

INTRAMOLECULAR HYDROGEN BONDING
IN NORBORNYL SYSTEMS

BY
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A dissertation submitted to the Faculty of Science, University
of the Witwatersrand, Johannesburg, in fulfilment of the
requirements for the degree of Master of Science

November, 1983

DECLARATION

I declare that this dissertation is my own, unaided work.
It is being submitted for the degree of Master of Science in
the University of the Witwatersrand, Johannesburg. It has
not been submitted for any degree or examination in any other
University.

A handwritten signature in cursive script, appearing to read 'Louis Denner', written in dark ink.

Louis Denner

ACKNOWLEDGEMENTS

I am most grateful to my supervisors, Prof. J.C.A. Boeyens and Dr. J.P. Michael, for their inspiring guidance and active assistance throughout the course of this study. It has been a privilege to have worked under them.

I would like to express my sincere gratitude to the following:

The Council for Scientific and Industrial Research and the University of the Witwatersrand for financial support for this project.

Jon Albain of the NPRL, C.S.I.R. for the intensity data collections of the crystal structures.

Demetrius Levendis for invaluable discussions as well as for proof-reading this manuscript.

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ABSTRACT

The crystal structure of 3-exo,6-exo-dichloro-5-endo-hydroxy-3-endo-nitrobicyclo[2.2.1]heptane-2-exo-carbonitrile, (7), was solved successfully. All the hydrogen atom positions could be located and it was established that an intramolecular hydrogen bond exists between the hydroxylic proton and an oxygen of the nitro group. The hydrogen bond is not bifurcated. This hydrogen bond was studied in solution by proton nuclear magnetic resonance and infrared spectroscopy. The results revealed that the hydrogen bond is weak and could even be bifurcated in solution.

Attempts to synthesise 6-endo-nitrobicyclo[2.2.1]heptan-2-endo-ol, (8), failed owing to the easy isomerisation of the nitro group, but two chloroalcohols, 3-exo-chloro-6-exo-nitrobicyclo[2.2.1]heptan-2-exo-ol, (60), and 3-exo-chloro-6-exo-nitrobicyclo[2.2.1]heptan-2-endo-ol, (59), were prepared instead. X-ray crystallography showed that intermolecular hydrogen bonding between the nitro and hydroxy groups is present in both these compounds; in the latter case the hydrogen bond is bifurcated. A model structure for (7) was calculated by empirical force-field calculations. The structure shows small differences regarding the orientations of the nitro and hydroxy groups if compared with the crystal structure. These differences were attributed to the effect of hydrogen bonding and packing forces.

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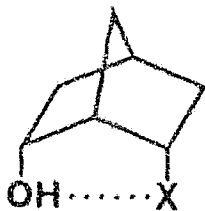
CHAPTER 1

INTRODUCTION

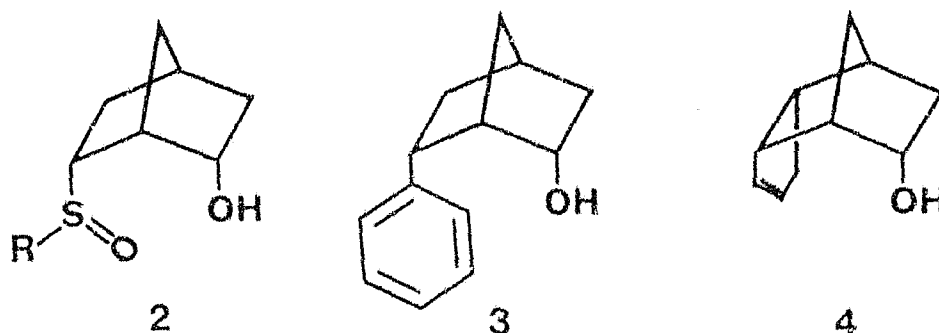
1.1. Origins of the project

Norbornyl derivatives have been used by chemists in a wide variety of synthetic and mechanistic investigations. This widespread use arises at least partly because the norbornyl skeleton possesses a rigid framework, and in consequence, the stereochemistry of substituents on this framework is, in theory, unambiguous. In practice, stereochemical assignments in substituted bicyclic systems may be attended with difficulties despite the rigid geometries involved. Of the physical methods available, proton magnetic resonance spectroscopy has been used with great success in elucidating the stereochemistry of norbornyl systems¹⁻⁵, but the more complex technique of X-ray crystallography⁶ is the best method yet available for structure elucidation. The structural parameters of norbornyl systems are well documented⁷⁻⁹ but the preferred orientations of many substituents on this system are not very well established.

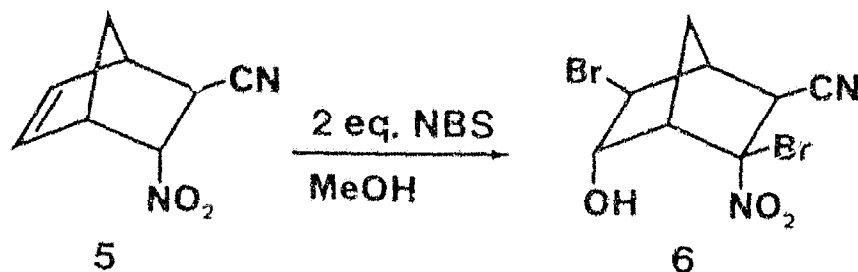
In general, exo substituents on the norbornyl skeleton are thermodynamically preferred over endo substituents. However, in the presence of overriding factors like hydrogen bonding, endo functional groups may be preferred, especially if an intramolecular hydrogen bond can emerge from such an arrangement of functional groups as shown in (1).



The degree of stabilisation gained from an intramolecular interaction obviously depends on the functional group X and on the way these interacting groups can orientate themselves to facilitate the energetically most favoured arrangement. Intramolecular hydrogen bonding has been found in compounds (2)-(4).¹⁰⁻¹²



Blom and Michael¹³ found a very interesting compound, namely 3-exo,6-exo-dibromo-5-endo-hydroxy-3-endo-nitrobicyclo[2.2.1]-heptane-2-exo-carbonitrile (6), in their study of norbornyl intermediates for the synthesis of alkaloids. This product was an unexpected product obtained from the reaction of 3-endo-nitrobicyclo[2.2.1]hept-5-ene-2-exo-carbonitrile, (5), with N-bromosuccinimide in methanol (Scheme 1). The reaction probably involves the nitro group as an intramolecular nucleophile, a rather rare occurrence.



Scheme 1

Compound (6) exhibits some interesting structural features. Most importantly, a crystal structure analysis revealed that both oxygen atoms of the nitro group were in close neighbourhood to that of the hydroxyl group. Both O...O distances, approximately 3 Å, were

short enough to indicate possible hydrogen bonding between the nitro and hydroxyl groups. Furthermore, in view of the near equality of the O...O distances this hydrogen bond might even be bifurcated. If these speculations are correct, the point of concern is whether hydrogen bonding is the sole factor determining the conformation of the nitro group. However, it was not possible to comment on the validity of any of these statements because the hydrogen atoms of (6) could not be located owing to the presence of two heavy bromine atoms.

All these questions prompted the work reported here. It was felt that if a compound analogous to (6) with chlorine atoms replacing bromine atoms could be prepared, then the essential features of the structure would remain unchanged. At the same time, the chances of locating the hydrogen atoms crystallographically should be improved by the substitution of the lighter halogen atoms. In other words, if hydrogen bonding really exists in these systems, it should be more easily detectable in (7) than in (6).



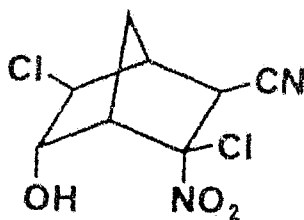
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In summary, the aims of the project are as follows:

- (a) to synthesise the dichloro compound (7) from (5), in the same way as compound (6) was prepared, but using N-chlorosuccinimide instead of N-bromosuccinimide;
- (b) to determine the molecular and crystal structures of compound (7) by means of X-ray diffraction;
- (c) to correlate the found structure with the spectroscopic behaviour of compounds (6) and (7);
- (d) to perform an in-depth conformational analysis of compound (7)

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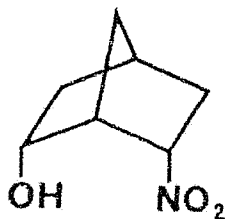
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- (d) to perform an in-depth conformational analysis of compound (7)

and suitable analogous norbornyl systems by means of empirical force-field calculations to determine preferred orientations of nitro and hydroxyl groups;

- (e) to synthesise a simplified model of (7), for instance 6-endo-nitrobicyclo[2.2.1]heptan-2-endo-ol, (8), and to investigate the nature of the hydrogen bonding in 2,6-nitronorbornanols in general.



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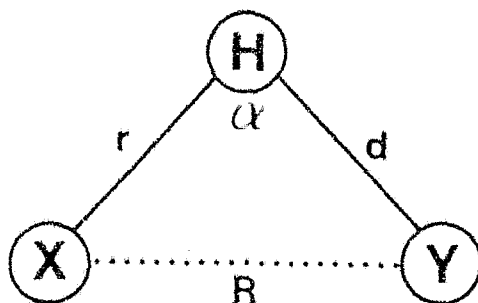
The main emphasis of this project is thus hydrogen bonding in nitronorbornanols. Hydrogen bonding was first recognised about 63 years ago by Huggins (1919)^{14,15} and Latimer and Rodebush (1920).¹⁶ Since then many important experimental and theoretical studies have been performed to provide some understanding of the nature of this interaction. An extensive literature exists on this subject and a number of books¹⁷⁻²⁴ and review articles²⁵⁻³⁶ have been published on this interesting topic. The determination of hydrogen bonding by infrared spectroscopy,^{37,38} proton nuclear magnetic resonance spectroscopy,³⁹⁻⁴¹ and X-ray crystallography^{42,43} is also very well documented. In the following section, brief surveys on the use of X-ray crystallography, proton nuclear magnetic resonance spectroscopy, and infrared spectroscopy in the investigation of hydrogen bonding will be given with special emphasis on nitroalcohols wherever such data can be obtained.

1.2. Hydrogen bonding as studied by X-ray crystallography

A definition commonly used states that a hydrogen bond between two groups X-H and Y exists when (a) there is evidence of bonding

X-H...Y; and (b) there is evidence that this bonding specifically involves the hydrogen in X-H.⁴⁴ These criteria evidently imply an energetic as well as a geometric requirement. Diffraction data can only provide direct information about the geometrical arrangement of the atoms. Generally spectroscopic methods are used to demonstrate whether the second criterion for the existence of a hydrogen bond is satisfied. The shift of the X-H stretching frequency is widely used to show the effect of an acceptor atom or group on a group X-H.

The hydrogen bond can be characterised geometrically by the parameters r , d , R and α .



Geometrically an X-H...Y interaction is considered to be a hydrogen bond if the distance H...Y is less than $(W_H + W_Y)$, and $110^\circ < \alpha < 180^\circ$, where W_H and W_Y are the van der Waals radii of hydrogen and the acceptor atoms respectively, and α is the angle X-H...Y.⁴⁵ The distance R between the atoms X and Y has often been used as indicator of possible hydrogen bonding, especially when heavy atoms are present in the molecule and the hydrogen atoms can not be detected. These criteria can only be applied with the knowledge of the positional parameters of the atoms involved. Single-crystal neutron diffraction studies of small molecules have shown that hydrogen atoms can be located to a precision of better than 0.02 angstroms.⁴⁶ The position of hydrogen atoms can neither be determined accurately by X-ray diffraction (because the X-rays are scattered by the electrons in an atom), nor can electron diffraction be employed successfully because of the low nuclear

charge of the hydrogen atom. The scattering factor for hydrogen falls off very rapidly with increasing scattering angle whereas it is found to be negative for neutrons. X-ray intensities are affected by temperature. The normal scattering-factor curves are calculated on the basis of the electron distribution in a stationary atom, but the atoms in a crystal are always vibrating about their rest points. The magnitude of the vibration depends on various factors like the temperature, the mass of the atom, and the firmness with which it is held in place by covalent bonds or other forces like hydrogen bonding. The effect of such thermal motion is to spread the electron cloud over a larger volume and thus to cause the scattering power of the real atom to fall off more rapidly than that of the ideal, stationary model.

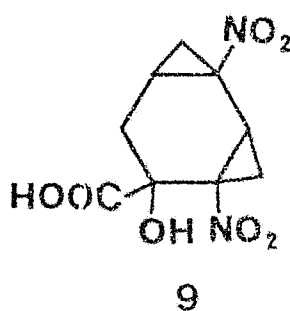
Hydrogen positions are commonly refined by standard least-squares methods, assuming spherical hydrogen scattering factors, but the electron cloud in a bond such as O-H is clearly deformed and the assumption of spherical scattering factors for hydrogens will give rise to a systematic shift in the apparent atomic positions. The atomic positions derived for a hydrogen atom from X-ray analysis thus approximate the centroid of the electron density rather than the actual nuclear position.⁴⁷

Before the time of accurately determined hydrogen positions by means of neutron diffraction it was generally accepted that nearly all hydrogen bonds were linear.⁴⁸ The present view, however, is that most hydrogen bonds in the solid state are not strictly linear.⁴⁹ In general, strong hydrogen bonding occurs only when the hydrogen atom is colinear with the bonded atoms. The strength of a hydrogen bond depends strongly on the X-H and Y type of interacting groups and it is normally much weaker than ordinary chemical bonds. Joesten and Schaad⁵⁰ proposed the following classification for hydrogen bonds: weak (< 3 kcal/mol), normal

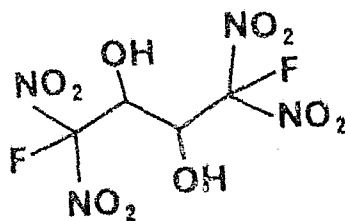
(3-10 kcal/mol) or strong (> 10 kcal/mol).

A variety of functional groups can participate in hydrogen bonding, but the system of concern here is the chelation of hydroxyl and nitro groups. A few examples of this interaction which have been uncovered by X-ray crystallography are discussed here.

Beintema⁵¹ reported that an intramolecular hydrogen bond joins an oxygen atom of the vicinal nitro group and a hydroxylic proton in the crystal structure of 2,3:4,5-dimethano-2,4-dinitro-1-hydroxycyclohexane-1-carboxylic acid, (9). He postulated that the hydrogen bond might be responsible for the significant difference between the bonds N-O(1) and N-O(2) of the nitro group vicin. to the hydroxyl group. The distances are 1.232 (hydrogen bonded) and 1.217 angstroms respectively.

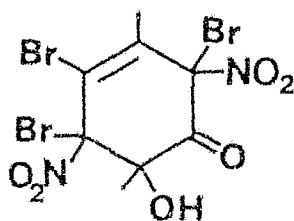


The X-ray structure elucidation of 1,4-difluoro-1,1,4,4-tetra-nitro-2,3-butanediol, (10), was reported by Dickinson and Holden.⁵² The fluorine atom and hydroxyl group are gauche to one another and no intramolecular hydrogen bond is formed. The hydroxyl group is oriented in such a way as to form a weak intermolecular hydrogen bond with a nitro group of the adjacent molecule, rather than an intramolecular or bifurcated system involving either the β -fluorine atom or a β -nitro group ($O...O = 2.99$ and $O-H...O = 2.27$ angstroms, $O-H...O = 170$ degrees).



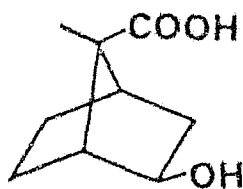
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Richards and co-workers⁵³ reported the X-ray structure of 2,4,5-tribromo-2,5-dinitro-6-hydroxy-3,6-dimethylcyclohex-3-enone, (11). On refinement, using full-matrix least-squares, it became apparent that the crystal was staticallystally disordered.



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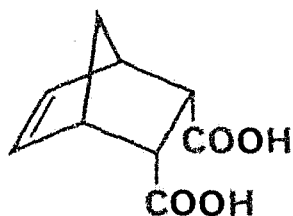
Hydrogen bonds in norbornyl systems have frequently been detected by X-ray crystallography. For example, Chapuis *et al.*⁵⁴ reported the structure of 2-exo-hydroxy-7-methylbicyclo[2.2.1]heptane-7-syn-carboxylic acid, (12), and concluded that the norbornane skeleton shows little distortion by the substituent groups. Each molecule is attached to three others by a total of four intermolecular hydrogen bonds, forming sheets of molecules parallel to (100).



12

Pfuger and co-workers⁵⁵ published the crystal and molecular structure of bicyclo[2.2.1]hept-5-ene-2-endo,3-endo-dicarboxylic acid, (13). The molecules are linked via intermolecular hydrogen bonding of the acid groups across centers of symmetry to form an infinite chain in the direction of the a-axis of the unit

cell. They observed large anisotropic thermal motions of the oxygen atoms of one carboxylic group and concluded that it is, presumably, the result of differences in the hydrogen bonding geometry.



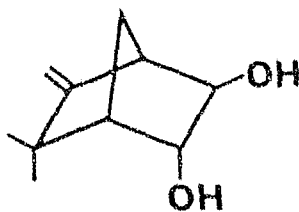
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Apgar and Ludwig⁵⁶ have studied the hydrobromide salt of (-)-exo-aminonorbornane-2-carboxylic acid, (14). They reported that each molecule makes four independent intermolecular hydrogen bonds involving an oxygen atom as well as three bromine atoms. The molecules are laid down in hydrogen-bonded sheets perpendicular to the b-axis of the unit cell.



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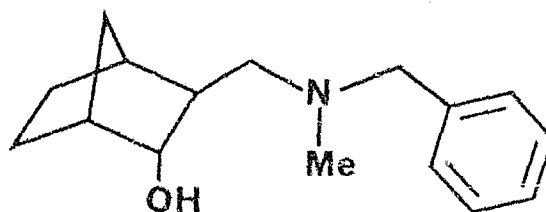
The structure of (-)-5-endo,6-exo-dihydroxycamphene, (15), was studied by Spencer and Trotter.⁵⁷ The nobornane skeleton was found to be slightly distorted as a result of intramolecular steric repulsion. Molecules are linked in the crystal by a double helical system of hydrogen bonds.



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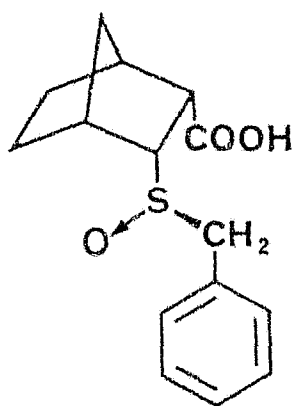
Karle and co-workers⁵⁸ reported the crystal and molecular

structure of 3-(N-benzyl-N-methylaminomethyl)-2-norbornanol, (16), and found that the molecules pack in such a manner as to form an intermolecular hydrogen bond between the hydroxyl group and the nitrogen atom.



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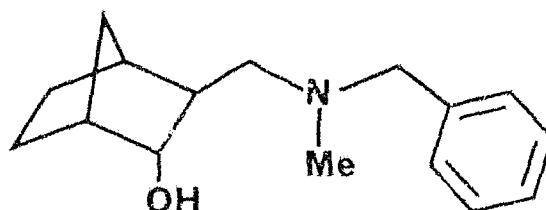
The crystal structure of 3-endo-benzylsulphonylbicyclo[2.2.1]-heptane-2-endo-carboxylic acid, (17), has been reported by Abrahamsson *et al.*⁵⁹ No intramolecular hydrogen bonding was found but rather strong intermolecular hydrogen bonding was detected between the acid moieties of pairs of molecules.



17

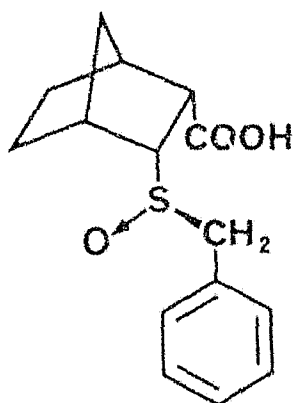
Hydrogen bonding is a complex phenomenon which besides the usual type X-H...Y may afford a variety of more complicated systems in which one proton acceptor centre Y may co-ordinate two hydrogens of the proton-donating X-H groups. Alternatively, the proton of the X-H group may be co-ordinated by two or even more Y centres. Bonds like these are called bifurcated hydrogen bonds. Bifurcated hydrogen bonds are a generally accepted phenomenon in the chemical literature.⁶⁰ Donohue⁴⁸ made a thorough study of some reported systems that contained bifurcated hydrogen bonds and discovered

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that several of these structures did not contain bifurcated hydrogen bonds at all. Bifurcated hydrogen bonds appear quite often in the literature and papers of this nature should be examined carefully especially where deductions of bifurcated hydrogen bonds are based solely on the positional parameters of the non-hydrogen atoms. As regards nitro groups, bifurcated hydrogen bonds appear to be unknown.

1.3. Spectroscopic studies of hydrogen bonding in nitroalcohols

1.3.1. Infrared spectroscopy

Infrared spectroscopy is the most important spectroscopic technique and the most frequently used tool for the studying of hydrogen bonds.⁶¹⁻⁶³ Spectroscopy can be used only to examine the characteristics of the bond adjacent to the hydrogen bond as was discussed in the previous section. Nevertheless, the indirect information obtained from such spectroscopic measurement enables one to deduce the spatial arrangement of the donor and acceptor groups participating in the hydrogen bond. X-ray diffraction and spectroscopy complement each other and deductions made on the grounds of spectroscopic evidence are often supported by a crystallographic analysis.⁶⁴ The hydroxyl group which participates in hydrogen bonding will have a different stretching frequency from that of the "free" hydroxyl group. This normally results in two absorption bands, with the lower frequency for the bonded O-H. The degree of difference between these bands is often used as a measure for strength of a hydrogen bond.

$$\Delta \nu(\text{OH}) = \nu(\text{OH})_f - \nu(\text{OH})_b$$

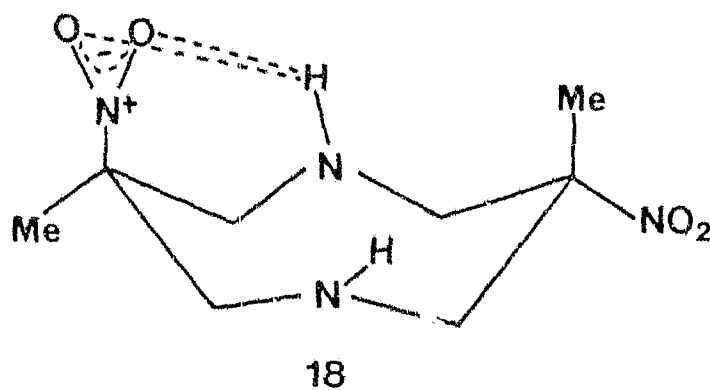
A fair number of spectroscopic investigations have been devoted to the existence of hydrogen bonding in 2-nitroalcohols and it is now

a generally accepted fact that hydrogen bonding does exist in these systems.⁶⁵ The interaction is classified as weak in comparison with the strength of hydrogen bonding in the resonance-stabilised *o*-nitrophenols.⁶⁶ Rao *et al.* suggested that the bond energies of nitro groups with alcohols is of the order of 1.5 kcal/mol.⁶⁷ The infrared spectra of nitroalcohols show that the structure of these compounds is largely dependent on intramolecular hydrogen bonding.^{68,69} Kuhn *et al.*⁷⁰ reported the infrared spectrum of 2-nitroethanol with free and bonded hydroxyl bands at 3623 and 3608 cm^{-1} respectively and a *gauche* conformation was assigned for this compound on the basis of weak intramolecular hydrogen bonding. The conformation of vicinal nitroalcohols was studied by Urbanski⁷¹ and it was found that the nitro and hydroxyl groups could have either the eclipsed or the *gauche* conformations.

Diallo⁷² published the infrared spectra of 2-nitropropan-1-ol and 2-methyl-2-nitropropane-1,3-diol and concluded that hydrogen bonding is present in these two systems. Urbanski *et al.*⁷³ studied the infrared, ultraviolet and nuclear magnetic resonance spectra of 2-methylpropan-1-ol and some of its derivatives that contained the nitro group and confirmed the presence of intramolecular hydrogen bonding in these compounds. These workers assumed the absorption bands for the nitro groups to remain unchanged under the action of hydrogen bonding. Krueger and Mettee⁷⁴ reported that nitro groups uniformly form weak hydrogen bonds as reflected in the very small spectral shifts of the hydroxyl vibrational band. They concluded that spectra obtained with high resolution are essential for the complete interpretation of the role that hydrogen bonds play in conformational equilibria and the investigation of the temperature dependence of such spectra is advisable since frequency displacements do not necessarily measure the strength of weak bonds.

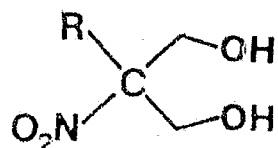
Ungnade and co-workers reported that 2-nitroalcohols are partially associated in carbon tetrachloride and almost monomeric in chloroform,^{75,76} and that the positions of the symmetrical stretches of the nitro group depends mainly on the degree of substitution on the carbon holding the nitro group. They interpreted the infrared spectra of 2-nitro-1,3-diols in terms of an interesting effect: the nitro group was believed to inhibit intramolecular hydrogen bonding between the two hydroxy groups. Similarly, an intermolecular hydrogen bond between alcohols was thought to be inhibited by nitromethane. The nitro and alcohol functions were considered to engage in an unspecified type of interaction that is responsible for this inhibition.⁷⁷ This suggestion was met with sharp criticism from Schleyer and his co-workers⁷⁸ who explained that Ungnade and Kissinger made their measurements with a spectrometer having a low resolution sodium chloride prism, which is inadequate for such investigations.

Kolinski *et al.*⁷⁹ have studied the intramolecular hydrogen bonding in 3,7-dialkyl-3,7-dinitro-1,5-diazacyclooctanes, (18), with infrared spectroscopy and dipole calculations. A possible bifurcated bond (as shown) was considered, but no tentative assignments were made about the actual conformation of the nitro group.

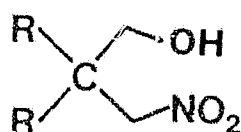


Calus *et al.*⁸⁰ reported their investigation of dipole moments of a number of nitroalcohols, (19)-(21). The calculated moment for

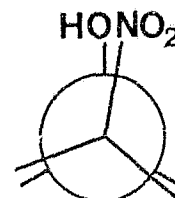
2-nitroethanol, (21), indicated that the two functional groups are eclipsed.



19



20

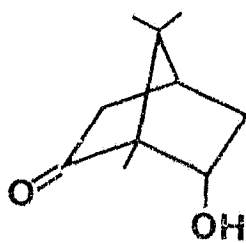


21

Kochany and co-workers⁸¹ confirmed the presence of hydrogen bonding in nitroalcohols based on dipole moment studies and concluded that dipole measurements are very sensitive functions of the atomic coordinates in molecules and it could therefore be used to exclude some conformations not favoured by hydrogen bonding.

In a semi-empirical treatment of the hydrogen bond, Reid reported⁸² that enhancement of the intensity by as much as 14 times can accompany the broadening of the hydroxyl frequency in hydrogen bonded systems. The broadening is undoubtedly due largely to the fact that hydroxyl frequency is dependent on O...O position, so that during an O...O vibration many different O-H frequencies occur.

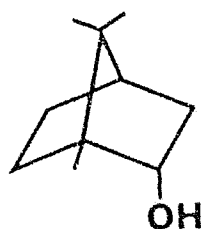
Some results on hydrogen bonding in simple norbornanols have been reported. The complex hydroxyl spectrum of 6-endo-hydroxycamphor, (22), was resolved by computer into a major band at 3606 cm^{-1} and a minor band at 3620 cm^{-1} by Schleyer and Joris.⁸³



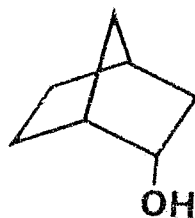
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By contrast they found that compounds (23) and (24) show only

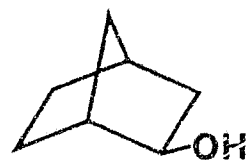
singlets for hydroxyl absorptions at 3627 and 3619 cm^{-1} , respectively. The absorption frequency for 2-exo-hydroxy-norbornane (25) was found to be 3619 cm^{-1} .



23



24



25

The possibility of intramolecular hydrogen bonding in 3-nitroalcohols remains almost entirely unexplored. To our knowledge, the sole example is due to Schleyer and co-workers,⁷⁸ who have shown that 3-nitropropanol is unlikely to possess even a weak intramolecular hydrogen bond. In this compound, and also in the general situation, it is probable that the preferred molecular conformation will be one in which the functional groups are too remote for interaction. The likelihood of observable intramolecular hydrogen bonding should be greater if the functional groups are effectively constrained into near neighbourhood as is the case with the groups attached to the rigid bicyclic skeleton.⁸⁴ The failure of the nitro group to engage to a greater extent in hydrogen bonding is surprising, but finds analogy in the case of the sulphone group.^{85,85}

1.3.2. Nuclear magnetic resonance spectroscopy

The changes in chemical shift in the nuclear magnetic resonance spectrum of a proton involved in hydrogen bonding are large⁸⁷ and can serve as an indication of hydrogen bonding in a similar manner to the changes in the infrared X-H frequency on formation of the hydrogen bond X-H...Y. Berkeley *et al.*⁸⁸ have studied the downfield shift of the signal of the proton involved in hydrogen bonding and concluded that the principal contributors are: (a) a contribution to the screening due to the distortion of the

electronic nature of the chemical bond; and (b) a contribution to the proton screening due to any magnetic anisotropy of the molecule to which the proton is hydrogen bonded. Urbanski *et al.*⁸⁹ reported that there is a prominent influence of the presence of the nitro group in alcohols on the chemical shift. The nitro group increases the value of hydroxyl chemical shift in monohydroxylic nitroalcohols by virtue of the intramolecular hydrogen bond. This is in agreement with findings already published on the nuclear magnetic resonance spectra of nitroanilides.⁹⁰ The chemical shifts of protons in nitroalkanes have been explained in terms of the inductive effect of the nitro group.⁶⁵ This effect can operate as far as the fourth carbon atom in a chain.

As with infrared spectroscopy, intramolecular hydrogen bonding can be distinguished from intermolecular hydrogen bonding by its constancy when the concentration of the compound is varied in a specific solvent.³⁹ Merrill correlated the hydroxyl proton chemical shift with infrared hydroxyl stretching frequency⁹¹ and discovered that the larger chemical shifts correspond to the lower hydroxyl frequency. Hydrogen bonding changes with temperature and concentration, and comparison of spectra taken under different conditions also serves to detect and measure it.⁹² Generally, a decrease in temperature causes the hydroxyl shift to move to lower field, the direction associated with stronger hydrogen bonding. Fales and Robertson⁹³ employed the exchange of active hydrogen for deuterium in spectroscopic studies. However, this method fails for strong intramolecular hydrogen bonds.

The observed shape of the proton nuclear magnetic resonance signal depends on a variety of factors of which chemical exchange is the most important factor in hydrogen bonding studies.⁹⁴ If the solute contains exchangeable protons, its spectrum may be quite dependent on the nature of the solvent in terms of exchange

lifetimes. If, in addition, the solvent contains exchangeable protons, there may be a rapid exchange between the solute and solvent. The rate of exchange between a solvent proton and one in an intramolecular hydrogen bond has been found to depend on the strength of the bond.⁹⁵ The rate of proton exchange also determines whether spin-spin coupling will be observed.

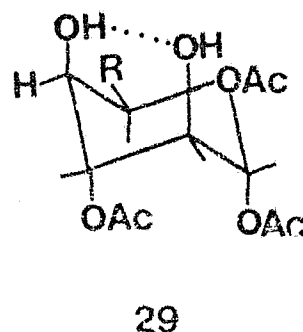
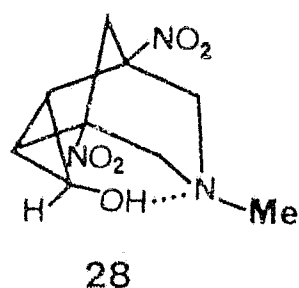
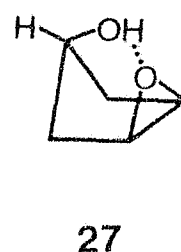
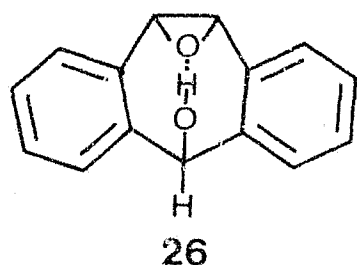
It should be generally accepted that parameters like the equilibrium constant, enthalpy and chemical shift for hydrogen bonded systems are functions of the particular solvent.⁹⁶ Conversely, the effect of solvents on the coupling constants is usually very small. The chemical shifts of hydrogen bonded to oxygen are extremely sensitive to structural and environmental changes and the change from chlorinated solvents to an aromatic solvent often causes drastic changes to the position and appearance of the signals.

Attractive forces like hydrogen bonding can cause a specific conformational preference for an acceptor or a donor group. The $^3J_{\text{HCOH}}$ coupling constant depends on the dihedral angle in a similar way as for HCCH-systems,⁹⁷ and the following is a frequently used empirical correlation for such systems:

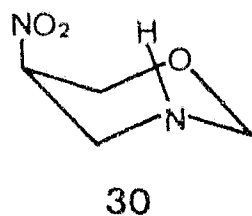
$$^3J_{\text{HCOH}}(\alpha) = 10.4\cos^2\alpha - 1.5\cos\alpha + 0.2 \quad (\text{Hz})$$

This effect is easily measureable with proton nuclear magnetic resonance spectroscopy in the form of coupling constants. Couplings between the vicinal proton and the hydroxylic proton have been found in cases where the hydroxyl proton is fixed by an intramolecular hydrogen bond, as in the structures of compounds (26)⁹⁸ ($J = 12.5 \text{ Hz}$), (27)⁹⁹ ($J = 12.3 \text{ Hz}$) and (28)¹⁰⁰ ($J = 12 \text{ Hz}$), where each compound has a nearly anti arrangement ($\alpha = 180^\circ$) with the respective vicinal hydrogen atom. For compound (29) a coupling

constant of 9.8 Hz was reported.¹⁰¹ Here the hydroxylic proton forms a hydrogen bond to O(2), and the dihedral angle, between H(4) and the hydroxyl proton is about 150°.

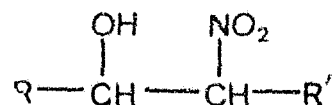


Very few studies of hydrogen bonding in nitronorbornanols by nuclear magnetic resonance spectroscopy have been reported. Urbanski⁷¹ reported the conformational analysis of some nitro and nitroso compounds using proton nuclear magnetic resonance spectroscopy as well as dipole moment measurements and concluded that nitroalcohols may exist in the gauche form due to hydrogen bonding between the nitro and hydroxy groups. No definite conclusion with regard to the conformation of the N-hydrogen, in (30), could be drawn from either dipole moment measurements or proton nuclear magnetic resonance spectra.



Kingsbury and co-workers⁷⁷ studied the conformational preferences in nitroalcohols, such as 3-nitrobutan-2-ol, by means of ¹H and ¹³C nuclear magnetic resonance coupling constants, dilution studies and effect of the solvent. The question of

interest was the effect of intramolecular hydrogen bonding between nitro and hydroxy groups. This effect proved to be weak and the hydroxyl signal was split into a doublet in certain cases. The tendency of CX₃ in (31) to be gauche to nitro when X = Br or Cl, raised the question of a possible charge-transfer interaction, but no evidence could be found for such an interaction.



31

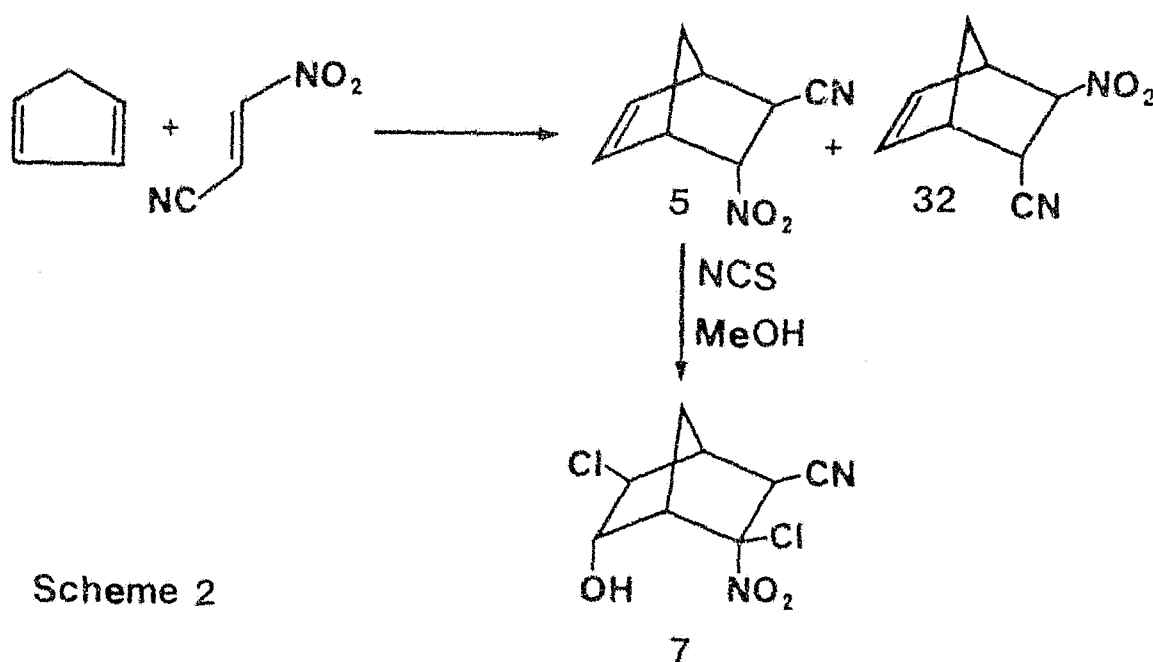
They found that whether or not hydrogen bonding existed, a strong tendency for the nitro and hydroxy functions to be gauche existed, and they disagreed that hydrogen bonding is a strong force that dominates the choice of conformation. The strongest alternative appears to be a two electron donor-acceptor interaction between the nitro and hydroxy groups.

CHAPTER 2

HYDROGEN BONDING IN 3-exo,6-exo-DICHLORO-5-endo-HYDROXY-3-endo-NITROBICYCLO[2.2.1]HEPTANE-2-exo-CARBONITRILE

2.1. The synthesis of the nitronorbornanol, (7)

The title compound was synthesised according to the following synthetic route (Scheme 2).



Scheme 2

This reaction was initially carried out by N.F. Blom¹⁰² and his method (see experimental) was used without modification in this work. The nitro-olefin was synthesised according to the method of Shechter *et al.*¹⁰³ using acrylonitrile and nitryl chloride as starting materials. The reaction of (E)-3-nitropropenenitrile with freshly cracked cyclopentadiene in dry diethyl ether proceeded smoothly at 0°C. Recrystallisation of the product from methanol resulted in a 62% overall yield of 3-endo-nitrobicyclo[2.2.1]-hept-5-ene-2-exo-carbonitrile, (5). This foamy-like substance decomposes slowly on standing at room temperature and could never be obtained entirely free of the isomer (32). Even at its purest, it melted over the range of 121-125°C. The infrared spectrum of (5)

shows the presence of a nitro group with strong absorption bands at 1545 and 1367 cm^{-1} as well as a weak, but sharp, absorption band at 2240 cm^{-1} for a nitrile group. Mass-spectral analysis confirmed a molecular ion peak at m/e 154. An abundant peak at m/e 118 arises from the loss of the nitro group from the molecule.

The proton nuclear magnetic resonance spectrum of the Diels-Alder adduct mixture reveals an isomer ratio 90:10 for the endo-nitro adduct, (5), to the exo-nitro adduct, (32) (Figure 1). These values were obtained from careful integration of the protons alpha to the nitro group. The spectrum (Figure 1) shows the presence of both isomers and the signals derived from the minor isomer are indicated with arrows.

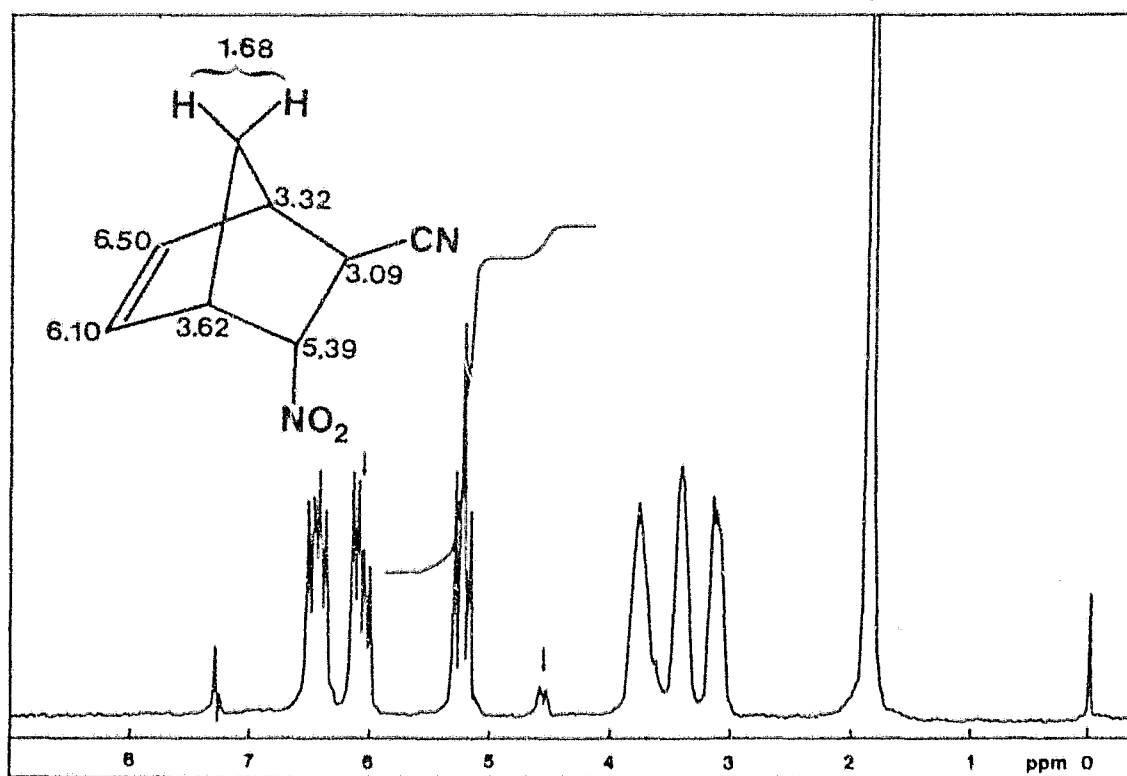
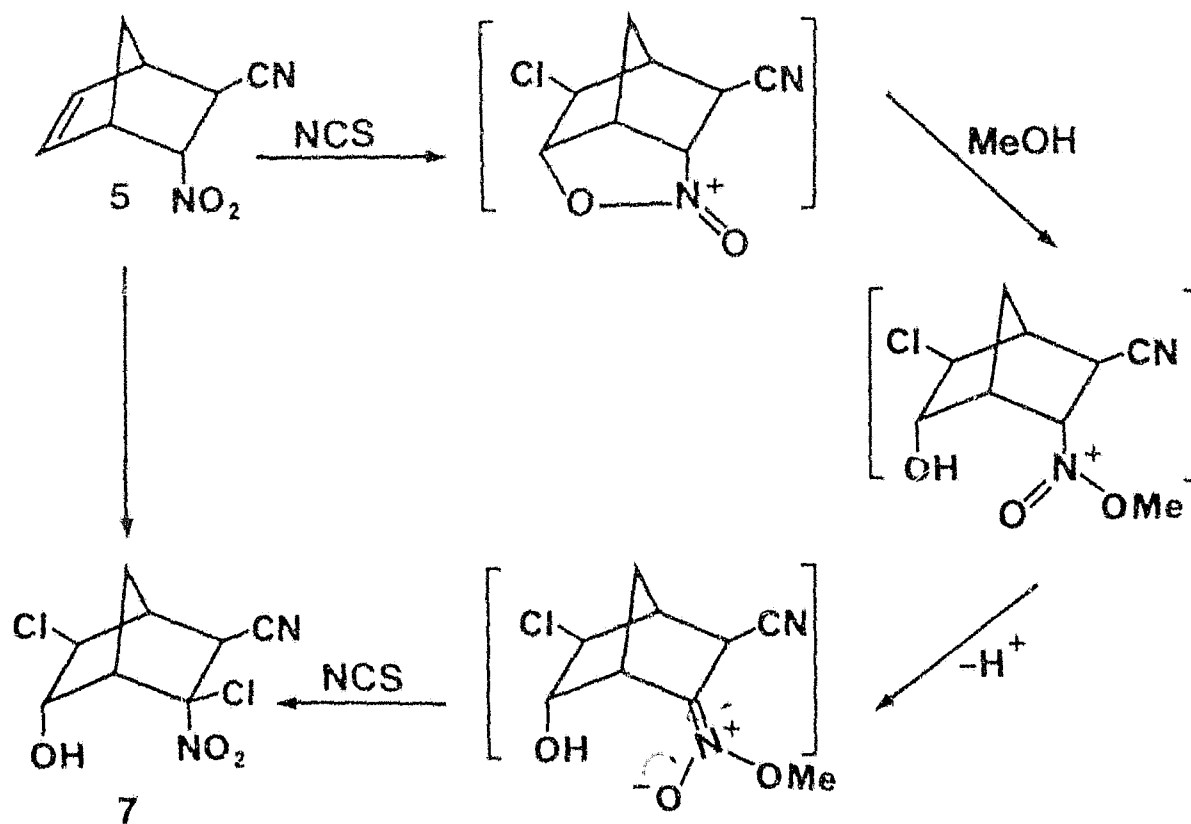


Fig. 1. ^1H NMR spectrum of (5), and the minor isomer (32), in deuteriochloroform.

The spectrum has two double-doublets at 6.50 and 6.10 ppm respectively with coupling constants of 5.4 Hz for cis vicinal coupling, and 3.0 Hz for coupling with the respective bridgehead

protons, H(1) and H(4). A triplet is found at 5.39 ppm for H(3) which couples with H(2) and H(4) resulting in a coupling constant of 3.80 Hz. The doublet from the minor isomer (indicated by the arrow) at 5.57 ppm originates from the coupling H(3) with H(2), and no coupling is observed for H(3) with H(4) as in the endo case. The broad signals at 3.62 and 3.32 ppm are assigned to protons H(4) and H(1). H(2) appears as a multiplet at 3.09 ppm and the protons H(7a) and H(7s) give rise to a singlet at 1.68 ppm.

The chlorination of the bicyclic alkene (5) with N-chlorosuccinimide in methanol afforded 3-exo,6-exo-dichloro-5-endo-hydroxy-3-endo-nitrobicyclo[2.2.1]heptane-2-exo-carbonitrile, (7). This reaction features the nitro group as an intramolecular nucleophile as depicted in Scheme 3, and has been investigated in the general case by Blom and Michael¹³.



Scheme 3

The crude product was recrystallised from methanol to give

prismatic-shaped crystals in a 60% yield; melting point 194-195°C. The infrared spectrum (KBr) of (7) shows the presence of a hydroxyl group (3435 cm^{-1}), a nitrile functionality (2288 cm^{-1}) and a nitro group (1578 and 1360 cm^{-1}). The mass- spectrum of (7) shows no molecular ion peak at m/e 250, but a peak at m/e 204, with typical isotope pattern for a chlorine atom, is observed for the loss of the nitro group from the molecule. A peak at m/e 178 is derived from the subsequent loss of the nitrile group. A further loss of a chlorine atom from the molecule leads to a peak at m/e 143.

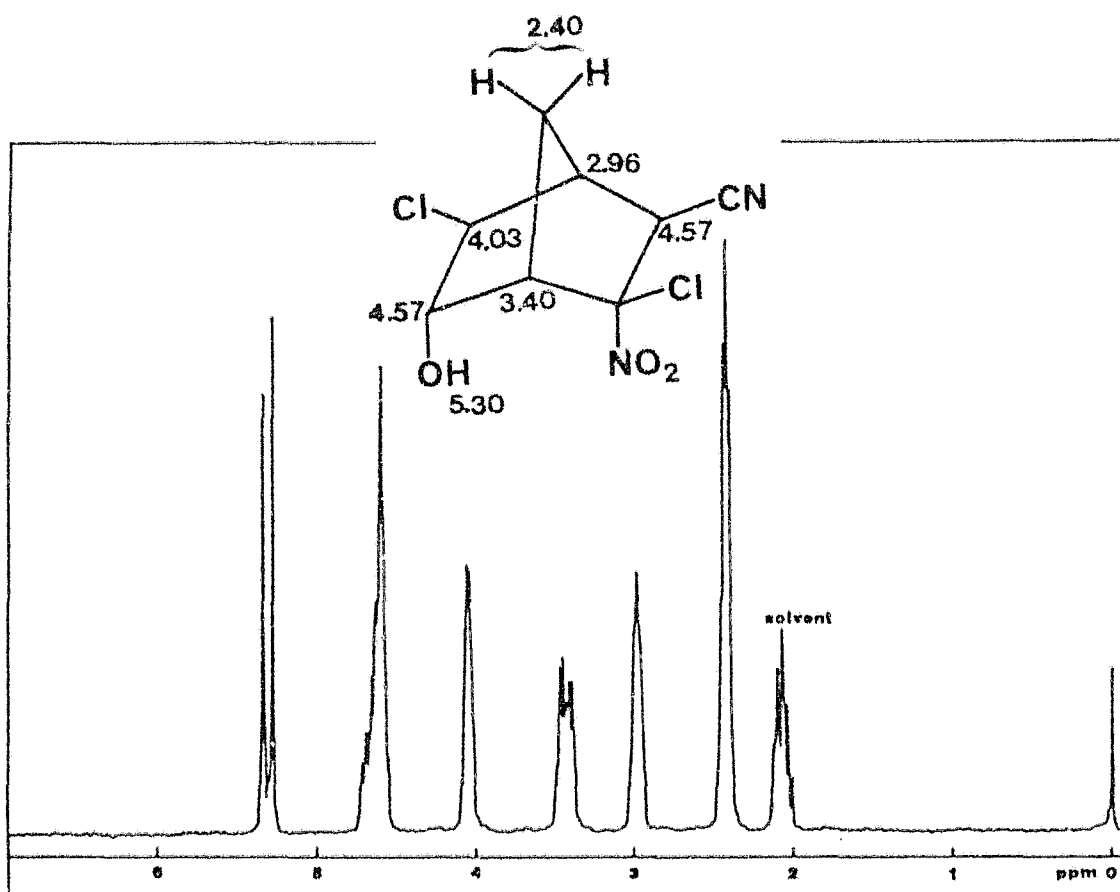


Fig. 2. ^1H NMR spectrum of compound (7) in deuterioacetone.

The proton nuclear magnetic resonance spectrum of (7) in deuterated acetone (Figure 2) has a doublet at 5.30 ppm for the hydroxylic proton with a coupling constant of 4.64 Hz to H(5), which appears together with H(2) as a multiplet at 4.57 ppm. H(6) appears as multiplet at a chemical shift of 4.02 ppm. The two bridgehead protons, H(1) and H(4), appear as multiplets at 2.96 and 3.40 ppm

respectively. The triplet at 2.40 ppm, with a coupling constant of 1.3 Hz and additional fine coupling, is assigned to the protons H(7s) and H(7a). Numerous nuclear magnetic resonance experiments were performed on this compound. It is largely on the basis of these spectra that intramolecular hydrogen bonding in this compound has been deduced, and these deductions will be presented in detail in section 2.3 (page 32).

2.2. X-ray crystallography of the nitronorbornanol, (7)

As was discussed in the introductory chapter, the structure of 3-exo,6-exo-dibromo-5-endo-hydroxy-3-endo-nitrobicyclo[2.2.1]-heptane-2-exo-carbonitrile, (6), was solved by Blom *et al.*¹³ resulting in a final *R* of 0.048. Hydrogen atoms could not be located owing to the two bromine atoms present and it was thus not possible to obtain any information regarding an intramolecular hydrogen bond. However, O...O distances of 2.99(4) and 3.08(4) angstroms for O(1)...O(2) and O(1)...O(3) respectively, suggested hydrogen bonding, possibly bifurcated. The analogous dichloro derivative, (7), was prepared in the hope that the hydrogen atoms could be located and the crystal structure analysis was performed to gain more information about these conformationally restricted 2,6-nitroalcohols.

Single, prism-shaped crystals of (7) were recrystallised from methanol and these crystals were found to be suitable for diffraction work. The space group and unit cell parameters were determined from Weissenberg, precession and oscillation photographs recorded with Cu-K α radiation. Table 1 lists the crystallographic and physical data for compound (7).

Table 1. Crystallographic and physical data.

<u>Crystal data</u>	
Formula	$C_8H_8N_2O_3Cl_2$
Molecular weight	251.069 g mol ⁻¹
Melting point	195°C
Crystallisation solvent	methanol
Crystal system	monoclinic
Space group	Cc (no. 9)
<u>a</u>	6.63(1) Å
<u>b</u>	15.97(1) Å
<u>c</u>	9.91(1) Å
β	92.91(1)°
<i>V</i>	1047.4 Å ³
<u>Z</u>	4
<i>D</i> _c	1.6 g cm ⁻³
<i>D</i> _m	1.6 g cm ⁻³
μ (Mo-K α)	5.45 cm ⁻¹
<i>F</i> (000)	512
<u>Data collection</u>	
Crystal dimensions	0.2x0.2x0.5 mm ³
Scan mode	ω -2 θ
Scan speed	0.043° θ s ⁻¹
Scan width	1.30° θ
Range scanned	3-23°
Stability of standard reflections	0.94%
Number of reflections collected	747
Number of observed reflections	714
Significance test	$F_o > \sigma(F_o)$
<u>Refinement</u>	
Number of variables	166
Weighting scheme	unit weights
Final conventional <u>R</u>	0.0378

Accurate cell parameters and intensities were measured with a Philips PW1100 four-circle diffractometer, using graphite monochromated Mo-K α radiation. After each group of 57 reflections three standard reflections were measured, but no significant change in these intensities were observed. The intensities were corrected for Lorentz and polarisation, but not absorption. The structure was solved by the heavy-atom method. The vectors corresponding to the two chlorine atoms were located on a Patterson map and a Fourier synthesis revealed the positions of all the non-hydrogen atoms. The structure was refined by full-matrix least squares with isotropic temperature factors for all the atoms during the first few cycles of refinement. Anisotropic temperature factors were assigned for all non-hydrogen atoms in subsequent cycles. All the hydrogen atoms could be located from a difference Fourier map. The final R was 0.0378 and a difference Fourier map revealed no peaks higher than $0.35 \text{ e } \text{\AA}^{-3}$. Structure factors (Appendix 1) were also calculated during the last cycle of refinement. The calculations for this structure determination were carried out on a CDC Cyber 174 computer of the C.S.I.R. with the SHELX-76 package of computer programs.¹⁰⁴

Results and discussion

The crystal structure and numbering scheme are depicted in Figure 3. Tables 2 and 3 give the fractional atomic coordinates and Tables 4 to 6 the molecular geometry. Components of vibrational tensors and structure factors are listed in Appendix 1.

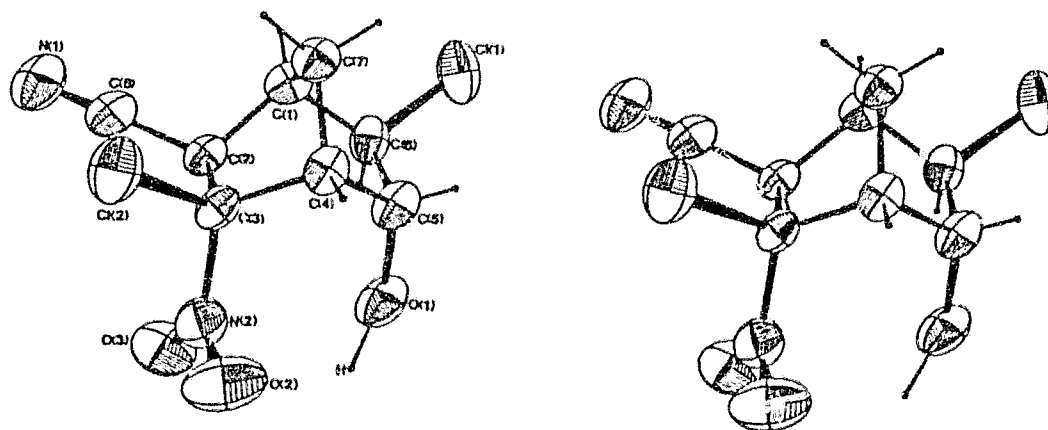


Fig. 3. Stereoscopic drawing of (7). This drawing was prepared by the program ORTEP¹⁰⁵. Thermal ellipsoids are scaled to enclose 50% probability.

Table 2. Fractional atomic coordinates for non-hydrogen atoms, ($\times 10^4$).

Atom	x/a	y/b	z/c
C(1)	0	-119(2)	5000(0)
C(2)	6046(5)	2713(1)	6133(4)
O(1)	4662(12)	37(4)	7395(7)
O(2)	7940(11)	1325(5)	7793(8)
O(3)	5459(12)	1642(5)	9066(7)
N(1)	1514(13)	3445(5)	7314(8)
N(2)	6181(12)	1544(4)	7962(8)
C(1)	1484(14)	1435(5)	5771(9)
C(2)	2609(12)	1890(5)	6997(8)
C(3)	4894(12)	1770(4)	6695(8)
C(4)	4779(13)	1111(5)	5563(8)
C(5)	3850(14)	284(5)	6104(9)
C(6)	1569(13)	507(5)	6149(11)
C(7)	3064(14)	1469(6)	4663(9)
C(8)	2001(14)	2771(5)	7160(8)

Table 3. Fractional atomic coordinates for hydrogen atoms, ($\times 10^3$).

H(1)	20(13)	162(5)	546(7)
H(2)	252(10)	153(5)	781(8)
H(4)	615(14)	105(5)	528(8)
H(5)	372(13)	-12(5)	553(8)
H(6)	145(12)	35(5)	697(9)
H(7s)	329(10)	205(5)	426(7)
H(7a)	268(12)	112(5)	390(9)
H (hydroxyl)	635(25)	23(13)	781(20)

Hydrogen atoms bonded to carbons have been given the same numbers as the carbon atoms to which they are attached. The designations syn (s) and anti (a) are defined relative to the nitrile group.

Table 4. Bond lengths (angstrom).

Cl(1)-C(6)	1.801(9)
Cl(2)-C(3)	1.787(7)
O(1)-C(5)	1.415(11)
O(2)-N(2)	1.234(9)
O(3)-N(2)	1.225(9)
N(1)-C(8)	1.134(10)
N(2)-C(3)	1.523(10)
C(1)-C(2)	1.568(12)
C(1)-C(6)	1.527(12)
C(1)-C(7)	1.554(10)
C(2)-C(3)	1.568(9)
C(2)-C(8)	1.472(11)
C(3)-C(4)	1.534(10)
C(4)-C(5)	1.561(11)
C(4)-C(7)	1.517(11)
C(5)-C(6)	1.553(11)
H(1)-C(1)	0.94(8)
H(2)-C(2)	0.99(8)
H(4)-C(4)	0.97(9)
H(5)-C(5)	0.86(8)
H(6)-C(6)	0.86(9)
H(7s)-C(7)	1.02(7)
H(7a)-C(7)	0.97(9)
O(1)-H (hydroxyl)	1.21(15)

Table 5. Selected bond angles (degrees).

Cl(1)-C(6)-C(1)	111.7(7)
Cl(1)-C(6)-C(5)	112.6(6)
Cl(2)-C(3)-N(2)	103.0(5)
Cl(2)-C(3)-C(3)	112.8(5)
Cl(2)-C(3)-C(4)	110.8(5)
O(1)-C(5)-C(4)	114.0(8)
O(1)-C(5)-C(6)	111.2(7)
O(2)-N(2)-O(3)	124.8(7)
O(2)-N(2)-C(3)	116.5(7)
O(3)-N(2)-C(3)	118.5(7)
N(1)-C(8)-C(2)	178.4(9)
N(2)-C(3)-C(2)	112.1(6)
N(2)-C(3)-C(4)	116.4(6)
C(1)-C(2)-C(3)	102.7(6)
C(1)-C(2)-C(8)	113.9(7)
C(1)-C(6)-C(5)	103.8(6)
C(1)-C(7)-C(4)	94.7(6)
C(2)-C(1)-C(6)	104.4(7)
C(2)-C(1)-C(7)	102.7(6)
C(2)-C(3)-C(4)	102.2(6)
C(3)-C(2)-C(8)	114.2(7)
C(3)-C(4)-C(5)	109.5(6)
C(3)-C(4)-C(7)	100.3(6)
C(4)-C(5)-C(6)	102.5(6)
C(5)-C(4)-C(7)	102.9(7)
C(6)-C(1)-C(7)	100.9(6)
H-O(1)-C(5)	122(10)
O(1)-H...O(2)	133(14)
H...O(2)-N(2)	76(6)

Table 6. Selected non-bonded distances (angstrom) and torsional angles (degrees).

O(1)...O(2)	3.00(1)
O(1)...O(3)	3.08(1)
O(1)...N(2)	2.65(1)
O(1)-H...O(2)	2.04(18)
O(1)-H...N(2)	2.11(20)
O(1)-H...Cl(1)	3.17 (intermolecular)
O(2)-N(2)-C(3)-C(2)	170.3(3)
O(3)-N(2)-C(3)-C(2)	-14.3(5)
C(4)-C(5)-O(1)-H	-26.8(6)
H(5)-C(5)-O(1)-H	109.1(4)

Torsional angles are presented in the range -180 to +180; the angle a-b-c-d is positive when the sense of rotation from a to d is clockwise as viewed along the b-c bond.

Bonds lengths and angles agree well with previously reported structures of related bicyclic systems¹⁰⁶⁻¹¹¹ as well as with the isomorphous dibromo derivative, (6).¹³

An interesting arrangement of oxygen atoms is found in the molecule; both the oxygen atoms of the nitro group were found to be about 3 angstroms from the oxygen atom of the hydroxyl group as can be seen from Table 6. It has frequently been pointed out that intramolecular hydrogen bonds are particularly readily formed when other bonds in the molecule constrain the atoms to favorable positions, as is the case for ortho-nitrophenols¹¹². This geometry of donor and acceptor groups suggested the possibility of an intramolecular bifurcated hydrogen bond but subsequent refinement of the structure showed clearly that the electron density of the hydroxylic proton was centred mainly between O(1) and O(2), with distances of 2.04 angstroms for O(1)-H...O(2) and 2.65 angstroms for O(1)-H...O(3). The sum of the van der Waals radii¹¹³ for O...O is about 2.8 angstroms. These distances seem to be typical for O...O hydrogen bonds although the information is rather limited for nitro-hydroxyl interactions.¹¹⁴⁻¹¹⁶ The O-H...O bond closes part of the molecule to a seven-membered ring and a non-linear arrangement of the bond was to be expected. The O(1)-H...O(2) angle is found to be 133 degrees. This hydrogen bond is a weak bond as supported by spectroscopic studies (Section 2.3,

page 32).

It is apparent that the hydrogen bond in (7) cannot be formed by the interaction with the lone pairs on the oxygen atoms of the nitro group (not that lone pair involvement is essential for hydrogen bonding^{115,117}). The angle formed by the H...O(2) vector and the plane of the nitro group, about 76 degrees, suggests that the hydrogen atom is interacting with a π orbital of the nitro group (probably the π non-bonding orbital), an interaction which can at best only give rise to weak hydrogen bonding.

The rigid bicyclic skeleton restricts the two groups from moving too close together to form a stronger hydrogen bond. The other degree of freedom for the nitro group is rotation about the C-N bond, which has a very small rotational barrier,^{118,119} but the bulkiness and repulsive action of the adjacent chlorine atom seem to prevent these functional groups from achieving closer proximity. A point of added interest arises from the pronounced elongation of the thermal ellipsoids (50% probability) for O(1) and O(2) towards the hydroxylic hydrogen atom (Figure 3), thereby lending further credence to an intramolecular hydrogen bond.

In conformational terms, the orientations of both the nitro group and hydroxy groups are rather surprising. The torsional angle in Table 6 shows that the C(3)-C(2) bond lies nearly in the plane of the nitro group; similarly, the dihedral angle between the O(1)-H and C(5)-C(4) bonds is unexpectedly small. With both functional groups adopting what would appear to be intrinsically high energy conformations, an overriding energy-lowering attractive interaction between them seems an inescapable conclusion. A molecular mechanics study on 2-endo-nitronorbornanes suggested that the nitro group can take up two conformations (as described in Chapter 4). However, no evidence of positional disorder could be found on the difference

Fourier map for O(2) and O(3) of the nitro group. It is probable that the hydrogen bond locks these functional groups together and thereby restricts free rotation about the C-N bond to form another conformer.

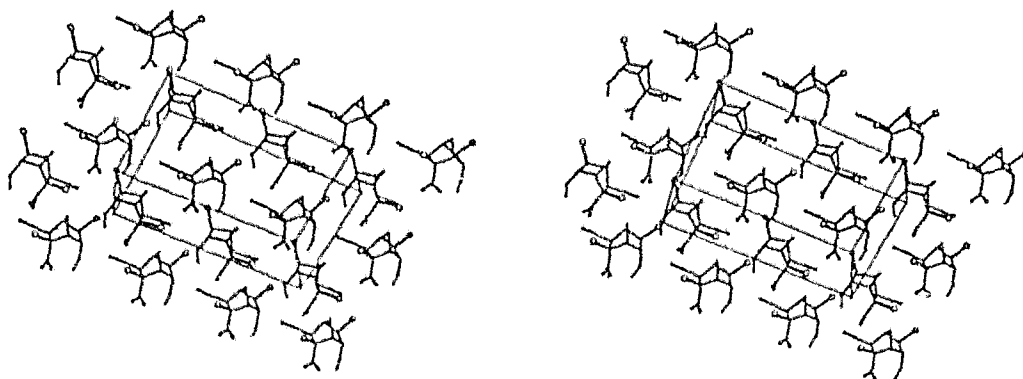


Fig. 4. A stereoview of the molecular packing in the unit cell of (7). Hydrogen atoms other than that of the hydroxyl group have been omitted for clarity.

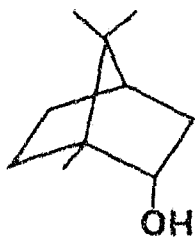
Figure 4 shows the packing of the molecules in the crystal lattice. The packing exhibits no unusual short non-bonded interactions and it is clear that the hydroxyl group cannot be involved in intermolecular hydrogen bonding, at least in the crystalline state. The closest intermolecular distance is between a hydroxyl proton and a chlorine atom with a distance of 3.17 angstroms which is too great for hydrogen bonding. Within each molecule, however, the same hydrogen atom is spatially positioned such that its interaction with the nitro group, as expected, is highly probable. Spectroscopic evidence supports the fact that the hydroxyl group is only intramolecularly bonded. (See discussion in Section 2.3).

Hence, it can be concluded that normal intramolecular hydrogen bonding is preferred in compounds (6) and (7), rather than a bifurcated hydrogen bond, which does not support the initial assumption based on the structure of the dibromo compound, (6).

2.3. Spectroscopic evidence for hydrogen bonding in the nitronorbornanol, (7)

The nature of hydrogen bonding in the solid state can change drastically once a compound has been dissolved in a specific solvent. Intermolecular hydrogen bonding with the solvent may be preferred above closely-packed, intramolecular hydrogen bonded units. Moreover, the orientations of the functional groups would also be effected to accommodate the new energetic requirements. Therefore, hydrogen bonding studies in solution do not necessarily have to correlate with experimental findings in the solid state.

Spectroscopic studies of compound (7), however, proved that the intramolecular hydrogen bond exists in solution too. The main drawback in the infrared spectroscopic study of (7) was the poor solubility of the compound in non-polar solvents. In chloroform, for instance, the maximum solubility of (7) was about 0.1% w/v (about 0.004 M), while in tetrachloromethane the solubility was about ten times poorer. The hydroxyl stretching frequency in chloroform was assigned to a weak but apparently symmetric band at 3605 cm^{-1} and no $\text{OH}\cdots\text{OH}$ intermolecular hydrogen bonding was observed. This absorption band was concentration independent in the range of 0.03-0.1% w/v. This absorption band was compared with that of borneol, (33), and 3-nitropropanol⁷⁸ which absorb at 3670 and 3639 cm^{-1} respectively. The difference of the hydroxyl absorption shift is small and the hydrogen bond is thus weak. No absorption bands arising from intermolecular hydrogen bonding were observed.

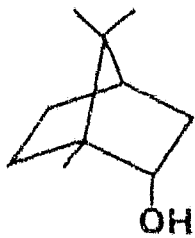


33

The results obtained from proton nuclear magnetic resonance spectroscopy also showed that an intramolecular hydrogen bond is

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33

The results obtained from proton nuclear magnetic resonance spectroscopy also showed that an intramolecular hydrogen bond is

present in solution. The chemical shift of the hydroxyl proton is concentration independent in the range 0.5-20% w/v (in deuterated acetone), which is a characteristic property of intramolecular hydrogen bonded systems in solutions. The multiplicity of the signal is a distinct doublet at 5.30 ppm ($J = 4.6$ Hz) owing to coupling with the vicinal proton on C(5). The results listed in Table 7 show that this coupling constant is independent of solvent and temperature. This is unusual, because normally no coupling is observed between the hydroxyl hydrogen and the vicinal hydrogens of ordinary alcohols. Under normal conditions, the rate of exchange of protons between alcohol molecules occurs at a rate faster than the time scale of the spectrometer. As in geminal coupling, however, there actually is coupling between these hydrogens, but spin-spin splitting is often not observed. The exchange in a mixture of 10% solute (in deuterated acetone) and one equivalent of water is also very slow and the hydroxyl doublet had only vanished after standing for four weeks at room temperature.

Owing to the likelihood of rotational averaging, the observed coupling constant may not be a reliable guide to the conformation of the hydroxyl group. However, in view of the invariance of the coupling constant with temperature, rotational averaging is unlikely, and the observation of coupling would appear to be a genuine result of conformational locking arising from an intramolecular hydrogen bond. In terms of the modified Karplus relationship introduced by Fraser and co-workers for H-C-O-H systems,⁹⁷ the observed ^3J value of 4.6 Hz corresponds to a dihedral angle for H-C(5)-O(1)-H of 125 degrees, which correlates reasonably well with the 109 degrees angle determined crystallographically. While one must take cognisance of the dangers of reading too much into a Karplus-type relationship. If the 125° angle is at all meaningful, then the implication is that, unless the conformation of the nitro group is also substantially altered,

the hydrogen bond in (7) may well be bifurcated in solution, in contrast to the situation in the solid state.

Table 7. Chemical shifts and coupling constants for the hydroxyl group of (7)

Solvent	Temperature	Concentration	Delta	J, Hz.
CDCl ₃	Ambient	0.1% w/v (ca.)	2.08 ^a	4.2
Acetone-d ₆	Ambient	0.5%-20%	5.30 ^a	4.6
Benzene-d ₆	Ambient	1%	0.80 ^a	4.6
Dioxan-d ₈	Ambient	1%, 10%	4.77 ^a	4.4
CD ₃ CN	Ambient	1%	4.00 ^a	4.6
DMSO-d ₆	Ambient	1%, 10%	6.22 ^a	4.6
Acetone-d ₆	303 K	1%	5.48 ^b	4.6
Acetone-d ₆	273 K	1%	5.68 ^b	4.6
Acetone-d ₆	243 K	1%	5.89 ^b	4.6
Acetone-d ₆	213 K	1%	6.17 ^b	4.6

^aAt 80 MHz ^bAt 500 MHz.

The downfield displacement of the chemical shift of hydrogen-bonded systems with increased solvent polarity is a well-known phenomenon¹²⁰, and is largely due to specific solute-solvent interactions. The solvents employed in this study are, in fact, mostly ones in which local ordering around polar centres of solute molecules is highly likely. For example, if one takes the chemical shift (delta 2.08) in chloroform, the solvent least likely to interact specifically with (7), as a reference point, a clear upfield ASIS effect¹²¹ is apparent in benzene (Table 7), while in solvents with pronounced electron-donating properties (in fact, themselves able to participate in hydrogen bonding with alcoholic solutes), large downfield shifts are observed. The range of solvents explored in this study was not large enough for a reliable correlation between chemical shift and solvent parameters to be

established. Nonetheless, within the limits of the experiment, no linear relationship between chemical shift and various solvent polarity or basicity parameters (for example, $E_T(30)$ values,¹²² aqueous pK_a values,¹²³ or Kamlet-Taft β values¹²⁴ appears to exist; and even with more complex relations like the Kirkwood function,¹²⁵ no linear relationship could be found. The last-mentioned case, at least, provides confirmation that non-specific interactions of the solvent with the hydrogen bond are unimportant. Finally, it should be pointed out that the nearly linear downfield displacement (in acetone) of the hydroxyl chemical shift with decreasing temperature is again a well-precedented phenomenon in hydrogen bonded systems, and has usually been ascribed to shifts in association equilibria favouring a smaller fraction of broken hydrogen bonds with decreasing temperature.¹²⁶ The experimental observation is illustrated in Figure 5.

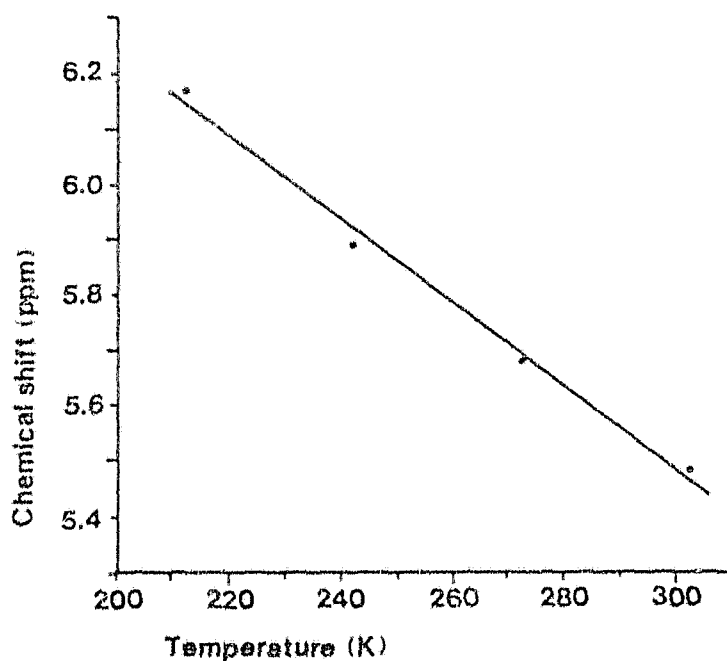


Fig. 5. Chemical shift versus temperature for compound (7).

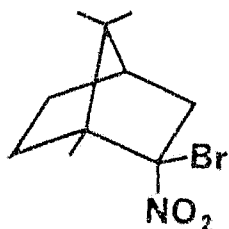
CHAPTER 3

THE PREPARATION AND CRYSTALLOGRAPHIC ANALYSES OF TWO CHLORONITRONORBORNANOLS

3.1. Introduction

The results obtained from the dichloro derivative, (7), regarding hydrogen bonding, prompted the investigation of other 2,6-functionalised bicyclic nitroalcohols. A point that was stressed in the discussion of the intramolecular hydrogen bond in compound (7) is the influence that neighbouring functional groups have on the specific orientation of the nitro group, in particular, the alpha chlorine atom. It was decided to study hydrogen bonding in 2,6-nitroalcohols in general.

Apart from the structure of (-)-2-bromo-2-nitrocamphane, (34), little information could be obtained from the literature regarding the orientation of an endo nitro group at the 2-position of the norbornyl system.¹⁰⁹



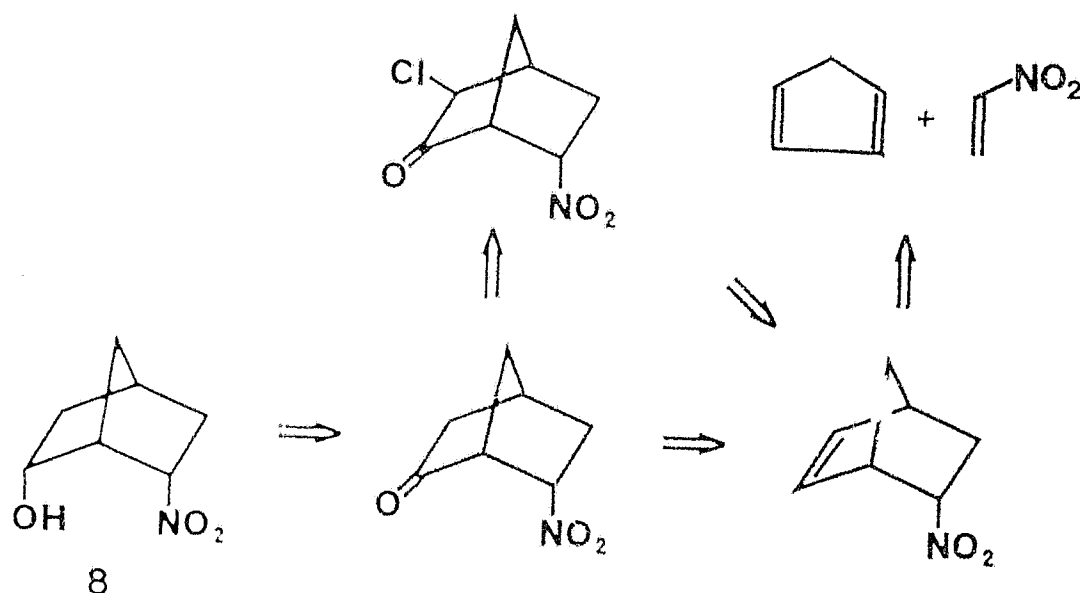
34

In order to investigate the structural consequences of such a system it was necessary to devise syntheses of molecules containing the relevant functional groups. The target molecule initially chosen was the simple system, 6-endo-nitrobicyclo[2.2.1]heptan-2-endo-ol, (8).

The hope in choosing this simple target molecule was that the

structural effects of non-essential substituents would be eliminated, since the nitro group in the molecule could be studied in the presence of the hydroxyl group alone. A further advantage is the absence of heavy atoms which could introduce difficulties in locating the hydrogen atoms crystallographically.

The most attractive retro-synthetic pathways chosen for compound (8) are depicted in Scheme 4.



Scheme 4

The merit of these disconnections of the target molecule lies in the utility of nitroethylene as a suitable synthon for the formation of the norbornene structure, and that relatively few functional group interconversions would produce the required compound.

Nitroethylene is conveniently prepared by heating 2-nitroethanol¹²⁷ with phthalic anhydride and allowing the nitroethylene to distil at reduced pressure.¹²⁸ Nitroethylene is stable as a standard solution in benzene for at least six months when stored in a refrigerator at ca. 10°C as was shown by Ranganathan and co-workers.¹²⁹

In the following section, the methods by which the transformations required in the retrosynthetic analysis have been accomplished in the literature will be briefly surveyed. In sections 3.3, 3.4 and 3.6, the different reactions performed, and the problems associated with them, will be described. Finally, the X-ray crystallographic determination of two nitronorbornanol structures initially prepared will be discussed.

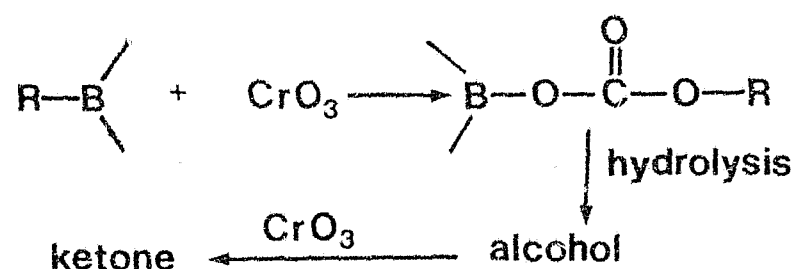
3.2. Literature survey of synthetic methods

3.2.1. Direct conversion of alkene to ketone

There are several methods for the preparation of ketones from alkenes but only those most suitable for the present study will be dealt with in this survey¹³⁰. These are based either on hydroboration-oxidation or the rearrangements of epoxides.

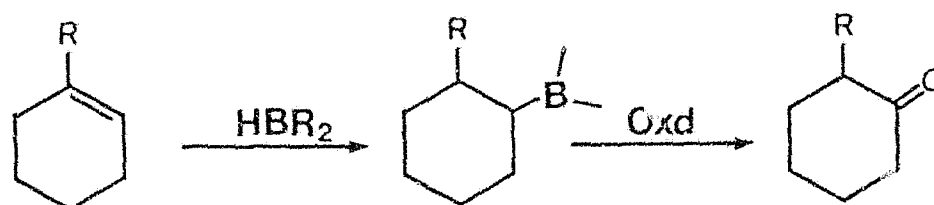
Brown and co-workers¹³¹ have extensively studied the reactivity of pyridinium chlorochromate¹³² towards several organoboranes. The olefins were transformed into the corresponding organoboranes by treatment with borane/dimethyl sulphide in dichloromethane and the resulting organoboranes, without isolation, were oxidised with excess pyridinium chlorochromate in the same solvent to give the ketones in very good yields. Lane reported¹³³ that borane-dimethyl sulphide has numerous advantages over other borane complexes mainly because of its miscibility with various solvents. Kao et al.¹³⁴ have published some work on medium-sized cyclic ketones employing this method but involving an anhydrous work-up procedure. They proposed that the oxidation of organoboranes with pyridinium chlorochromate probably proceeds via the formation of the alcohols which are subsequently oxidised to the ketones. Analysis of an incomplete reaction mixture by infrared and gas-liquid chromatography showed the presence of alcohol and

ketone. The proposed mechanism is outlined in Scheme 5.



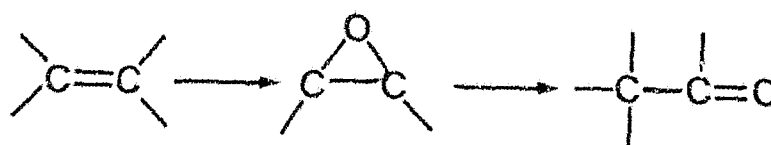
Scheme 5

The oxidation of organoboranes with aqueous chromic acid¹³⁵ is known to give ketones in fair yields and the reaction sequence is shown in Scheme 6. The tedious extractive work-up and strong acidic conditions employed limit the utility of these reactions.



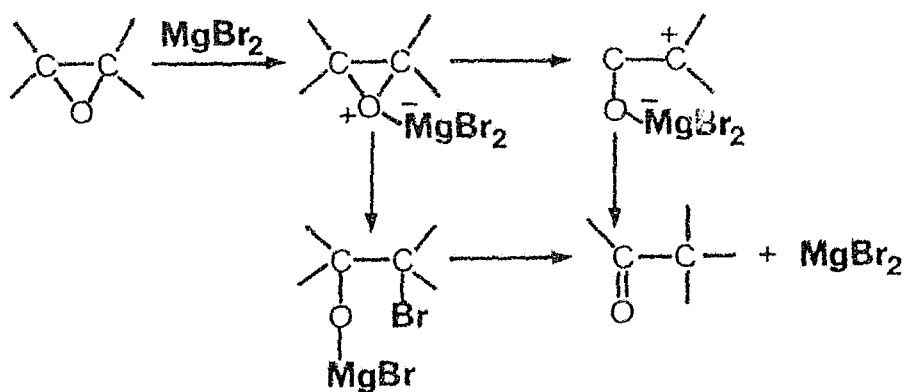
Scheme 6

A useful synthetic reaction of epoxides is their acid-catalysed rearrangement to carbonyl compounds as was reviewed by Parker and Isaacs.¹³⁶ The rearrangement is outlined in Scheme 7.



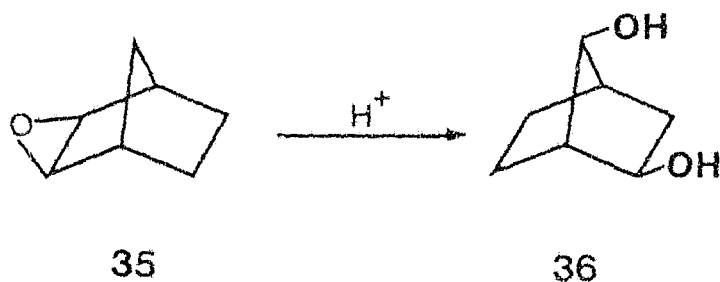
Scheme 7

Mineral acids or Lewis acids such as boron trifluoride etherate or magnesium bromide are frequently used as catalysts. House¹³⁷ suggested that the isomerism of a substituted oxirane to a carbonyl compound in the presence of magnesium bromide may follow two different reaction paths as shown in Scheme 8.

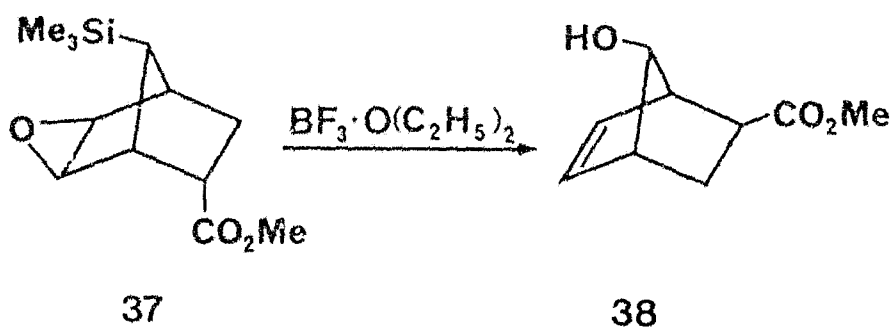


Scheme 8

Kwart and Vosburgh¹³⁸ showed that 2,3-*exo*-epoxynorbornane, (35), could be hydrolysed to the 2,7-diol, (36). Obviously, rearrangement of the carbon skeleton has occurred.

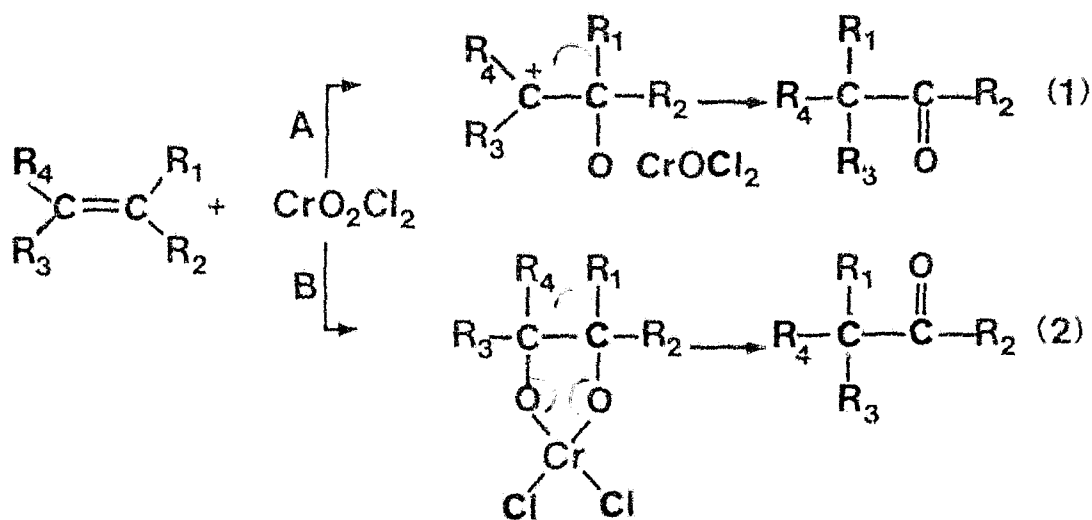


Other cases of rearrangement of the carbon skeleton have been observed. Fleming and Michael¹³⁹ reported the rearrangement of the epoxide (37) with boron trifluoride diethyl etherate to give 7-hydroxynorbornane (38) in 67% yield. The two examples show that ketone synthesis by rearrangement of epoxides may not be useful in the present work.



3.2.2. Conversion of alkene to ketone via the α -chloroketone
 Sharpless *et al.*¹⁴⁰ have found that reaction of disubstituted olefins with chromyl chloride in acetone produces the alpha-chloroketones. The addition of zinc dust to the crude reaction

mixture results in reduction of the chloro ketones to the corresponding ketones in a high yield. The key to the success of this procedure appears to be the use of the more polar solvent in comparison with previously reported halogenated organic solvents. The reaction presumably involves an electrophilic attack of chromyl chloride at the double bond via eqs. 1 or 2 to give the intermediates A or B, either of which could rearrange to give a carbonyl product.¹⁴¹



Meinwald *et al.*¹⁴² reported the addition of nitrosyl chloride to norbornene to form norbornene nitrosochloride which can be converted directly into the chloro ketone, (39), by warming with levulinic acid and hydrochloric acid.



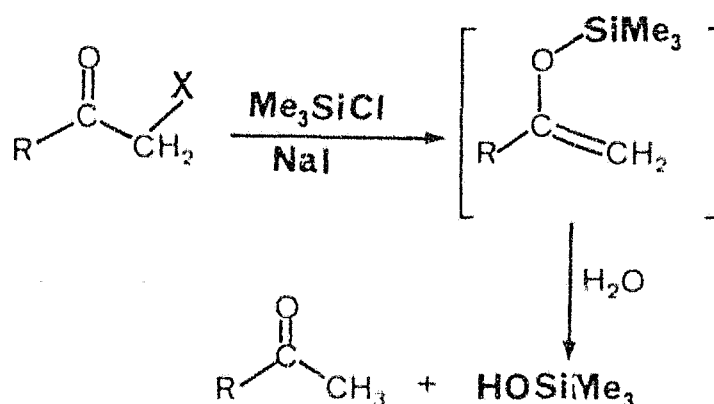
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3.2.3. Hydrogenolysis of α -haloketones

Hydrogenolysis in organic chemistry is defined as the cleavage of a single bond uniting carbon with another atom or group, resulting in replacement of that atom or group by hydrogen. Recently Pinder conducted a survey on hydrogenolysis of carbon-halogen

bonds.¹⁴³ Generally, for organic halides the order of ease of reductive dehalogenation in the same type of structural environment is: $I > Br > Cl > > F$. Sometimes caution has to be exercised when reducing a halogen from a molecule that contains a sensitive group like the nitro group.

Olah *et al.*¹⁴⁴ employed chlorotrimethylsilane/sodium iodide effectively for the reduction of both alpha-haloalkanones as well as alpha-halocycloalkanones. The mechanism of the reaction may be represented as in Scheme 9.



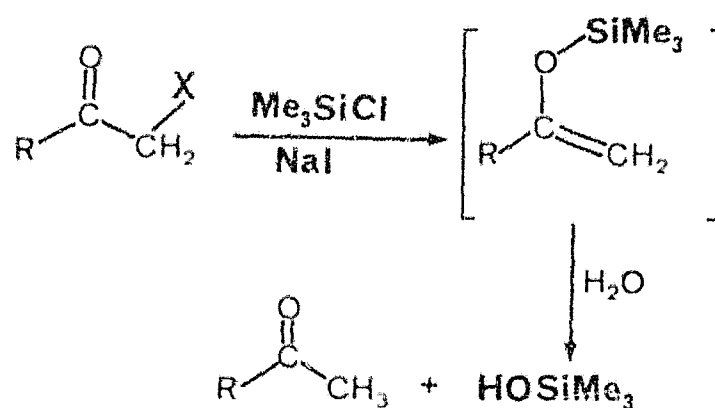
Scheme 9

Chlorotrimethylsilane and sodium iodide are readily available, are inexpensive and give good yields in simple and easy-to-carry-out reactions under mild conditions. α -Halogenated cycloalkanones are reduced at room temperature in the presence of excess iodide and ketones are obtained in 75-98% yield in 8-12 hours.

Tse-Lok Ho¹⁴⁵ has found that iodotrimethylsilane in chloroform or acetonitrile can hydrodehalogenate alpha-haloketones at room temperature as shown in Scheme 10.

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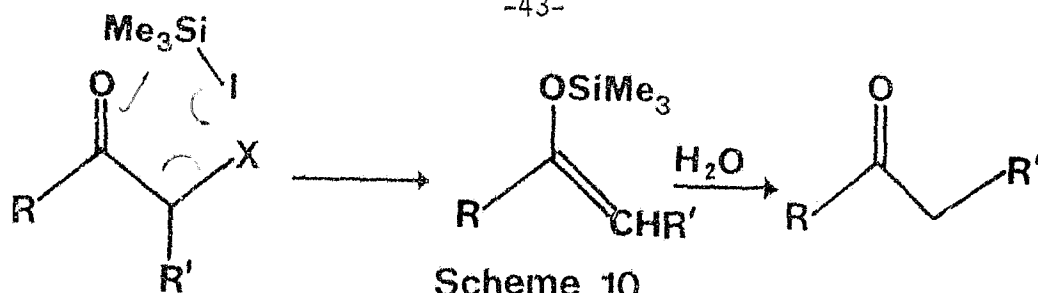
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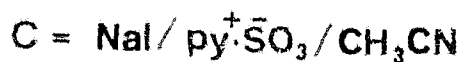
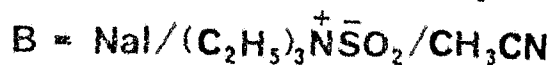
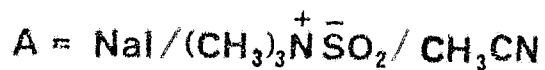
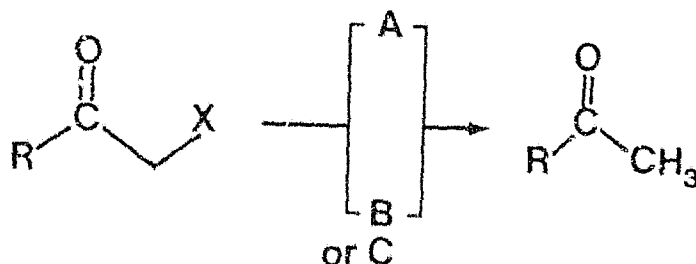
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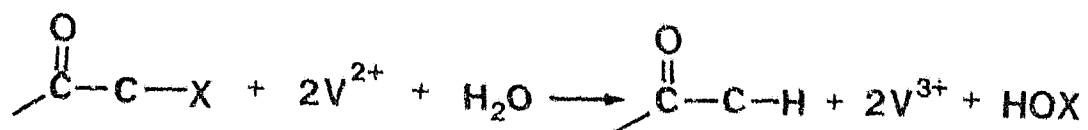


He claimed that the facility of this process originates from the favourable six-centered transition state wherein hard-hard centres interact at one end and soft-soft centres interact at the other end.

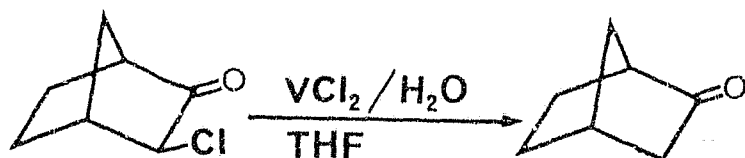
Sodium iodide/trialkylamine/sulphur dioxide complexes are specific reagents for the reduction of aryl alpha-haloalkanones, whereas sodium iodide/pyridine/sulphur trioxide complex can be used as a general reducing system for alpha-haloketones.¹⁴⁶ Sodium iodide removes the alpha-halogen atom as indicated, assisted by polarisation of the C-X bond, brought about by complexing the carbonyl group by sulphur trioxide.



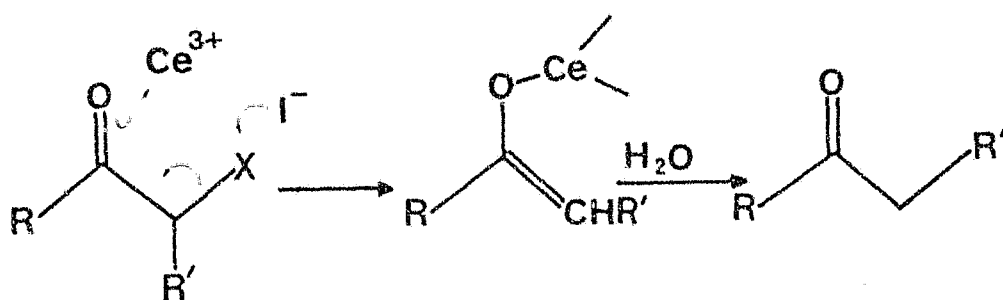
Olah and Ho¹⁴⁷ reported the facile hydrodehalogenation of alpha-haloketones by vanadium(II) chloride, which proceeds according to the following stoichiometry:



They achieved the following hydrodehalogenation in an 80% yield.



An efficient procedure for the hydrogenolysis of alpha-haloketones with cerium(III) iodide was reported by Ho.¹⁴⁸ The system that contains cerium(III) and iodide ions functions as shown in Scheme 11.

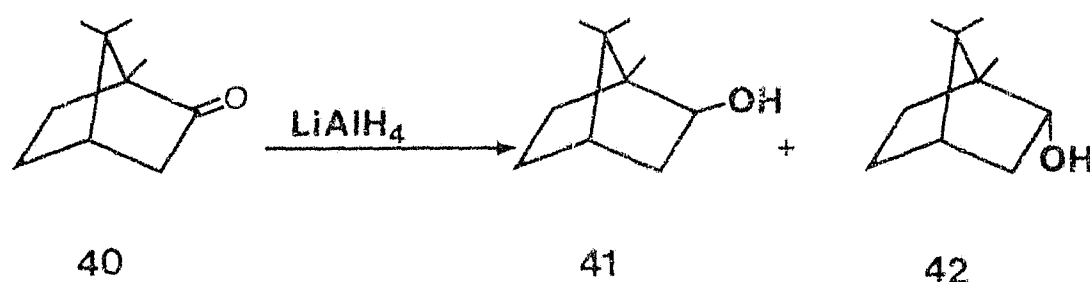


Scheme 11

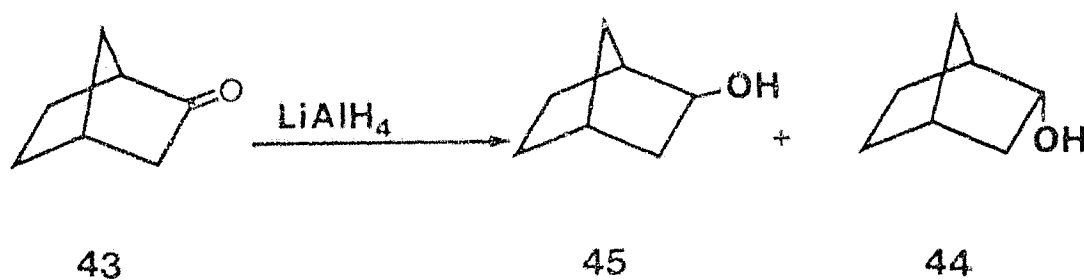
3.2.4. Reduction of bicyclic ketones with metal hydrides

Complex metal hydrides offer the most convenient method for the reduction of ketones to the corresponding alcohols, and reactions which proceed by transfer of hydride ions are widespread in organic chemistry.^{149,150} Lithium aluminium hydride, a highly reactive, powerful reducing agent, rapidly and efficiently reduces ketones as well as a number of other functional groups including the nitro group. Sodium borohydride, a much milder reagent, is often used in methanol and under these conditions it rapidly reduces ketones, but it is inert towards most other functional groups. The disadvantage of the usual reagents like lithium aluminium hydride and sodium borohydride is that they reduce relatively unhindered cyclic ketones either with little or no stereoselectivity or give predominant formation of the thermodynamically more stable isomer. In a bridged ring system, with a methyl group in the 7-position, the carbonyl group is much more hindered from the exo face than

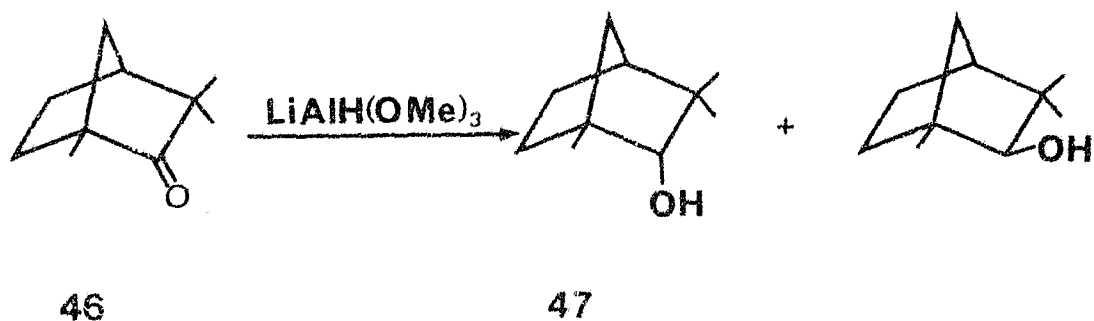
from endo face and many reductions of bicyclic ketones have been reported. Camphor, (40), for example, reacts with lithium aluminium hydride in diethyl ether to give an 80% yield of a mixture of 89% isoborneol (2-exo-hydroxybornane), (41), and 11% borneol (42) (2-endo-hydroxybornane).¹⁵¹



Ketones with an unsubstituted bridge, such as norcamphor (43) and its derivatives, are attacked (because of the electrostatic repulsion of the nucleophilic carbonyl group) mainly from the exo side, which in this case is less hindered. Lithium aluminium hydride in diethyl ether reduces norcamphor in 90% yield,¹⁵² with a 91:9 ratio of α -norborneol (2-endo-hydroxynorbornane), (44) and β -norborneol (2-exo-hydroxynorbornane), (45).



The introduction of alkoxy substituents into lithium aluminium hydride provides a simple, convenient means of modifying the steric requirements and reducing properties of this powerful reducing agent.¹⁵³ With norcamphor, (43), lithium trimethoxyaluminium-hydride gave much higher stereoselectivity than lithium aluminium hydride (2% exo-norborneol (45) and 98% endo-norborneol (44)). The reduction of fenchone, (46), yielded endo fenchyl alcohol (47) in a purity of at least 97%.



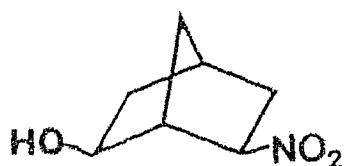
The selectivity obtained in these reactions increases with the steric demand of the reducing agent, and some remarkably stereoselective reactions have been achieved using complex hydride reagents specifically designed for the purpose, like the trialkylborohydrides for the stereoselective reduction of ketones.^{154,155} The lithium and potassium tri-sec-butylborohydrides (generally known as selectrides), are probably the best reagents yet available for the stereoselective reduction of bicyclic ketones.¹⁵⁶

3.2.5. Syntheses of nitronorbornanols

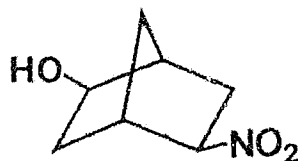
Grob and co-workers¹⁵⁷ reported the syntheses of certain exo, exo disubstituted nitronorbornanols. The starting material was prepared from the cycloaddition of nitroethylene with cyclopentadiene. The mixture of epimers (**48**) and (**48b**) could be separated by fractional distillation under vacuum.



The pure isomer, (**48b**), was then hydroborated and the resulting organoborane was cleaved with hydrogen peroxide and 3M sodium acetate solution to give a mixture of 6-exo and 5-exo-nitroalcohols, (**48c**) and (**48d**).



48c



48d

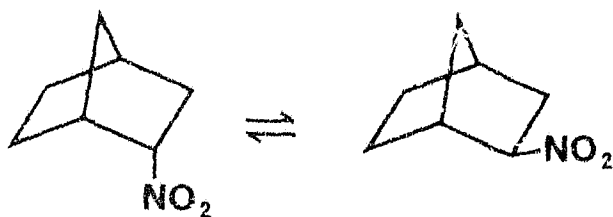
In a subsequent paper Grob and his co-workers¹⁵⁸ published their attempted syntheses of some endo, endo disubstituted nitronorbornanols. They found that the hydroboration of (48) was not very successful, because of the very ready epimerisation of the nitro group, and that the nitroalcohols (48c) and (48d) were formed instead.

These results are thus in agreement with the results we obtained before the latter paper was published.

3.3. Attempted preparation of ketone from alkene

As indicated in section 3.1 (page 36), the synthetic approaches to simple nitronorbornanols adopted in the present work all begin with 5-endo-nitrobicyclo[2.2.1]hept-2-ene, (48). Roberts and co-workers¹⁵⁹ reported the [4+2] cycloaddition of nitroethylene with cyclopentadiene to produce almost exclusively the 5-endo-nitrobicyclo[2.2.1]hept-2-ene, (48), isomer as a colourless semi-solid at room temperature.

The reaction was found to proceed at a temperature as low as -100°C but for practical reasons, however, the addition is performed normally at temperatures of -15 to 0°C .¹⁶⁰ The stereochemical preference of the nitro group in the 5-position of bicyclo[2.2.1]-heptene has been determined by base equilibration using potassium *t*-butoxide in *t*-butyl alcohol.¹⁶¹



The exo/endo ratio was found to be 1.80 at 75°C. These workers could not separate the two isomers even on an analytical scale.

In the present work nitroethylene was conveniently prepared from 2-nitroethanol¹²⁷ and phthalic anhydride in a 76% overall yield according to the procedure of Buckley and Scaite.¹²⁸ The Diels-Alder reaction of nitroethylene and cyclopentadiene produced 5-endo-nitrobicyclo[2.2.1]hept-5-ene, (48), in almost 100% yield.¹²⁹

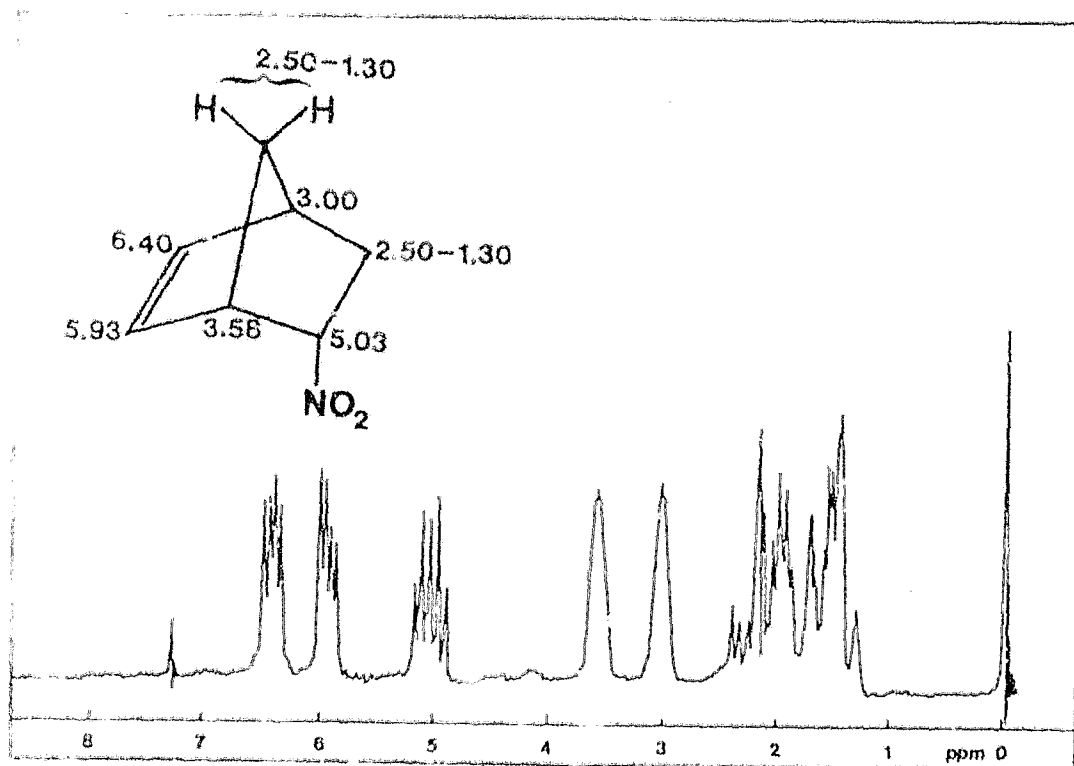
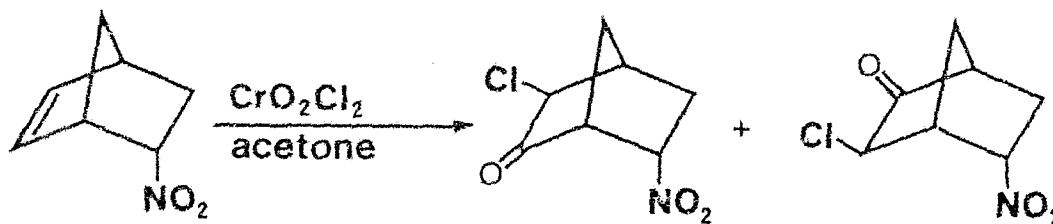


Fig. 5. ¹H NMR spectrum of compound (48) in deuteriochloroform.

The proton nuclear magnetic resonance spectrum¹⁶² of this

compound (Figure 5) shows a double doublet at 6.40 ppm for H(2) with coupling constants of 6 and 3 Hz to H(3) and H(1) respectively. The double doublet at 5.93 ppm corresponds to the coupling of H(3) to H(2) and H(4), resulting in coupling constants of 6 and 3 Hz. The multiplet at 5.03 ppm (J ca. 4 Hz) originates from the coupling of the proton alpha to the nitro group to H(1), H(6x) and H(6n). The resonances at 3.58 and 3.00 ppm are due to the two bridgehead protons, H(1) and H(4). The broad patterns of these peaks are derived from several coupling interactions with other protons in this rigid system. The complex multiplet at 2.50-1.30 ppm corresponds to four protons, namely H(7s), H(7a), H(6n) and H(6x). The mass spectrum of the compound shows no molecular ion peak for compound (48), but there is a relative^{-ly} abundant peak at m/e 93 which is due to the loss of the nitro group. The base peak appears at m/e 66 and is typical of a retro Diels-Alder fragmentation route.

The initial approach adopted for functionalising the C=C double bond was the Sharpless¹⁴⁰ one. The alkene was converted to the alpha-chloroketones with chromyl chloride in acetone at -78°C as shown in Scheme 12.



Scheme 12

Work-up gave a viscous, yellow oil in a 58% crude yield. Thin-layer chromatography indicated that the mixture contained two major components. An attempt to separate the mixture into its different components produced only a few fractions that were significantly separated leaving the bulk of the product still as a mixture. The

separated fractions, however, yielded white solids.

The more polar was identified as (49), and the less polar as (50). Compound (49) was identified as 3-exo-chloro-6-endo-nitro-bicyclo[2.2.1]heptan-2-one and has the following spectral features. The infrared spectrum shows characteristic stretching absorption bands for an alpha-haloketone (1762 cm^{-1}), and a nitro group (1550 and 1368 cm^{-1}). The molecular ion peak in the mass-spectrum is found at m/e 189 and the isotope pattern clearly indicates one chlorine atom. The subsequent loss of the nitro group accounts for peaks at m/e 143. The removal of a unit of carbon monoxide from molecule (49) gives a peak at m/e 115. The base peak appears at m/e 79.

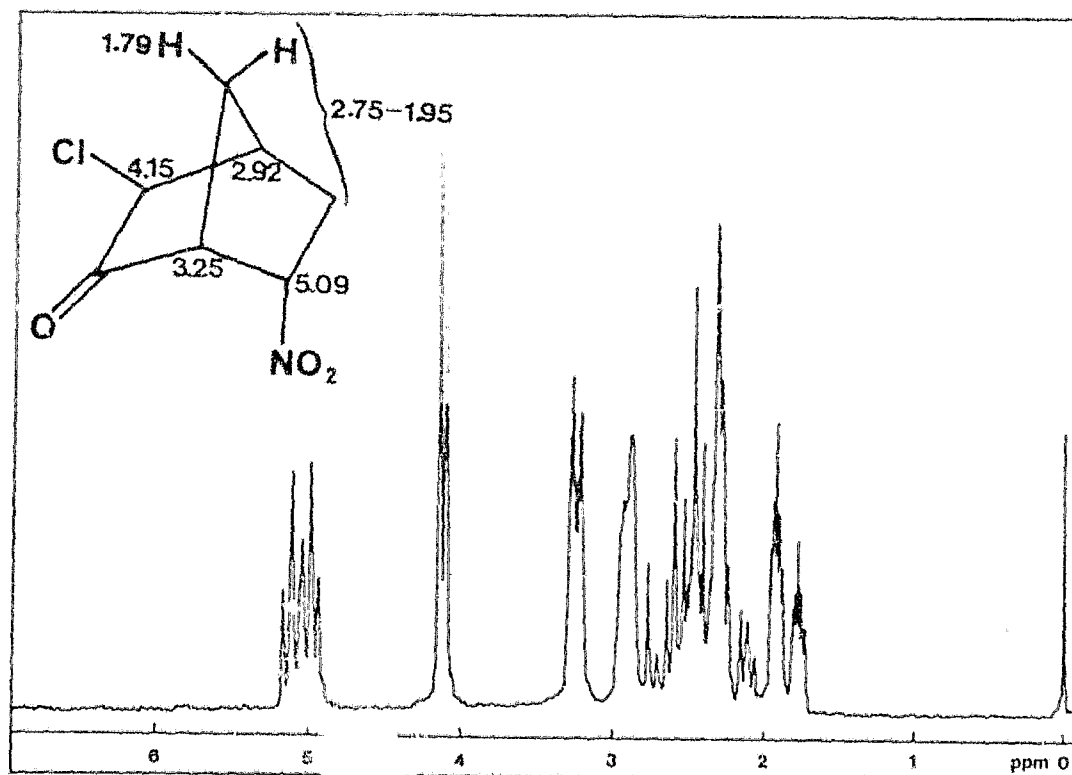


Fig. 6. ^1H NMR spectrum of compound (49) in deuteriochloroform.

The proton nuclear magnetic resonance spectrum (Figure 6) of (49) contains of a five-line multiplet at 5.09 ppm for proton H(6).

Coupling between H(6), H(5x) and H(1) (J ca. 4.5 Hz) indicates that the nitro group is endo. A well defined doublet at 4.15 ppm ($J = 3.4$ Hz) corresponds to proton H(3), which is engaged in long-range coupling to H(7s). The coupling between H(3) and H(4) is zero since the dihedral angle between them approximates ninety degrees. H(1) and H(4) appear as multiplets at 3.25 and 2.92 ppm. Three protons, namely H(5x), H(5n) and H(7s), are superimposed as a complex multiplet in the region 2.75-1.95 ppm. H(7a) is a doublet at 1.79 ppm ($J = 12$ Hz) which exhibits some additional fine coupling too.

Compound (50), 3-exo-chloro-6-exo-nitrobicyclo[2.2.1]heptan-2-one, m.p. 78-79°C, is an isomer of (49). The infrared spectrum shows the cyclic alpha-haloketone by a peak at 1762 cm^{-1} , as well as a nitro group (1550 and 1367 cm^{-1}). The mass-spectrum confirms the molecular mass of compound (50) as 189, and again the isotope pattern characteristic of chlorine is present. The peak at m/e 142 is due to the loss of the nitro group, and the further loss of the chlorine atom gives a peak at m/e 107.

The proton nuclear magnetic resonance spectrum (Figure 7) has a four-line multiplet at 4.56 ppm for H(6) with a coupling constant of ca. 3.9 Hz. This splitting pattern arises from coupling with protons H(5x), H(5n) and H(7s). Long-range W-coupling¹⁶³⁻¹⁶⁵ with H(7a) causes the signal of proton H(3) to split up into a doublet with a coupling constant of 2.7 Hz. The broad multiplets at 3.39 and 2.86 ppm are the bridgehead protons H(1) and H(4). The multiplet from 2.60-2.90 ppm accounts for the protons H(5x) and H(5n). The protons H(7s) and H(7a) couple to form doublets at 2.31 and 2.00 ppm resulting in a coupling constant of 11 Hz.

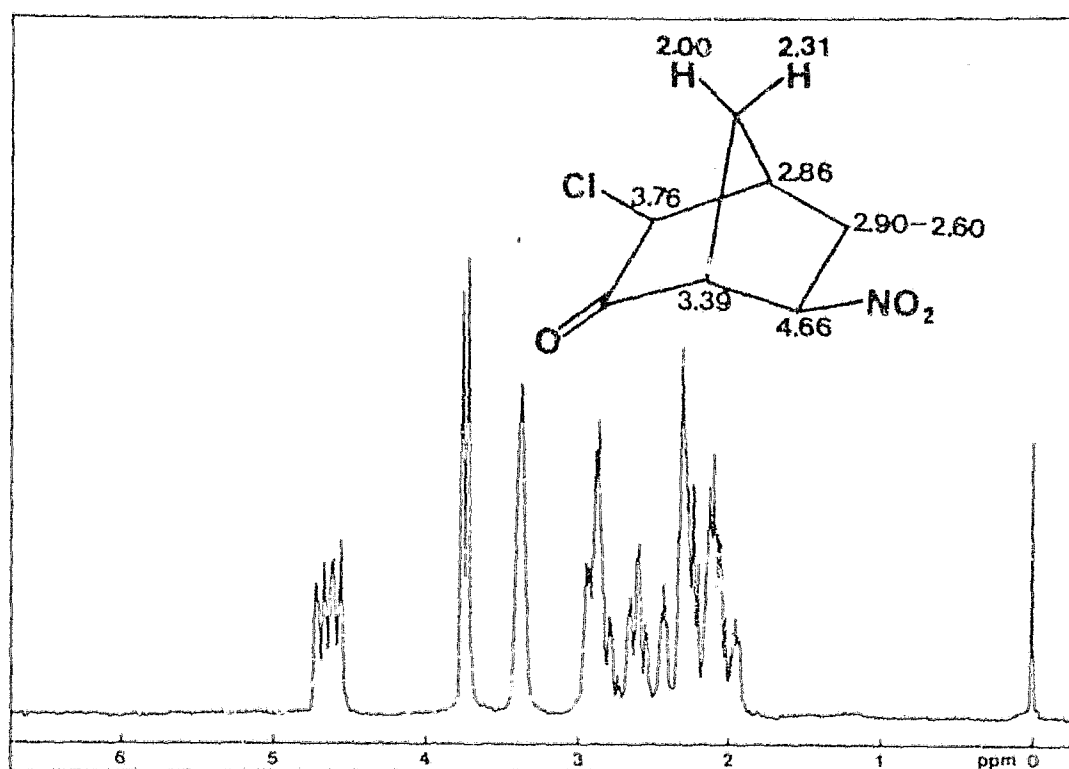
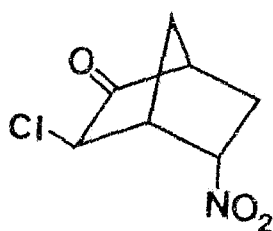
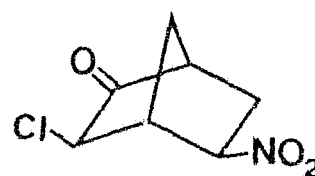


Fig. 7. ^1H NMR spectrum of compound (50) deuteriochloroform.

The fact that none of the other positional isomers (51 and 52) could be isolated from the reaction mixture is quite surprising in view of the proposed electrophilic attack of the chromyl chloride at the symmetrical double bond (see section 3.2.2, page 41) which should contain at least (51). However, it is possible that these compounds were formed, but were not separated chromatographically. The purified products (49) and (50) represent only a 19% recovery from the column.



51



52

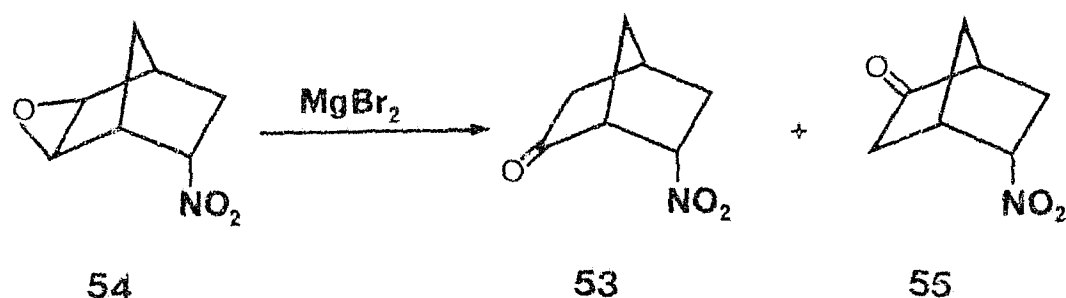
The next step in the synthesis was the hydrodehalogenation of the

chloroketones to furnish the ketones. The presence of the nitro group in these compounds introduced some difficulty in this step because most of the frequently used dehalogenation reagents might also reduce the nitro group. Nonetheless, a few milder reagents were tried instead. The first method employed was the method of Olah and co-workers¹⁴⁴ which uses sodium iodide/chloro-trimethylsilane. The reduction was performed under a nitrogen atmosphere but even after 48 hours at room temperature and 26 hours of refluxing in acetonitrile no change had occurred as indicated by thin-layer chromatography. Olah reported that alpha-halogenated cycloalkanones are reduced at room temperature and ketones are obtained in 75-98% yield in 8-12 hours, but also concluded that 2-chlorocyclopentanone and 2-chlorocyclohexanone are exceptions and require more time ca. 48 hours).

The second method tried was the method of Ho¹⁴⁸ which utilises cerium(III) iodide, but again without any successful dechlorination of the bicyclic chloro ketones. Desyl chloride is the only chloro compound studied by Ho; most of his examples are bromo ketones. A method that uses suspended vanadium(II) chloride¹⁶⁶ in tetrahydrofuran was employed as well,¹⁴⁷ but only starting material was recovered in a quantitative yield. The conventional method of zinc in acetic acid resulted in a complex mixture containing several products. An explanation for the failure of these methods to effectively dechlorinate the chloro ketones could be the steric barrier experienced with bicyclic ketones compared with normal open chain or monocyclic halo-ketones.

In view of the failure to hydrogenolise these alpha-chloroketones by mild methods, it was decided to attempt the conversion of alkene (48) to ketone directly. An alternative approach to the ketone (53) via the rearrangement of a suitable epoxide was felt to be a potentially useful approach.¹³⁶ This would involve the

acid-catalysed (or Lewis-acid catalysed) rearrangement¹³⁷ of (54), to produce a mixture of the two ketones (53) and (55) as outlined in Scheme 13.



Scheme 13

2,3-exo-Epoxy-5-endo-nitrobicyclo[2.2.1]heptane, (54), was prepared as a crystalline substance from 5-endo-nitrobicyclo[2.2.1]hept-5-ene, (48), in a 94% crude yield using m-chloroperbenzoic acid in dichloromethane without the aid of a buffer. The substance was recrystallised from diisopropyl ether to give a white solid in an 87% yield, m.p. 105-107°C. The mass spectrum shows a molecular ion peak at m/e 156 and the base peak appears at m/e 139 which corresponds to the opening of the epoxide ring and the subsequent loss of a hydroxyl group. The infrared spectrum shows the presence of a nitro group with absorption bands at 1540 and 1375 cm^{-1} .

The proton nuclear magnetic resonance spectrum (Figure 8) has a 6-line multiplet at 4.83 ppm for proton H(5), alpha to nitro group, which couples with the bridgehead proton, H(4), and hydrogens H(6x) and H(6n) respectively. The coupling constants in norbornyl systems are well defined because of the rigidity of the skeleton and some typical values are: $J_{\text{H}(4)\text{-H}(5)}$ is normally 3-5 Hz, $J_{\text{H}(5)\text{-H}(6x)}$ is 7-10 Hz and $J_{\text{H}(5)\text{-H}(6n)}$ is 4-6 Hz.^{167,168} These values agree with those calculated from Dreiding models using the Karplus equation⁹⁷ relating the dihedral angle of protons on vicinal carbon atoms to their coupling constant. The multiplet centered at 3.20 ppm originates from the similar chemical shifts of H(2), H(3)

and H(4). The signal at 2.65 ppm is due to proton H(1). Spin-decoupling was used to deduce the structure of this compound and irradiation at 2.65 ppm causes the signals at 2.14 and 2.05 ppm to collapse to two broad singlets. The signals at 2.14 and 2.05 ppm are assigned to the protons H(6x) and H(6n). The protons H(7s) and H(7a) give rise to the signals at 1.53 and 0.88 ppm, respectively, with a coupling constant of 11 Hz. Irradiation at 0.88 ppm causes the doublet at 1.53 ppm to collapse to a singlet.

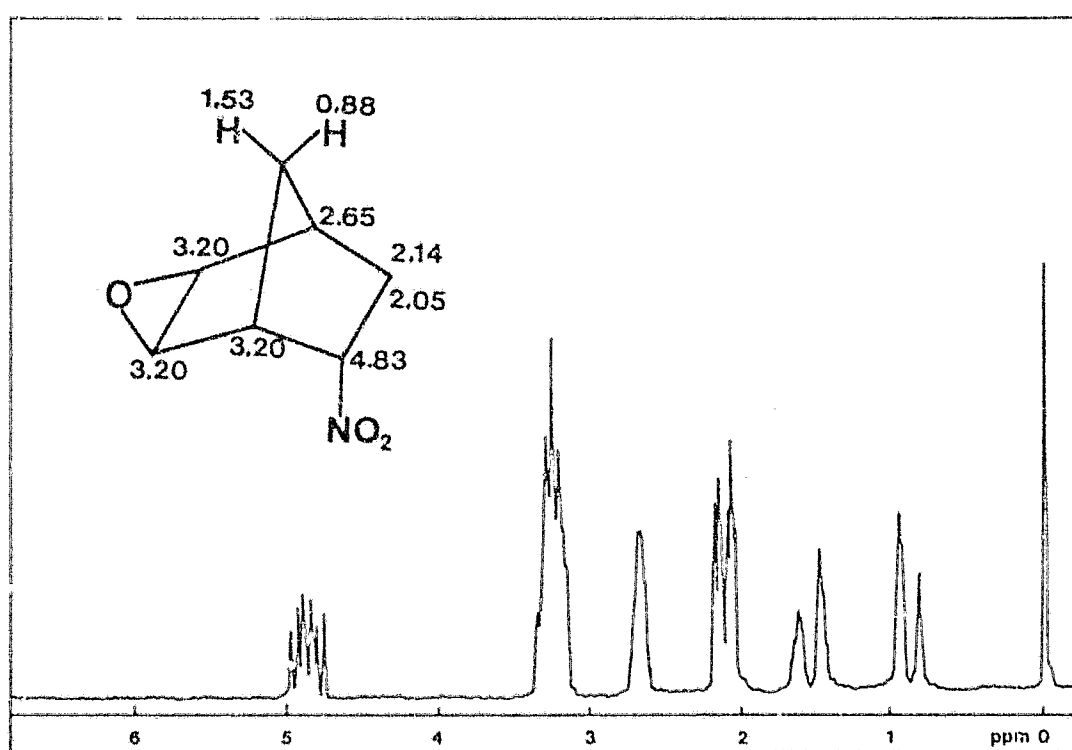
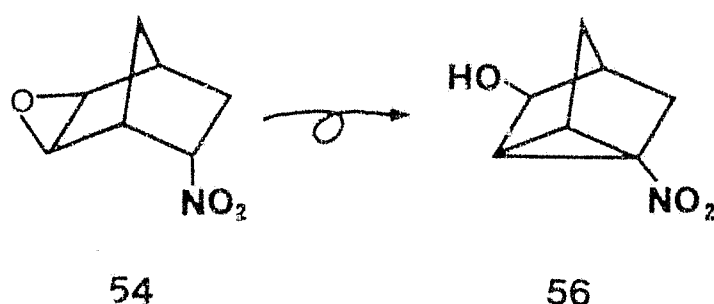


Fig. 8. ^1H NMR spectrum of compound (54) in deuteriochloroform.

The rearrangement of (54) was attempted using magnesium bromide as a Lewis acid.¹³⁷ The mixture was stirred at room temperature for 35 hours after which thin-layer chromatography showed that no starting material had remained. A white crystalline solid was obtained in an 89% yield after removal of the solvent, and recrystallisation of this substance from cyclohexane and ethyl acetate produced a pure compound in 54% overall yield, m.p. 77-78°C.

A thin-layer chromatography plate sprayed with 2,4-dinitro-diphenylhydrazine showed no evidence of a carbonyl functionality. Microanalysis was found to be consistent with the proposed structure, but the infrared spectrum showed a broad absorption band at 3260 cm^{-1} for the presence of a hydroxyl group and strong bands at 1510 and 1374 cm^{-1} for a nitro group. The mass spectrum showed a molecular ion peak at $m/e\ 157$, a peak at $m/e\ 139$ for the loss of a water molecule and a peak at $m/e\ 111$ for the loss of the nitro group. The consideration of these facts clearly indicated that the expected product had not formed, but instead a rather unexpected product had been produced as can be seen in Scheme 13. The product was identified as being 5-nitrotricyclo[2.2.1.0^{3,5}]heptan-2-ol, (56).



Scheme 13

The proton nuclear magnetic resonance spectrum (Figure 9) shows a singlet at 4.13 ppm for $H(2)$ and the hydrogens $H(6x)$ and $H(6n)$ appear as a singlet at 2.60 ppm . A multiplet is located at 2.14 ppm for $H(1)$ and hydrogens $H(7s)$ and $H(7a)$ give rise to a doublet at 2.01 ppm with a coupling constant of ca. 2 Hz . The chemical shift of $H(3)$ is 1.77 ppm and the hydroxyl proton, which exchanges with D_2O , appears at 1.65 ppm .

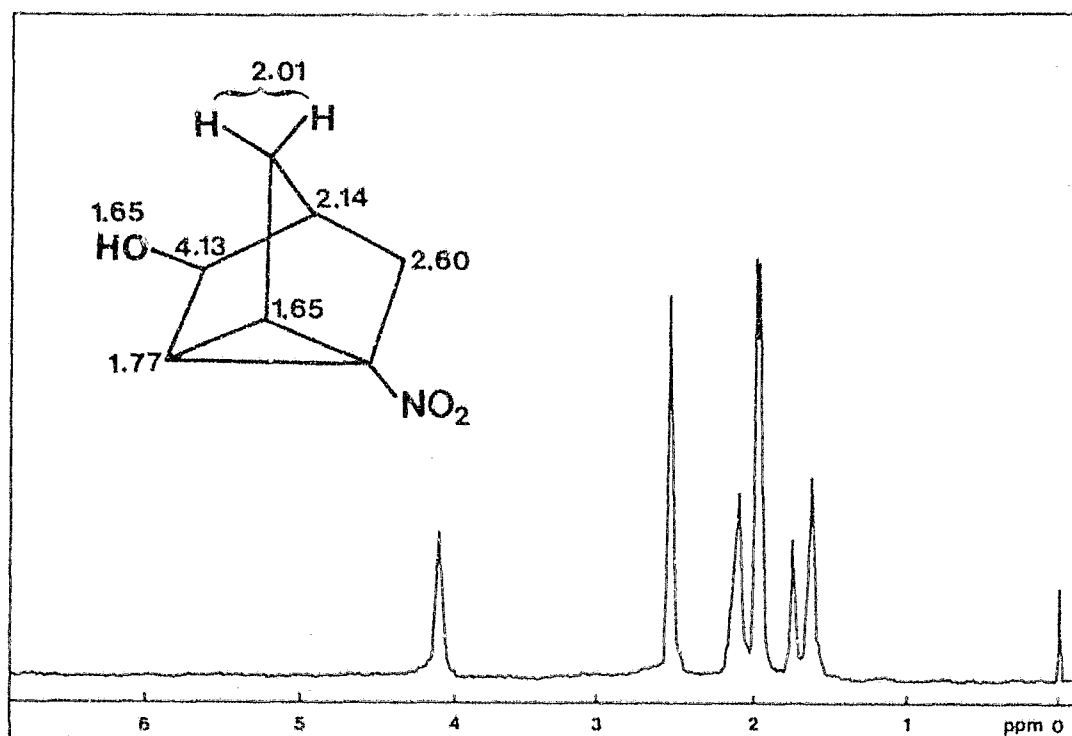
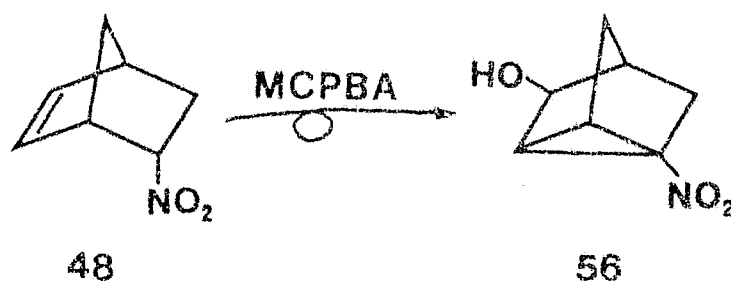


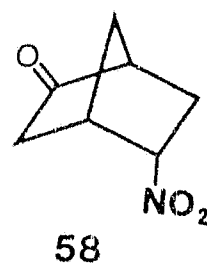
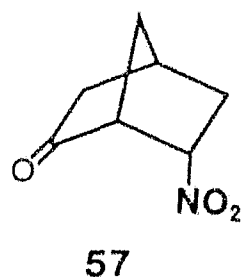
Fig. 9. ^1H NMR spectrum of compound (56) in deuteriochloroform.

The epoxide is unstable when standing at room temperature and the white solid decomposes to form a yellow substance within three weeks. In a subsequent reaction to prepare more of (54) it was found that the epoxide rearranged spontaneously to the tricyclo substance (56) on stirring at room temperature in the presence of *m*-chlorobenzoic acid.



In view of the failure of the epoxide to rearrange as desired, the final approach towards the preparation of the ketones was the hydroboration/oxidation of the alkene to produce the

ketones.¹³¹ Borane/dimethyl sulphide was used for the hydroboration step because it has certain advantages above some of the other ether-boranes.¹³³ The organoborane was oxidised with pyridinium chlorochromate¹³² and the mixture was quenched by pouring it into an ice-cold sodium bisulphite solution. The green mixture was filtered through a pad of anhydrous magnesium sulphate and neutral alumina, and evaporation of the solvent gave as product a yellow oil. Thin-layer chromatography indicated the presence of three compounds in the mixture. The low yield is attributed to the black tacky solid that formed in the reaction flask shortly after the pyridinium chlorochromate was introduced. This solid was washed several times with anhydrous ether to try and obtain a granular solid as described in the paper by Corey and Suggs.¹⁶⁹ Column chromatography was used for the separation of the mixture but resulted in an incomplete separation of the isomers. A white crystalline substance was obtained from the column and it was recrystallised from diisopropyl ether to give 43 mg of the pure compound, m.p. 126-128°C which was assigned tentatively as 6-endo-nitrobicyclo[2.2.1]heptan-2-one, (57). The spectroscopic evidence available does not allow one to decide between this structure and the alternative one, (58).



The infrared spectrum of the compound shows a strong absorption band at 1755 cm^{-1} for the presence of a ketone in a five-membered ring as well as strong bands at 1550 and 1373 cm^{-1} for unsymmetrical and symmetrical stretching vibrations of the nitro group.

The proton nuclear magnetic resonance spectrum (Figure 10) of compound (61) has a five-line multiplet with a coupling constant of ca. 4.5 Hz for proton H(6) owing to coupling with H(1), H(5x) and H(5n). H(1) appears as a multiplet at 3.08 ppm and the other bridgehead proton, H(4), is a multiplet at 2.78 ppm. The protons, H(3x), H(3n), H(5x) and H(5n), appear as a multiplet around a chemical shift of 2.25 ppm. The protons, in the 7-position of the norbornyl structure give rise to a singlet at 1.83 ppm.

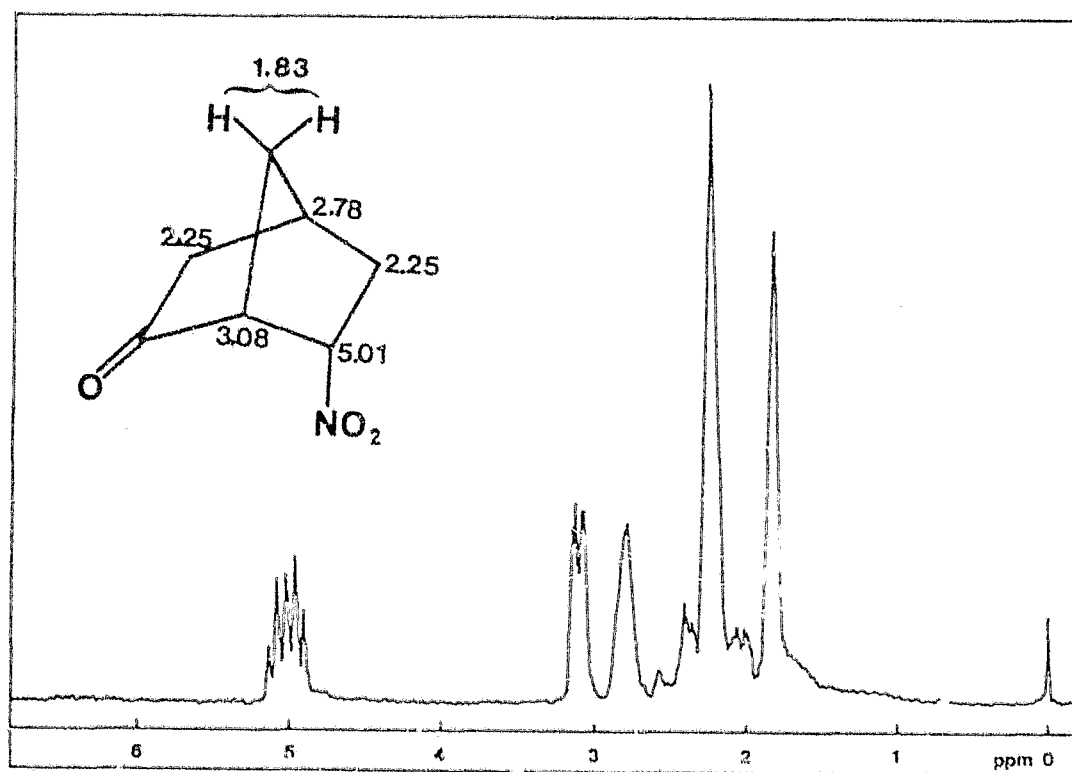


Fig. 10. ^1H NMR spectrum of compound (57) in deuteriochloroform.

3.4. Reduction of chloroketones to chloroalcohols

It was apparent at this point that the attempt to synthesise simple nitronorbornanols had been far less successful than was originally hoped. The best functionalisation of the C=C bond was with chromyl chloride, but the removal of chlorine was a failure. The decision was therefore made that, since the chloroketones were rather readily accessible, these should be reduced to chloroalcohols, since these products, though more substituted than was strictly

desirable, would nevertheless possess structural features which might encourage intramolecular OH...NO₂ hydrogen bonding.

It was initially decided to reduce the total mixture of alpha-chloroketones to the corresponding alcohols using sodium borohydride and then to attempt separation of the isomers. The reason for using sodium borohydride and not a more bulky reagent to enforce endo stereoselectivity of the hydroxyl group is that both endo and exo isomers could be obtained, and that it would be advantageous to have the spectra of all possible isomers. This reduction resulted in a crude yield of 92% in the form of a yellow oil which was subsequently separated by column chromatography. The first set of fractions gave a white solid on evaporation of the solvent and recrystallisation from diisopropyl ether gave a solid, 3-exo-chloro-6-exo-nitrobicyclo[2.2.1]heptan-2-endo-ol, (59), in a 31% yield, m.p. 117-119°C. The second set gave 3-exo-chloro-6-exo-nitrobicyclo[2.2.1]heptan-2-exo-ol, (60), in an 17% yield, m.p. 94-95°C. Other products could not be separated clearly.

The structure of (59) was unambiguously decided by X-ray crystallography (Section 3.5, page 69), but its chief spectroscopic features are as follows. The infrared spectrum shows a broad band of medium intensity for the hydroxyl stretching vibration at 3480 cm⁻¹, strong bands at 1533 and 1370 cm⁻¹ for the nitro group and a strong band at 1060 cm⁻¹ for carbon-oxygen stretching vibration. The mass-spectrum of (59) shows no molecular ion peak, but a peak at m/e 145 showing a chlorine isotope pattern is present for the loss of the nitro group from the molecule. The further loss of a unit of hydrochloric acid corresponds to a peak at m/e 108 and the base peak is found at m/e 66.

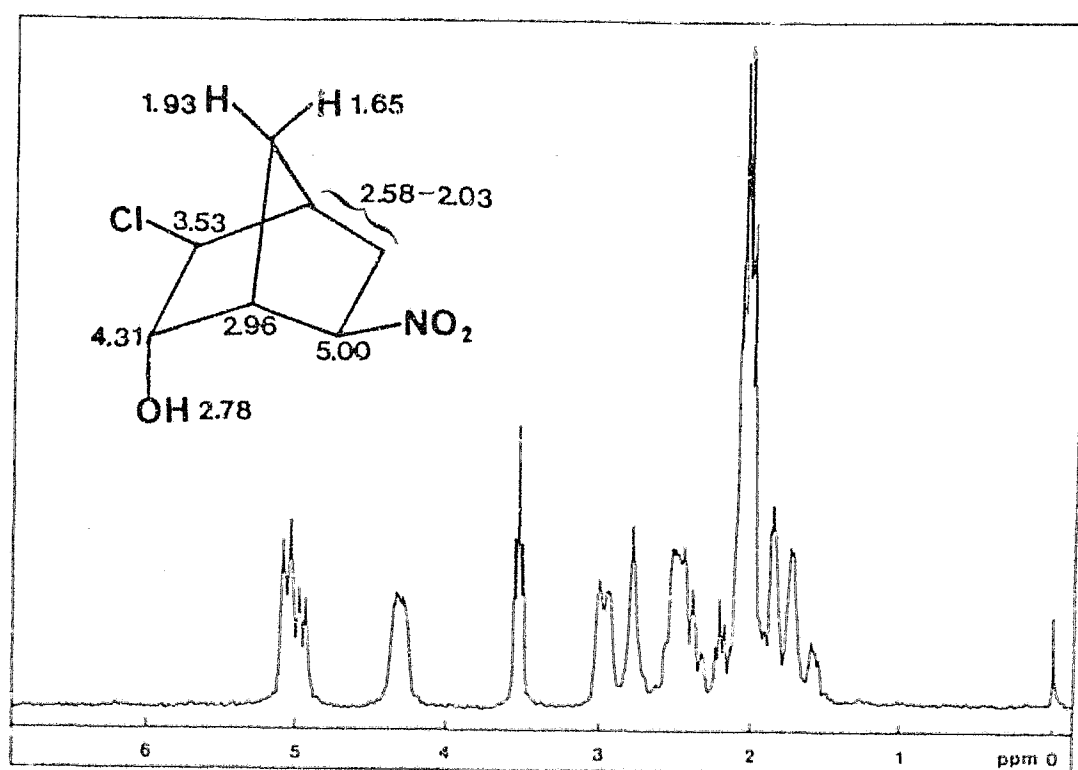


Fig.11. ^1H NMR spectrum of (59) in deuterioacetone.

The proton nuclear magnetic resonance spectrum (Figure 11.) of (59) displays a four-line multiplet at 5.00 ppm with a coupling constant of ca. 4.2 Hz. The nitro group is therefore exo. H(2) is a multiplet at 4.31 ppm and H(3) is accounted for by the double-doublet at 3.53 ppm with coupling constants of 2.3 and 2.1 ppm due to spin-spin interaction with the protons H(2) and H(7a) respectively. The bridgehead proton, H(1), resonates at 2.96 ppm and appears as a multiplet. The hydroxylic proton, which is D_2O -exchangeable, is the broad singlet at 2.78 ppm. The complex multiplet in the region 2.58-2.03 ppm is assigned to H(5x), H(5n) and H(4) with the solvent peak obscuring some of this splitting pattern. The signals at 1.93 and 1.65 ppm are the protons H(7s) and H(7a) and appear as doublets ($J = 11$ Hz) with additional fine coupling.

A second component obtained pure was similarly identified by X-ray crystallography (Section 3.5, page 65) as 3-exo-chloro-6-exo-nitrobicyclo[2.2.1]-heptan-2-exo-ol, (60). The mass-spectrum does not show a molecular ion peak, but a peak at m/e 45 is observed for the elimination of the nitro group from (64). The loss of a hydrochloric acid molecule causes a peak at m/e 108. The base peak is at m/e 66 and is indicative of a retro Diels-Alder fragmentation sequence.

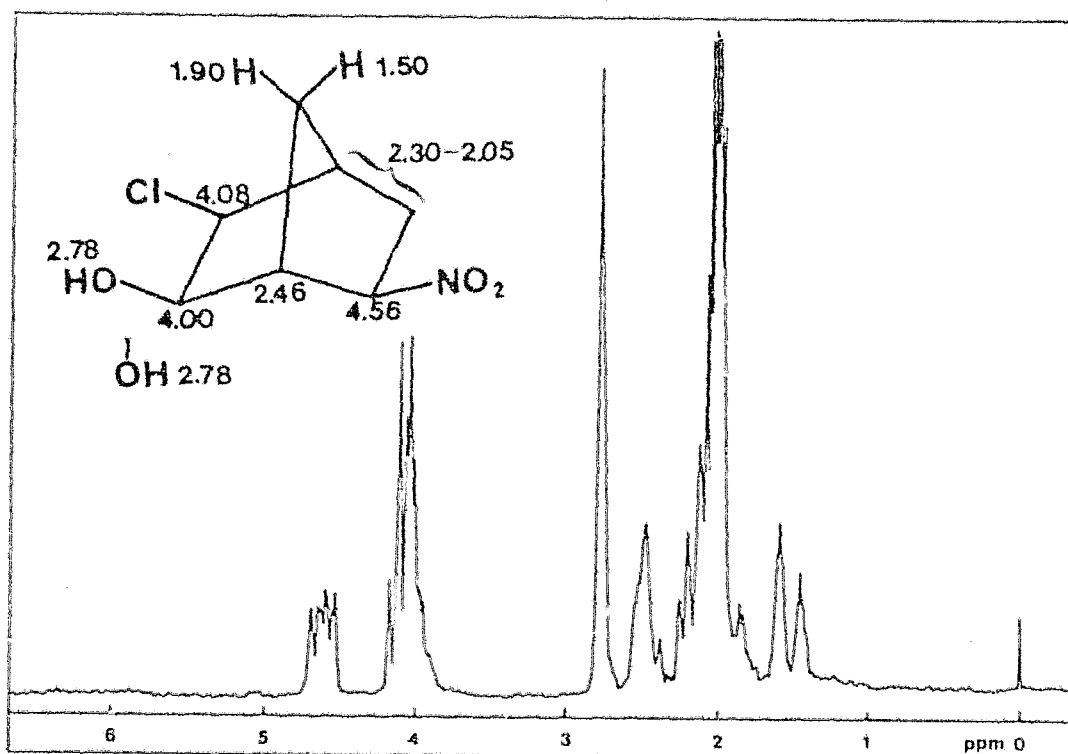


Fig. 12. ^1H NMR spectrum of compound (60) in deuteriochloroform.

The proton nuclear magnetic resonance spectrum (Figure 12) shows a four-line multiplet at 4.56 ppm for H(6) (J ca. 4.2 Hz). Proton H(3) appears as a double-doublet at 4.08 ppm with coupling constants of 5.6 and 3.0 Hz owing to coupling with H(2) and H(7a). The multiplet at 4.00 ppm is assigned to H(2) and the hydroxylic proton, which is D_2O -exchangeable, is a singlet at 2.78 ppm. The one bridgehead proton, H(1), is found at 2.46 ppm as a multiplet and the other bridgehead proton, H(4), resonates together with H(5x) and H(5n), in the region 2.30-2.05 ppm. The remaining

two protons, H(7s) and H(7a), are situated at 1.90 and 1.50 ppm respectively as doublets with a coupling constant of 11.4 Hz. These signals exhibit some unresolved fine coupling.

3.5. The crystal structures of 3-exo-chloro-6-exo-nitrobicyclo[2.2.1]heptan-2-exo-ol, (60), and 3-exo-chloro-6-exo-nitrobicyclo[2.2.1]heptan-2-endo-ol, (59)

3.5.1. Experimental

The two title compounds (59) and (60) were prepared from the crude mixture of chloroketones, presumably containing (49) and other products, by reduction with sodium borohydride in methanol as described in Section 3.4. The physical and crystallographic data for these structures appear in Table 8. Microanalyses were found to be consistent with the proposed structures. Crystals suitable for X-ray diffraction analysis were obtained by the vapour-diffusion technique¹⁷⁰ using hexane and carbon tetrachloride. Preliminary unit cell and space group data were obtained from oscillation and Weissenberg photographs using Cu-K α radiation. Accurate cell parameters were obtained by a least-squares fit on a Philips PW1100 four-circle diffractometer using graphite monochromated Mo-K α radiation. Three reference reflections were periodically monitored during the intensity data collection to ensure crystal stability. The intensities were corrected for Lorentz and polarisation effects but not for absorption.

3.5.2. Solution of the Structures

The structures of compounds (59) and (60) were solved with the centrosymmetric direct-methods option of SHELX-76.¹⁰⁴ Four E-maps were calculated for each structure from reflections with E > 1.2. All the non-hydrogen atoms could be located in these electron density maps. These coordinates were then refined by full-matrix least squares refinement and difference Fourier maps revealed all

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the hydrogen atoms for both the structures. Subsequent refinement using anisotropic temperature factors for all non-hydrogen atoms and isotropic temperature factors for hydrogen atoms, converged at a conventional R of 0.0420 for compound (60) and 0.0440 for compound (59). The residual electron densities on the final difference Fourier maps were $0.24 \text{ e } \text{\AA}^{-3}$ for compound (60) and $0.22 \text{ e } \text{\AA}^{-3}$ for compound (59) respectively. The computations for these structures were performed on a CDC Cyber 750 computer of the C.S.I.R.

Table 8. Crystallographic and physical data for 3-exo-chloro-6-exo-nitrobicyclo[2.2.1]heptan-2-exo-ol, (60), and 3-exo-chloro-6-exo-nitrobicyclo[2.2.1]heptan-2-endo-ol, (59)

<u>Crystal data</u>	<u>Compound 60</u>	<u>Compound 59</u>
Formula	$\text{C}_7\text{H}_{10}\text{NOCl}$	$\text{C}_7\text{H}_{10}\text{NOCl}$
Molecular weight	191.61	$191.61 \text{ g mol}^{-1}$
Melting point	94-95	$117-119^\circ\text{C}$
Crystallisation solvent	hexane/ CCl_4	hexane/ CCl_4
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
<u>a</u>	10.57(1)	$6.90(1) \text{ \AA}$
<u>b</u>	7.75(1)	$9.96(1) \text{ \AA}$
<u>c</u>	10.17(1)	$12.11(1) \text{ \AA}$
β	$93.03(1)$	$92.36(1)^\circ$
V	832.93	$833.30 \text{ \AA}^3$
<u>Z</u>	4	4
D_c	1.53	1.53 g cm^{-3}
D_m	1.51	1.54 g cm^{-3}
$\mu(\text{Mo-K}\alpha)$	3.67	3.67 cm^{-1}
$F(000)$	400	400
<u>Data collection</u>		
Crystal dimensions	$0.1 \times 0.2 \times 0.2$	$0.3 \times 0.2 \times 0.3 \text{ mm}^3$

Scan mode	ω -2 θ	ω -2 θ
Scan speed	0.053	0.040°/s s ⁻¹
Scan width	1.60	1.20°
Range scanned	3-23	3-23°
Stability of standard reflections	0.73	1.04%
Number of reflections collected	1244	1229
Number of observed reflections	1079	1083
Significance test	$F_o > \sigma F_o$	$F_o > \sigma F_o$
<u>Refinement</u>		
Number of variables	149	149
Weighting scheme	unit weights	unit weights
Final conventional R	0.0420	0.0440

3.5.3. Results and discussion

3.5.3.1. The structure of 3-exo-chloro-6-exo-nitrobicyclo[2.2.1]heptan-2-exo-ol, (60)

The molecular structure and atomic numbering of the title compound is shown in Figure 13 in the form of an ORTEP¹⁰⁵ drawing.

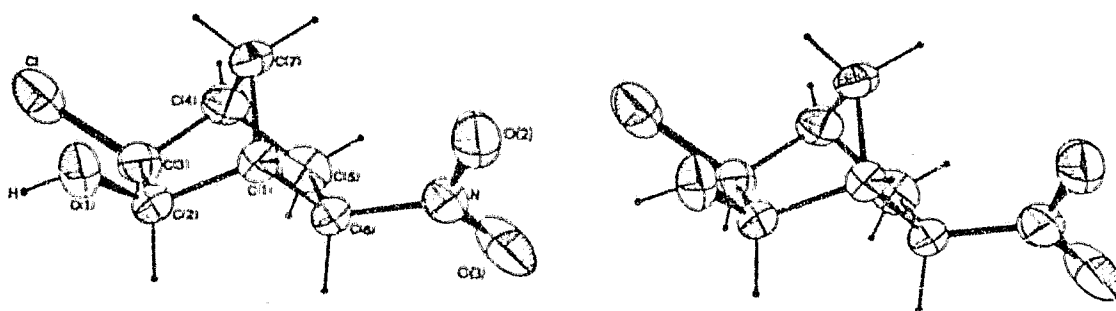


Fig. 13. Stereopair showing the molecular conformation. Thermal ellipsoids are drawn to enclose 50% of the probability distribution.

Final fractional atomic coordinates, bond lengths, bond angles, torsion angles and selected non-bonded distances are listed in Tables 9 to 13. Observed and calculated structure factors as well as thermal parameters appear in Appendix 2.

Table 9. Fractional atomic coordinates for non-hydrogen atoms, ($\times 10^4$).

Atom	x/a	y/b	z/c
Cl	1104(1)	-3676(1)	4096(1)
O(1)	3501(2)	-2738(3)	5425(2)
O(2)	3655(2)	3594(3)	4974(2)
O(3)	3874(3)	4115(3)	2930(2)
N	3658(2)	3129(3)	3825(3)
C(1)	3274(3)	162(4)	4708(3)
C(2)	3343(3)	-1737(4)	4268(3)
C(3)	2048(3)	-1970(4)	3456(3)
C(4)	1406(3)	-220(4)	3605(3)
C(5)	2085(3)	1080(5)	2742(3)
C(6)	3399(3)	1266(4)	3492(3)
C(7)	1867(3)	341(4)	4987(3)

Table 10. Fractional atomic coordinates for the hydrogen atoms, ($\times 10^3$).

Atom	x/a	y/b	z/c
H(1)	384(2)	41(3)	543(3)
H(2)	405(3)	-192(4)	369(3)
H(3)	217(3)	-225(4)	253(3)
H(4)	50(3)	20(4)	342(3)
H(5x)	169(3)	221(5)	271(3)
H(5n)	217(3)	64(4)	182(3)
H(6)	412(3)	94(4)	293(3)
H(7s)	163(3)	-47(4)	569(3)
H(7a)	160(3)	154(4)	522(3)
H (hydroxyl)	354(4)	-373(5)	524(4)

Table 11. Bond lengths (angstrom).

Cl-C(3)	1.800(3)
O(1)-C(2)	1.412(4)
O(2)-N	1.222(3)
O(3)-N	1.220(3)
N-C(6)	1.507(4)
C(1)-C(2)	1.542(4)
C(1)-C(6)	1.516(4)
C(1)-C(7)	1.535(4)
C(2)-C(3)	1.571(4)
C(3)-C(4)	1.529(5)
C(4)-C(5)	1.540(5)
C(4)-C(7)	1.527(4)
C(5)-C(6)	1.556(4)
H(1)-C(1)	0.944(26)
H(2)-C(2)	0.989(28)
H(3)-C(3)	0.979(29)
H(4)-C(4)	0.964(30)
H(5x)-C(5)	0.971(37)
H(5n)-C(5)	1.008(33)
H(6)-C(6)	1.013(27)
H(7s)-C(7)	0.990(32)
H(7a)-C(7)	1.002(31)
O(1)-H (hydroxyl)	0.790(40)

Table 12. Selected bond angles (degrees).

C1-C(3)-C(2)	112.3(2)
C1-C(3)-C(4)	111.1(2)
O(1)-C(2)-C(3)	115.8(2)
O(1)-C(2)-C(1)	106.8(2)
O(2)-N-O(3)	122.6(3)
O(2)-N-C(6)	119.2(2)
O(3)-N-C(6)	118.2(3)
N-C(6)-C(5)	110.3(3)
N-C(6)-C(1)	112.4(2)
C(1)-C(2)-C(3)	102.1(2)
C(1)-C(6)-C(5)	103.5(2)
C(1)-C(7)-C(4)	94.0(2)
C(2)-C(1)-C(6)	107.2(2)
C(2)-C(1)-C(7)	101.6(2)
C(2)-C(3)-C(4)	103.0(2)
C(3)-C(4)-C(5)	107.6(3)
C(3)-C(4)-C(7)	102.9(3)
C(4)-C(5)-C(6)	102.2(2)
C(5)-C(4)-C(7)	101.7(3)
C(6)-C(1)-C(7)	103.1(2)
H-O(1)-C(2)	109.9(3)

Table 13. Selected non-bonded distances (angstrom) and torsion angles(degrees).

O(1)...O(2)	2.888
O(1)...O(3)	3.125
O(1)...N	3.074
O(1)-H...O(2)	2.101
O(1)-H...O(3)	2.924
O(1)-H...N	3.103
C1...O(2)	3.507
C1...O(3)	3.644
O(2)-N-C(6)-C(5)	110.0(4)
O(3)-N-C(6)-C(5)	-70.6(5)
C(1)-C(2)-O(1)-H	179.7(3)
H(2)-C(2)-O(1)-H	59.1(6)

The contents of the unit cell are shown in Figure 14.

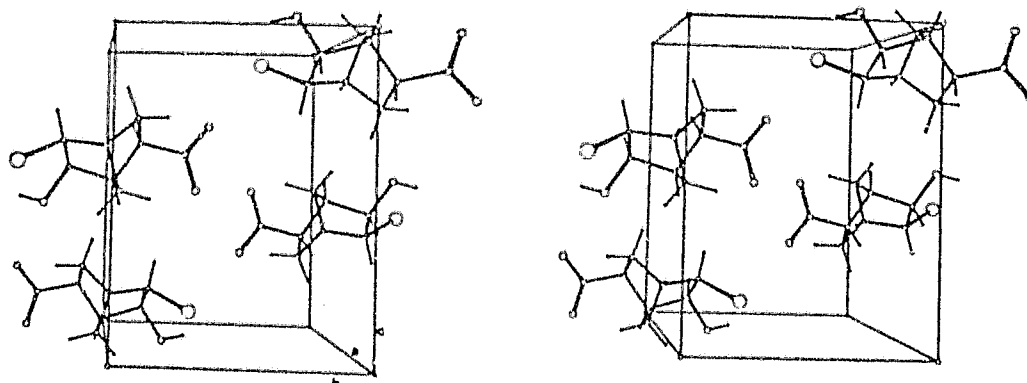


Fig. 14. Packing arrangement of the molecules in the crystal.

There is no intramolecular hydrogen bonding present in this molecule due to the arrangement of the functional groups, but intermolecular hydrogen bonding is feasible for this compound in the solid state. Hydrogen bonding occurs along the b-axis of the cell as infinite chains of bonded molecules. These bonds are illustrated with dotted lines in Figure 15.

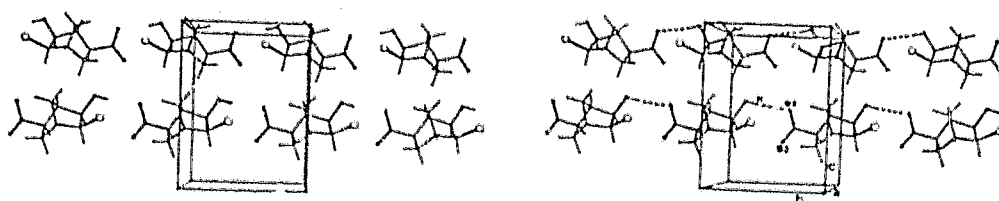


Fig. 15. Perspective view of hydrogen bonds in crystal.

A single intermolecular distance between the hydroxyl proton at the symmetry position x, y, z and O(2) of the nitro group of a neighbouring molecule at symmetry position $x, 1+y, z$ is noted, with the distance being 2.888 angstrom for O(1)...O(2) or 2.107 angstrom for H...O(3). The dihedral angle, which depicts the orientation of the hydroxyl group, C(1)-C(2)-O(1)-H is 179.7 degrees and the orientation of the nitro group is given by the dihedral angle C(5)-C(6)-N-O(3) of -70.6 degrees and again these angles deviate from what would be expected, but it must be borne in mind that additional stabilisation is gained from the formation of hydrogen bonds.²⁶ There are no other unusual short non-bonded contacts. It is interesting to note that bifurcated hydrogen bonding is not present in this structure. A possible reason for the specific orientation of the exo nitro group in this molecule could just be due to the electrostatic interaction between O(2) of the nitro group and the chlorine atom of the neighbouring molecule, which prevents the nitro group from participating in possible bifurcated hydrogen bonding. In conclusion, normal intermolecular hydrogen bonding is preferred in this molecule where both donor and acceptor groups are

exo.

3.5.3.2. The structure of 3-exo-chloro-6-exo-nitrobicyclo[2.2.1]heptan-2-endo-ol, (59)

An ORTEP¹⁰⁵ drawing and atomic numbering scheme of the abovementioned compound is given in Figure 16.

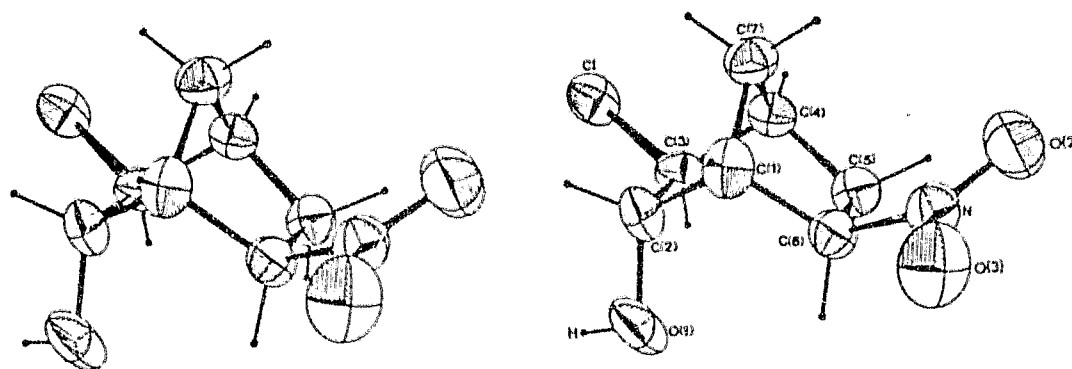


Fig. 16. Stereopair showing the molecular conformation. Thermal ellipsoids are drawn to enclose 50% of the probability distribution.

The fractional atomic coordinates, bond lengths, bond angles, torsion angles and non-bonded distances are listed in Tables 14 to 18. Structure and temperature factors are listed in Appendix 3.

Table 14. Fractional atomic coordinates for non-hydrogen atoms, ($\times 10^4$).

Atom	x/a	y/b	z/c
Cl	3090(1)	4275(1)	708(1)
O(1)	-849(4)	1713(3)	1278(2)
O(2)	-4413(3)	3121(3)	3910(2)
O(3)	-2198(4)	4116(3)	4878(2)
N	-2713(4)	3442(3)	4085(2)
C(1)	-1498(5)	3806(3)	2225(3)
C(2)	-355(4)	3098(3)	1332(3)
C(3)	1783(4)	3353(3)	1728(3)
C(4)	1599(4)	4152(3)	2785(3)
C(5)	850(4)	3178(4)	3652(3)
C(6)	-1283(4)	2956(3)	3267(2)
C(7)	-191(5)	5009(3)	2506(3)

Table 15. Fractional atomic coordinates for the
hydrogen atoms, ($\times 10^3$).

Atom	x/a	y/b	z/c
H(1)	-264(5)	402(3)	204(2)
H(2)	-55(4)	351(3)	55(3)
H(3)	242(4)	251(3)	182(2)
H(4)	271(4)	460(3)	299(2)
H(5x)	83(4)	361(3)	440(3)
H(5n)	157(5)	230(4)	364(3)
H(6)	-168(4)	202(3)	313(2)
H(7s)	1(4)	559(3)	186(3)
H(7a)	71(4)	552(3)	315(3)
H (hydroxyl)	-24(6)	149(4)	67(3)

Table 16. Bond lengths (angstrom).

C1-C(3)	1.810(3)
O(1)-C(2)	1.423(4)
O(2)-N	1.227(3)
O(3)-N	1.214(3)
N-C(6)	1.508(4)
C(1)-C(2)	1.537(4)
C(1)-C(6)	1.523(4)
C(1)-C(7)	1.531(5)
C(2)-C(3)	1.555(4)
C(3)-C(4)	1.517(4)
C(4)-C(5)	1.537(4)
C(4)-C(7)	1.529(4)
C(5)-C(6)	1.543(4)
H(1)-C(1)	0.840(30)
H(2)-C(2)	1.035(32)
H(3)-C(3)	0.952(29)
H(4)-C(4)	0.916(28)
H(5x)-C(5)	1.007(32)
H(5n)-C(5)	1.008(34)
H(6)-C(6)	0.988(31)
H(7s)-C(7)	0.990(31)
H(7a)-C(7)	1.010(32)
O(1)-H (hydroxyl)	0.897(40)

Table 17. Selected bond angles (degrees).

C1-C(3)-C(2)	111.5(2)
C1-C(3)-C(4)	111.7(2)
O(1)-C(2)-C(3)	113.3(3)
O(1)-C(2)-C(1)	110.4(3)
O(2)-N-O(3)	121.9(3)
O(2)-N-C(6)	116.8(3)
O(3)-N-C(6)	121.3(3)
N-C(6)-C(5)	113.5(3)
N-C(6)-C(1)	108.8(2)
C(1)-C(2)-C(3)	102.5(2)
C(1)-C(6)-C(5)	103.3(2)
C(1)-C(7)-C(4)	94.4(3)
C(2)-C(1)-C(6)	107.0(3)
C(2)-C(1)-C(7)	101.6(3)
C(2)-C(3)-C(4)	103.6(2)
C(3)-C(4)-C(5)	106.7(3)
C(3)-C(4)-C(7)	101.7(3)
C(4)-C(5)-C(6)	103.2(2)
C(5)-C(4)-C(7)	102.2(3)
C(6)-C(1)-C(7)	102.4(3)
H-O(1)-C(2)	99.1(3)

Table 18. Selected non-bonded distances (angstrom) and torsion angles (degrees).

O(1)...O(2)	3.078
O(1)...O(3)	3.205
O(1)...N	3.500
O(1)-H...O(2)	2.257
O(1)-H...O(3)	2.418
O(1)-H...N	3.371
C1...O(2)	3.623
C1...O(3)	3.529
O(2)-N-C(6)-C(5)	169.5(3)
O(3)-N-C(6)-C(5)	-10.4(5)
C(1)-C(2)-O(1)-H	171.0(3)
H(2)-C(2)-O(1)-H	44.9(6)

The bond lengths and angles do not deviate noticeably from what is ordinarily observed for functionalised bicyclo[2.2.1]heptanes.¹⁰⁶⁻¹¹¹ The dihedral angle C(1)-C(2)-O(1)-H for the hydroxyl group is 171.0 degrees and the orientation of the nitro group is given by an angle of 10.4 degrees for C(5)-C(6)-N-O(3), which is remarkably different from the value found for the previous structure (compound 60) and it shows very well how the nitro group can rotate to attain a favoured orientation as a hydrogen bonding acceptor. A possible explanation for this vast difference in orientations of the two nitro groups can be seen from Figure 17. Both the nitro and hydroxyl groups are exo which create an unfavourable steric interaction between the nitro of one molecule

and the chlorine atom in an adjacent molecule if a bifurcated hydrogen bond was to be preferred.

The packing of the molecules in the crystal is stabilised by a system of hydrogen bonds as illustrated in Figure 17.

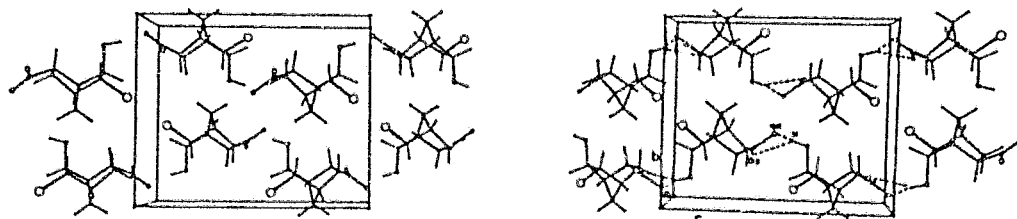


Fig. 17. A stereoscopic view of the contents of the unit cell. Hydrogen bonds are indicated with dotted lines.

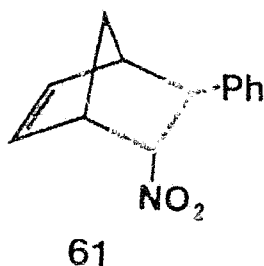
The dotted lines represent the hydrogen bonds. All the hydroxyl protons are involved in the formation of these bonds and the nitro group of each molecule act as an acceptor for these hydrogens to establish chains of bonded molecules throughout the whole crystal lattice. The direction of binding is along the c-axis of the unit cell and it involves both molecules of the centrosymmetric pair. The higher estimated standard deviations in the positional coordinates of O(1), O(2), and O(3) as well as the short O(1)...O(3) and O(1)...O(3) distances, suggested that the hydroxylic proton is shared between the oxygens of neighbouring molecules related by a two-fold screw axis. The intermolecular contacts, H...O(2) and H...O(3) of 2.257 and 2.418 angstroms respectively, are considerably shorter than the sum of the van der Waals radii. So, it can be concluded that the interaction observed in the crystal is an interesting example of a weak unsymmetrical bifurcated hydrogen bond.

Thus, while the bifurcated hydrogen bond does not appear to be twice as stable as a normal hydrogen bond, it does nevertheless

constitute an energetically favourable interaction and provides a mechanism which more than compensates for energy costs associated with markedly bent hydrogen bonds.⁴⁸

3.6. Reactions using 5-endo-nitro-6-exo-phenylbicyclo[2.2.1]-hept-2-ene

Attempts to prepare simple norbornanes containing endo-hydroxy and nitro groups have so far all ended in defeat, in the final analysis because of the unexpectedly easy isomerisation of the endo-nitro group to the exo position. In order to circumvent this last problem, it seemed likely that one could use steric features to inhibit this isomerisation. It was felt that, if one used the Diels-Alder adduct of β -nitrostyrene rather than that of nitroethylene, the presence of the vicinal exo-phenyl group would sterically disfavour the isomerisation of the nitro group. Accordingly, the last group of syntheses in this project were attempts to functionalise the C=C double bond of adduct (61) with an endo-hydroxyl group.

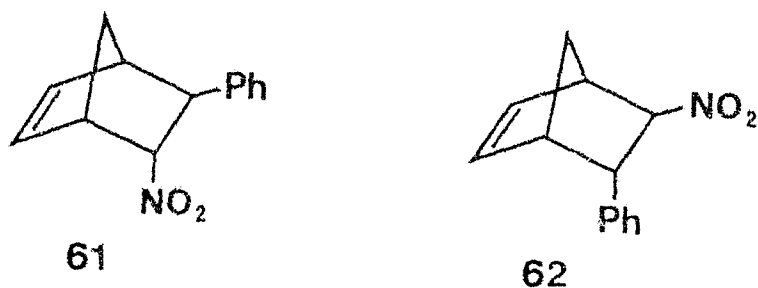


β -Nitrostyrene was prepared from nitromethane and benzaldehyde as described by Worrall.¹⁷¹ The infrared spectrum shows stretching absorption bands at 1632 and 1575 cm^{-1} for the aromatic C=C vibration, and at 1550 and 1342 cm^{-1} for the nitro group. The proton nuclear magnetic resonance spectrum shows a singlet at 7.53 ppm for the five aromatic protons and two doublets at 7.53 and 8.02 ppm respectively for the olefinic hydrogens. The coupling constant of 14 Hz between the latter protons is in agreement with what is normally measured for trans coupling between vicinal hydrogens in

alkenes.

The reaction of cyclopentadiene and β -nitrostyrene leads to 2-nitro-3-phenylbicyclo[2.2.1]hept-2-ene as described in the literature by Poos *et al*¹⁷² and other authors.^{173,174}

Poos and his co-workers found a 3:1 ratio of isomeric adducts (61) and (62) from several runs of the diene condensation although temperature and times of heating were varied.



In the present work the [4+2] cycloaddition of β -nitrostyrene and cyclopentadiene at the refluxing temperature of the mixture produced the two possible isomers (61) and (62) in a 90% yield. The ratio of endo:exo nitro isomers was found to be 80:20 using nuclear magnetic resonance spectroscopy. This ratio was based on the careful integration of the proton alpha to the nitro group. The infrared spectrum shows the presence of a nitro group by absorption bands at 1530 and 1365 cm^{-1} as well as unsaturated C=C bonds with absorption bands at 1598 and 1493 cm^{-1} . The mass spectrum has a molecular ion peak at m/e 215, a peak at m/e 185 which corresponds to the loss of a nitroso fragment, and a peak at m/e 169 which accounts for the loss of the nitro group. The peak at m/e 66 indicates that a retro Diels-Alder reaction has occurred during the fragmentation sequence.

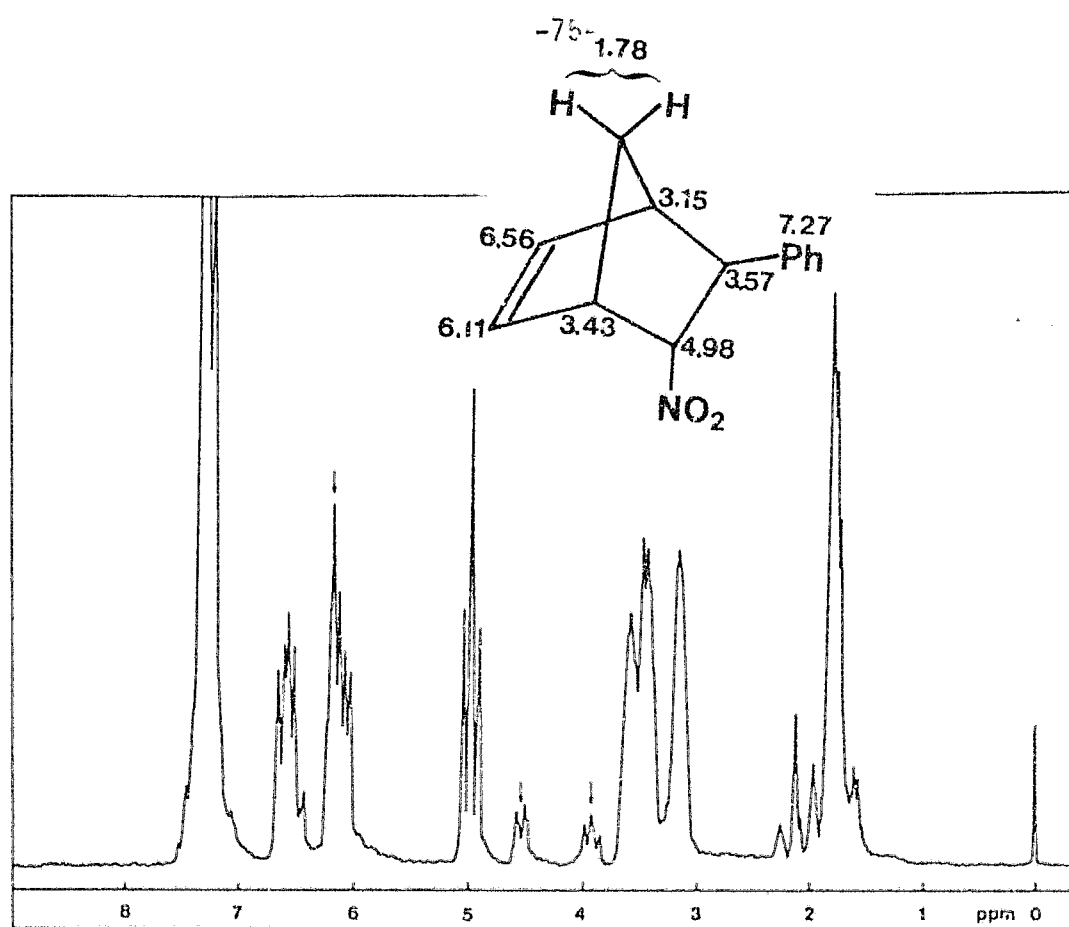
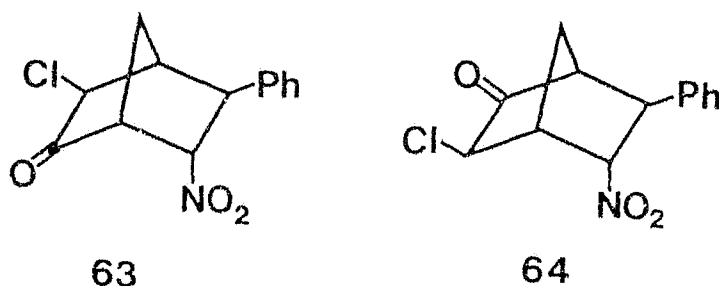


Fig. 18. ^1H NMR spectrum of compound (61), and the minor isomer, (62), in deuteriochloroform.

The proton nuclear magnetic resonance spectrum (Figure 18) indicates a multiplet at 7.27 ppm which corresponds to the aromatic protons. Two double doublets appear at 6.56 and 6.11 ppm for H(6) and H(5) respectively, with a coupling constant of 5.6 Hz for cis vicinal coupling between the olefinic protons. The coupling constant to the respective bridgehead protons is 2.5 Hz. Proton H(3) appears as a triplet at 4.98 ppm owing to the similar coupling constants of ca. 3.6 Hz to H(4) and H(2). The bridgehead protons, H(1) and H(4), are broad singlets at 3.15 and 3.43 ppm. The proton alpha to the phenyl group is found at 3.57 ppm in the form of a broad singlet. The broadness of this peak can be understood in terms of long-range W-coupling with the proton H(7a), which is a common type of coupling in norbornyl systems.¹⁶³⁻¹⁶⁵ A multiplet appears around 1.78 ppm for the protons H(7s) and H(7a) (arrowed peaks indicates minor isomer).

The mixture of Diels-Alder adducts (61) and (62) (80:20) was treated with chromyl chloride¹⁷⁵ in acetone to produce an isomer mixture of chloroketones in a 78% crude yield.¹⁴⁰ An attempt to distil some of the product resulted in a very poor recovery due to decomposition, and the proton nuclear magnetic resonance spectrum showed that the distilled product had the same composition as crude product. Two attempts using column chromatography also failed to separate the isomers successfully. However, low pressure chromatography (8.35 g) gave a fair separation of the isomers in some of the fractions. The less polar compound ($R_f = 0.52$; ethyl acetate-hexane; 1:3) was obtained as a white solid (0.277 g) which was recrystallised from diisopropyl ether to yield needle-shaped crystals with a melting point of 125-126°C. This compound was tentatively assigned as 3-exo-chloro-5-endo-nitro-6-exo-phenylbicyclo[2.2.1]heptan-2-one, (63).

The second set of fractions ($R_f = 0.42$) was isolated as a yellowish oil (0.537 g) which solidified after standing for four weeks at room temperature. Recrystallisation from ethyl acetate and diisopropyl ether afforded a white solid, with a melting point of 79-80.5°C, which was identified tentatively as 3-exo-chloro-6-endo-nitro-5-exo-phenylbicyclo[2.2.1]heptan-2-one, (64).



The infrared spectrum of (63) shows stretching absorption bands for the following functionalities: a ketone (1762 cm^{-1}), a nitro group (1540 and 1382 cm^{-1}) and bands at 1600 and 1495 cm^{-1} for aromatic unsaturated bonds. The mass-spectrum of (63) has a

molecular ion peak at m/e 265 as well as a peak at m/e 230 for the loss of the chlorine atom. Subsequent loss of the phenyl substituent accounts for a peak at m/e 152. The infrared spectrum of (64) exhibits characteristic absorption bands for a ketone at 1765 cm^{-1} as well as for a nitro group at 1550 and 1362 cm^{-1} . Aromatic unsaturated carbon bands are present at 1600 and 1495 cm^{-1} .

The third fraction gave also a yellow oil after the solvent had been removed and was assigned to a product derived from the minor isomer. No further attempts were made to accomplish complete separation of all the fractions.

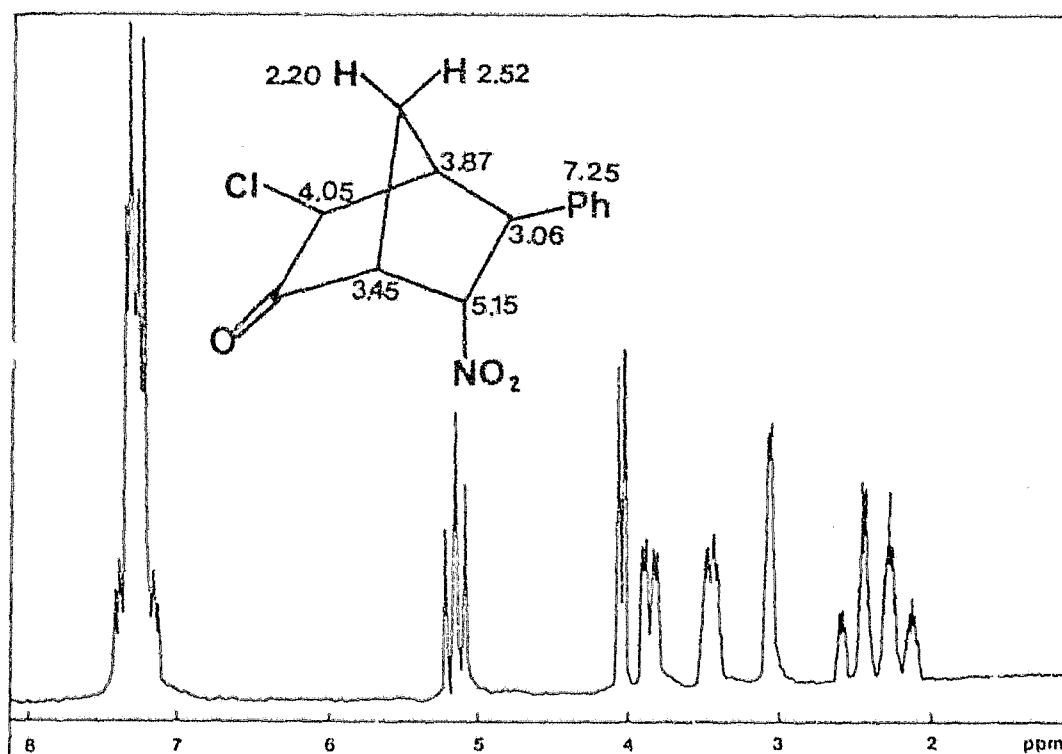


Fig. 19. ^1H NMR spectrum of compound (63) in deuteriochloroform.

The proton nuclear magnetic resonance spectrum of (63) and (64) are shown in Figures 19 and 20. Extensive spin-decoupling experiments were performed, without success, in attempts to assign the structures unambiguously. The proton nuclear magnetic resonance spectrum of (63) has a multiplet at 7.25 ppm for the aromatic

protons as well as a double-doublet at 5.15 ppm for H(6), which couples with H(5) and H(1). A well-defined doublet is observed at 4.05 ppm for H(3) owing to spin-interaction with H(7a) through long-range coupling. The three multiplets at 3.87, 3.45 and 3.06 ppm are assigned to H(1), H(4) and H(5) respectively. The two doublets, with a coupling constant of 12 Hz, at 2.52 and 2.20 ppm originates from coupling between H(7a) and H(7s).

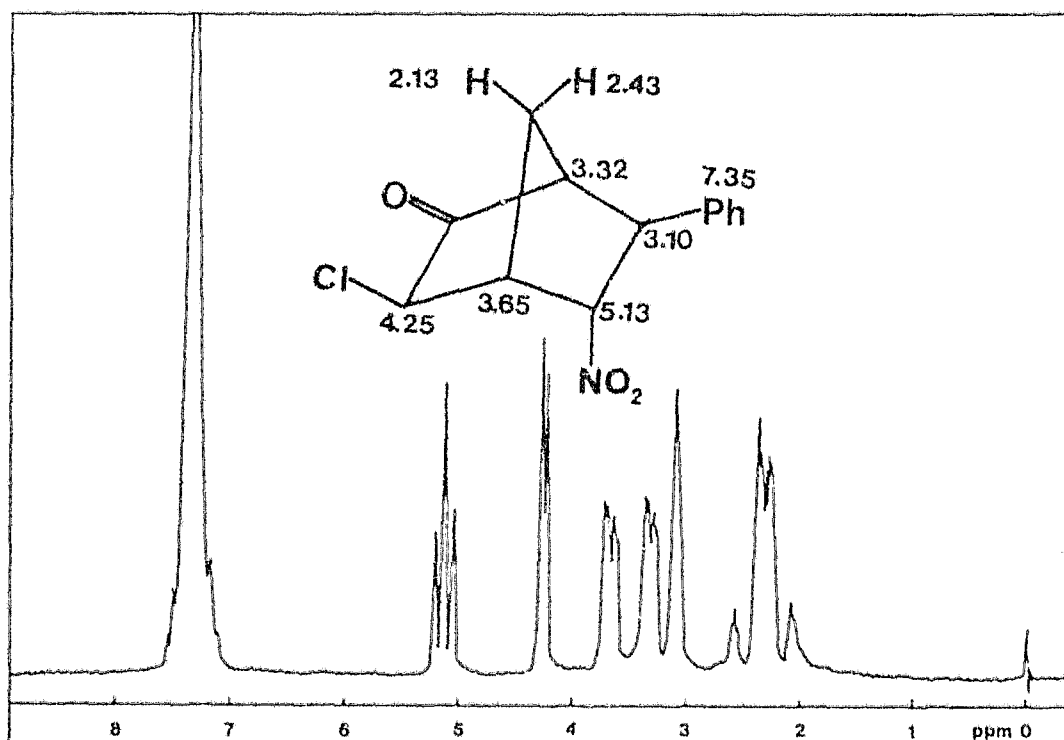
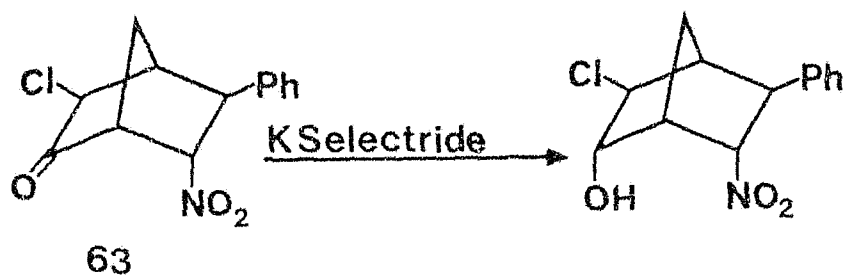


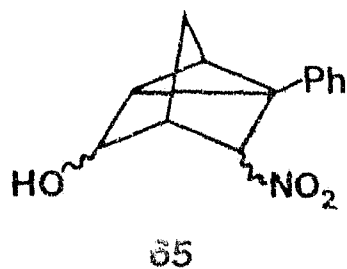
Fig. 20. ¹H NMR spectrum of compound (64) in deuteriochloroform.

The proton nuclear magnetic resonance spectrum of (64) has a multiplet situated at 7.35 ppm for aromatic protons as well as a double-doublet situated at 5.13 ppm for H(5) owing to coupling with H(6) and H(4). The doublet ($J = 2.4$ Hz) at 4.25 ppm arises from the spin-spin interaction of H(3) with H(7a). The multiplets at 3.65 and 3.32 ppm are assigned to the bridgehead protons, H(4) and H(1). The broad singlet at 3.10 ppm accounts for the proton alpha to the phenyl substituent. The doublets, which show additional fine coupling, at 2.43 and 2.13 ppm are assigned to H(7a) and H(7s).

It was decided to reduce some of (63) and (64) to assist in deducing the structures of the former two chloro-ketones, since it was felt that the more extensively coupled systems in the reduced products might be more amenable to investigation by spin-decoupling experiments. A bulky reducing agent which should attack only from the less hindered exo face was used to avoid the formation of even more isomers.



Compound (63) was reduced successfully with 1.25 equivalents of potassium tri-sec-butylborohydride in tetrahydrofuran under an inert atmosphere.¹⁵⁶ Thin-layer chromatography indicated that two components (R_F -values 0.98 and 0.29; ethyl acetate-hexane 1:2) were present in the product after work-up. This mixture was separated easily by column chromatography. The first compound was identified as some derivative of the reducing agent. The second product from the column was an alcohol, but clearly not the desired chloro-alcohol. Microanalysis indicated a molecular formula of $C_{13}H_{13}NO_3$, i.e. the chlorine atom was lost during the reaction. On the basis of this and of spectroscopic data, the structure of the product is tentatively proposed as (65).



Compound (65) has the following spectral features: the infrared

spectrum shows a broad, but sharp, absorption band for a hydroxyl group as well as absorption bands for the presence of the phenyl group (1603 and 1453 cm^{-1}). There are strong bands at 1512 and 1372 cm^{-1} owing to the presence of a nitro group. The mass-spectrum of (65) has a molecular ion peak at 231 and a peak at $m/e\ 167$ due to the loss of the nitro group and a unit of water from the molecule. An abundant peak at is found at $m/e\ 153$ for the loss of the phenyl substituent from the molecule.

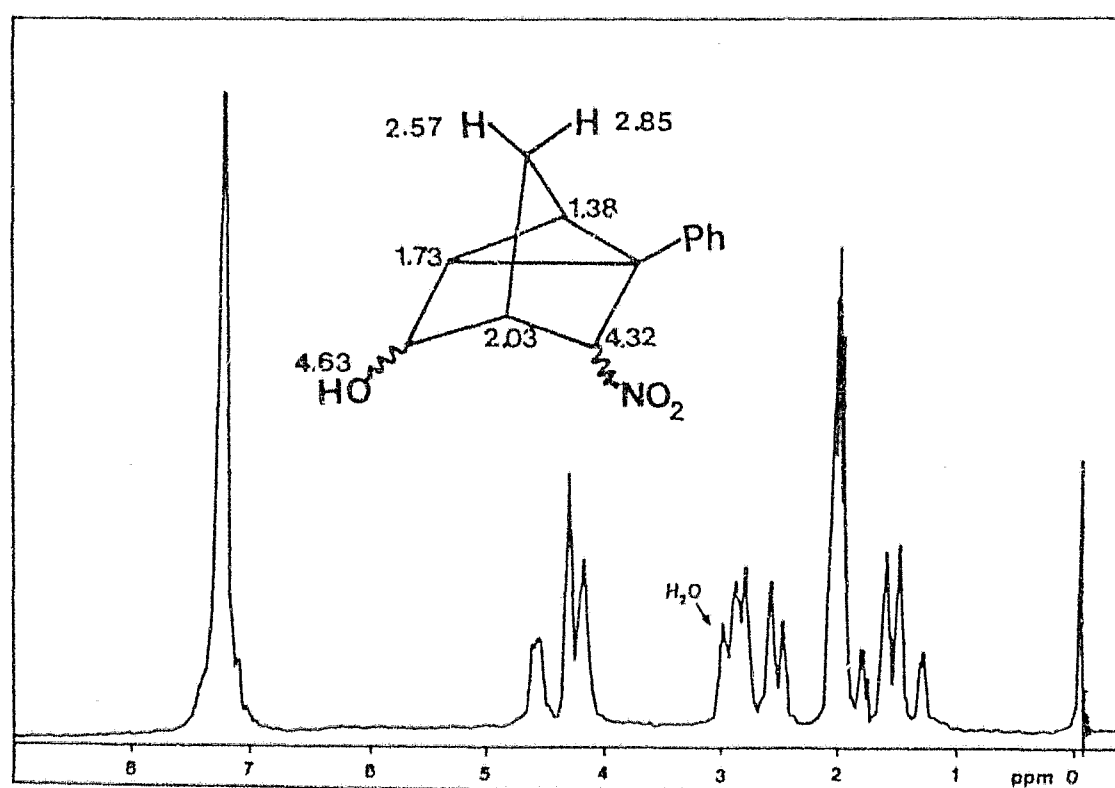


Fig. 21. ^1H NMR spectrum of (65) in deuterioacetone.

The proton nuclear magnetic resonance spectrum (Figure 21) has a multiplet at 7.22 ppm for the aromatic hydrogens. The signal for the hydroxyl proton is situated at 4.63 ppm . The latter is D_2O -exchangeable. The proton alpha to the nitro group is found at a chemical shift of 4.32 ppm and it appears as a singlet. The reason that no coupling is observed with $\text{H}(1)$ might mean that the nitro group has isomerised to the exo position. $\text{H}(2)$ resonates at

4.18 ppm as a multiplet which sharpens upon exchange of the hydroxyl proton with D₂. The two protons in the 7-position, H(7a) and H(7s), are found at 2.87 and 2.57 ppm. They appear as doublets ($J = 6$ Hz), with additional fine coupling, owing to geminal coupling between them. The signal for H(1) is obscured by the acetone peak at 2.03 ppm. Finally, the protons attached to the cyclopropyl ring show vicinal coupling ($J = 10$ Hz) and appear at 1.73 (H(3)) and 1.38 ppm (H(4)), respectively.

The assignment of this structure is not unambiguous, but it fits in with the available spectroscopic data. Furthermore, it was on the basis of this structure that the structures of the precursors, (63) and (64), were proposed. It is obviously highly desirable to obtain more concrete evidence for the structure of (65), and at the present time, attempts are under way to grow suitable crystals of this compound for X-ray crystallography.

CHAPTER 4

CONFORMATIONAL ANALYSIS BY MEANS OF MOLECULAR MECHANICS

4.1. INTRODUCTION

The crystal structure of 3-exo,6-exo-dichloro-5-endo-hydroxy-3-endo-nitrobicyclo[2.2.1.]heptane-2-exo-carbonitrile, (7), revealed two interesting structural features: an unusual position for the hydroxyl proton, and an unexpected orientation of the nitro group, both of which could be entirely due to the hydrogen bonding between these groups. On the other hand, it is possible that even in the absence of hydrogen bonding, these conformations may be the intrinsically preferred ones. Hence, this problem of conformation was felt to be suitable for study by means of empirical force-field calculations to determine the preferred orientation(s) of the substituents in compound (7) and other related nitronorbornanols.

The ability of the molecular mechanics method to calculate accurately the geometries of molecules is best suited to quantitative conformational analysis.¹⁷⁶ Molecules are considered strained if they contain internal coordinates which deviate from values regarded as strain-free or normal;¹⁷⁷ and the molecular force field describes, within certain limits, the potential energy of a molecule relative to the energy of a reference geometry. The primary objective of these molecular mechanics calculations is to obtain structural properties rather than thermochemical data like heats of formation or vibrational parameters. A comparison of force fields as derived by different authors is possible only to a limited extent and generally it is found that calculated structural parameters are less sensitive to changes of potential constants than energetic or vibrational quantities are. In a number of cases it is essential to know the

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4.1. INTRODUCTION

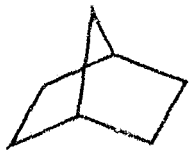
The crystal structure of 3-exo,6-exo-dichloro-5-endo-hydroxy-3-endo-nitrobicyclo[2.2.1.]heptane-2-exo-carbonitrile, (7), revealed two interesting structural features: an unusual position for the hydroxyl proton, and an unexpected orientation of the nitro group, both of which could be entirely due to the hydrogen bonding between these groups. On the other hand, it is possible that even in the absence of hydrogen bonding, these conformations may be the intrinsically preferred ones. Hence, this problem of conformation was felt to be suitable for study by means of empirical force-field calculations to determine the preferred orientation(s) of the substituents in compound (7) and other related nitronorbornanols.

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barriers of transition from one conformation to another. If a molecule has only one energy minimum the calculation is quite simple. However, in complex situations, particularly when a molecule contains many single bonds, one can never be sure that the program will give a global minimum and it is therefore advisable to examine the entire energy surface.¹⁷⁸ A situation can arise in which an energy surface may have many minima of similar depth rather than an absolute minimum. In this case it cannot be guaranteed that the global minimum always corresponds to the real structure.

In the present work, the different orientations of the hydroxyl and nitro groups in compound (7) were calculated with a standard molecular mechanics program to decide whether intramolecular hydrogen bonding could exist between them, and also to establish whether a bifurcated hydrogen bond between these groups would be possible. The influences that neighbouring substituents have on these groups were also taken into account to explain the structural features exhibited by 2-endo,6-endo-nitroalcohols in the norbornyl system.

Although the norbornane ring system, (66), has been important in the field of organic and structural chemistry for many years, the structural parameters are not very accurately known, despite all the data accumulated by chemical and physical methods with particular emphasis on the effect of intramolecular strain.¹⁷⁹



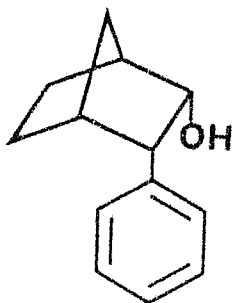
66

A number of investigations have shown that unconstrained ab initio

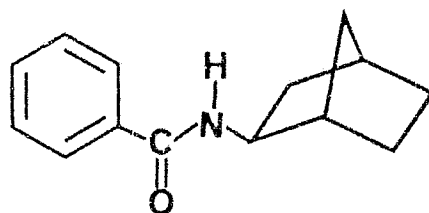
calculations produce geometries that are consistently close to experimental.¹⁸⁰⁻¹⁸² Various workers have calculated different structural models for norbornane derived from a variety of molecular mechanics approaches.¹⁸³⁻¹⁹⁰ However, the quality of geometrical constraints derived from ab initio calculations was shown to be better than that calculated by molecular mechanics.¹⁸⁰ Nevertheless, the latter method has often produced useful results with medium strained hydrocarbons.¹⁹¹ Altona and Sundaralingam¹⁹² reported a quantitative description of the skeletal torsion angles of eleven norbornanes, camphanes, and norbornenes. The geometrical details of the molecules from X-ray structure determinations were compared with those obtained by computer calculations (full relaxation molecular mechanics approach), and showed reasonable agreement.

Futher support for the strain in norbornane is given by nuclear magnetic resonance studies.¹⁹³ The microwave spectrum of norbornane has been recorded and interpreted as well.¹⁹⁴ Investigations on the free molecule by gas-phase electron diffraction have resulted in four structural models¹⁹⁵⁻¹⁹⁸ that differ from one another in important details, particularly in the CC bond lengths and CCC valence angles. From this published work, it appears that the detailed structure of norbornane cannot be determined from gas electron diffraction alone, and since the molecule is too big to be conveniently studied by microwave techniques, use of the crystallographic method was clearly indicated.¹⁷⁹ because the molecule is nearly spherical, disordered crystals might be expected and have been found in various derivatives.^{8,199} To avoid disorder, a crystalline derivative which is reasonably high melting and which has an opportunity for hydrogen bonding is preferred. Two X-ray diffraction studies of 2,3-disubstituted norbornanes have been published^{58,200} and a preliminary report on a neutron diffraction

analysis of 3-endo-phenylbicyclo[2.2.1]heptan-2-endo-ol,²⁰¹ (67), is available. Newton and co-workers¹⁷⁹ have solved the X-ray crystal structure of exo-N-(2-norbornyl)benzamide, (68), to determine accurate bond lengths and angles for the parent norbornane. This system is evidently distorted by the substituent group, by crystal packing forces, or by both.



67



68

It appears that the presently available averaged norbornane skeleton as obtained by X-ray diffraction gives useful information about the valence angles in free norbornane. Unfortunately, the same cannot be said about bond lengths obtained with this technique.

The best composite structure for norbornane was published recently by Doms and co-workers²⁰² who reported a study in which gas-electron diffraction is augmented by all presently available spectroscopic data (microwave, Raman and infrared). The data were combined with geometrical constraints obtained from ab initio calculations after complete relaxation (MOCED model). For comparison a second model was used with constraints calculated by molecular mechanics using the force field of Ermer and Lifson.²⁰³ They concluded that, even with the combination of the abovementioned techniques, it was not possible to say whether C(1)-C(2) is longer than C(1)-C(7).

In the present work, the bicyclic skeleton of (66) was taken as the

basis of all the calculations and a model structure for (7) was constructed from (66) and successive placing of the different functional groups. This gradual construction of the molecule made it possible to examine the effects caused by neighbouring functional groups and it also provided a different starting set of coordinates on the energy surface, which enabled the program to converge from different points on this surface.

4.2. The Force-Field Study ²⁰⁴

The method of Boyd,²⁰⁵ as modified by Snow,²⁰⁶ using a general force-field was used in this work. The molecular mechanics method is a purely empirical method to calculate the structure of a molecule. The molecule is presented as though constructed from a number of balls joined together by springs with four potential energy functions which define the force-field. The four energy terms are:

$$U = \sum_{ij} U(r_{ij})_B + \sum_{ij} U(r_{ij})_{NB} + \sum_{ijk} U(\theta_{ijk}) + \sum_{ijkl} U(\phi_{ijkl}) \quad (1)$$

$U(r)_B$ is the potential energy for bond deformation between bonded atoms i and j , $U(r)_{NB}$ the non-bonded potential energy between two atoms i and j , $U(\theta)$ the potential energy contribution for angle deformation between bonded atoms $i-k$, and $U(ijkl)$ the potential energy for torsional strain about the bonded atoms $i-l$.

The bond-stretching and valence-angle deformation are assumed to have harmonic restoring forces. Hooke's law is therefore obeyed and the potentials are of the forms (2) and (3),

$$U(r_{ij})_B = 0.5 k_{r_{ij}} (r_{ij} - r_{ij}^0)^2 \quad (2)$$

$$U(\theta_{ijk}) = 0.5 k_{\theta_{ijk}} (\theta_{ijk} - \theta_{ijk}^0)^2 \quad (3)$$

where theta and r represent strain-free angles and bond-lengths respectively. The stretching and bending force constants, $k(r)$ and $k(\theta)$ are listed in Table 1 of Appendix 4. Bond-stretching and valence-angle deformation terms have been included for all the bonds and angles within the molecule. The non-bonded potential function between a pair of atoms i and j has been based on a Buckingham-type potential, viz (4),

$$U(r_{ij})_{NB} = a \exp(-br_{ij}) - (c/r_{ij}^6) \quad (4)$$

where the r_{ij} term represents the attractive forces and the exponential term approximates the repulsive forces. The constants a, b and c are listed in Table 2 of Appendix 4. All the interactions between non-bonded atoms up to a distance of 1.2 times the sum of their van der Waals radii¹¹³ have been included in the calculations.

According to Scott and Scheraga²⁰⁷ the torsional strain in a molecule can be computed from a equation that considers contributions from non-bonded and quantum-mechanical components separately, viz (5),

$$U(\phi_{ijkl}) = U_{NB} + U(V/2)(1 + \cos 3\phi_{ijkl}) \quad (5)$$

where V is that part of the experimental barrier not accounted for in the non-bonded term U_{NB} , and $\phi(ijkl)$ is the torsion angle generated by bond twisting about the bonded atoms j and k. All interactions arising from bond twisting have been included, and the contribution per interaction is taken as 0.80 kcal/mol.

A modified Newton-Raphson method of minimisation has been used to vary all the independent coordinates of the four energy terms simultaneously with respect to the total conformational potential

energy of the molecule. This frequently used method for minimisation has been described adequately and it will not be discussed further.^{205,206,208,209} Convergence was considered complete when all the root-mean-square shifts were less than 0.002 angstrom.

A very important point to notice is that this molecular mechanics program only accounts for an isolated molecule in the gas-phase and thus excludes phenomena like the crystal packing forces and hydrogen bonding. Various workers have shown that a hydrogen bond interaction can be taken into account in the atom-atom potential scheme using the following potential function for the Morse curve:^{210,211}

$$V_{HB} = D[1 - \exp(-n\Delta r)]^2 - D$$

where: D = hydrogen bond dissociation energy,

$\Delta r = r - r_0$,

r_0 = equilibrium H...O distance,

n = empirical parameter.

Most conformational calculations are conducted for "free" molecules, in other words without taking into consideration the effect of the medium. Kitaigorodsky¹⁷⁸ has emphasised that the crystal field does not affect the lengths of the bonds in any way and alters but insignificantly the values of the valence angles. However, if rotation about single bonds is possible, it often involves insignificant use of energy and is affected by the crystal-field forces. Thus, the minimum of an energy surface yields both packing parameters and values of internal rotation angles, which may be significantly different from the value for the optimal conformation of an isolated molecule.

The main emphasis in this study was thus to look for the

differences between the calculated and the actual structure which were then attributed to the effect of hydrogen bonding and packing forces.

4.3. Results and Discussion

The calculated structure of norbornane, (66), is compared with the structures published by other authors (Table 19). The two main discrepancies are the C(1)-C(2) bond length and the angle theta which defines the angle between the two planes in the six-membered ring. The values are sufficiently close, however, that one has no hesitation in basing the subsequent calculations on this model.

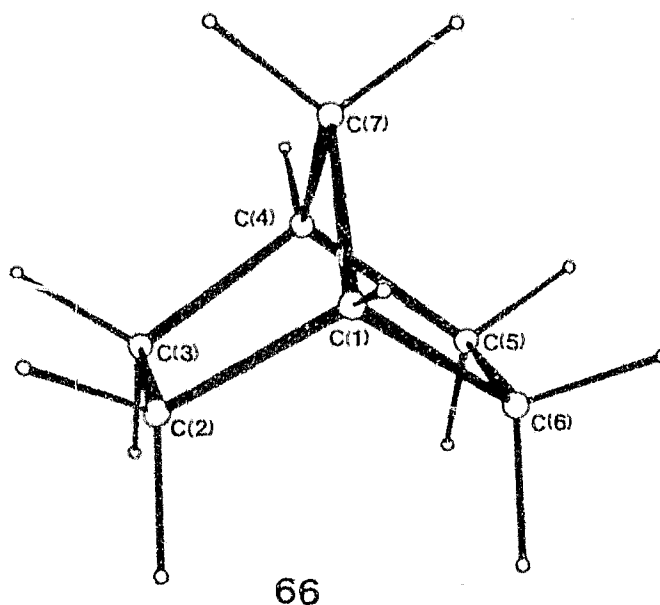
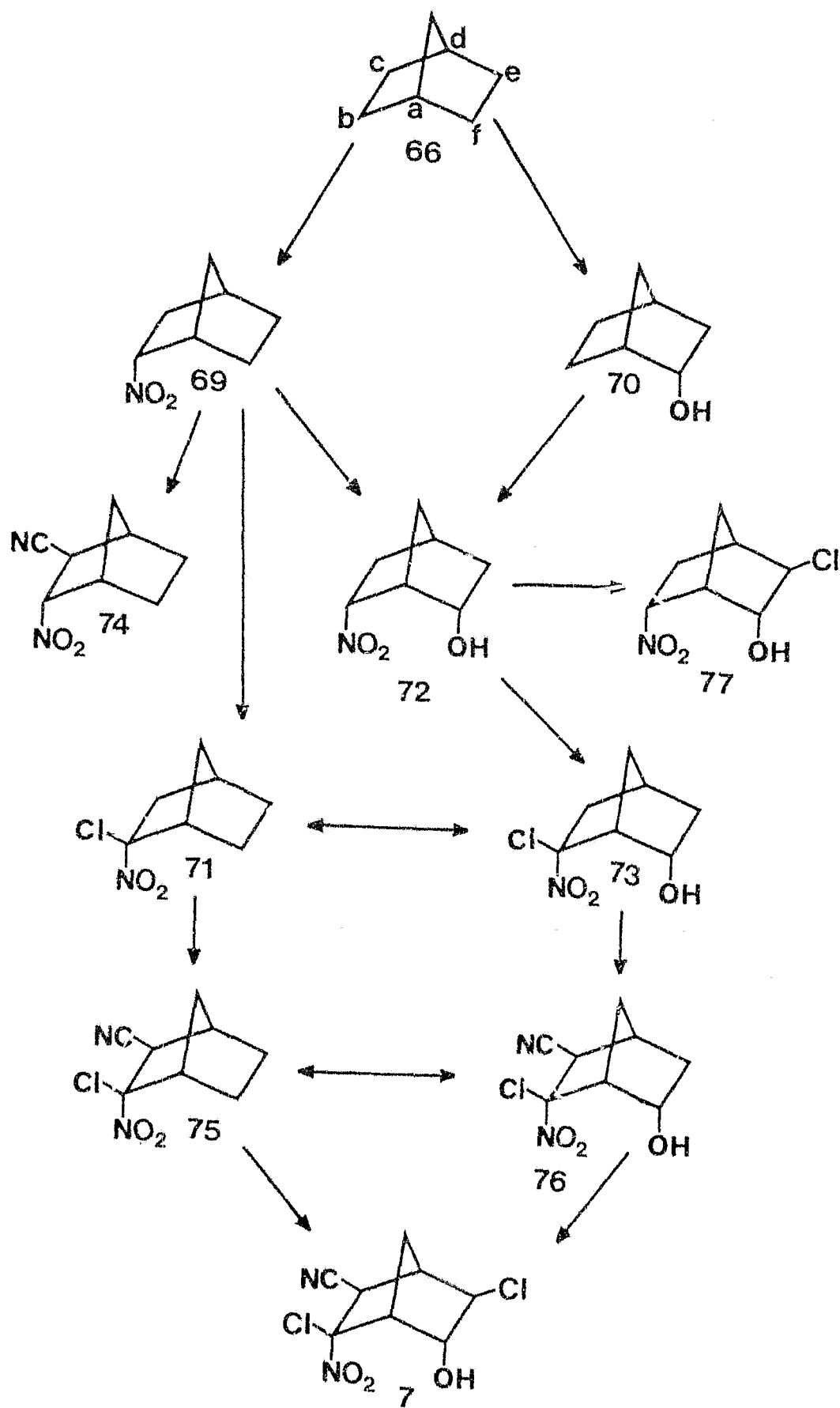


Table 19. Comparison of structural parameters determined in norbornane.

	STRUCT.1	STRUCT.2	STRUCT.3	STRUC.4	THIS STUDY
Ref.	197	196	198	202	
<CC>	1.549	1.545	1.555	1.5479	1.547
C(1)-C(2)	1.542	1.534	1.556	1.536	1.548
C(2)-C(3)	1.543	1.578	1.551	1.573	1.549
C(1)-C(7)	1.570	1.535	1.559	1.546	1.541
<CH>	1.126	1.11	1.11	1.113	1.097
C(1,7,4)	93.2	95.3	96	93.41	93.31
C(7,1,2)	101.2	100.4	101.6	102.04	102.03
C(1,2,3)	103.9	104.9	104.1	102.71	102.93
C(1,2,6)	108.1	105.6	103.4	108.97	108.35
theta	113	111.3	108	113.1	108.35

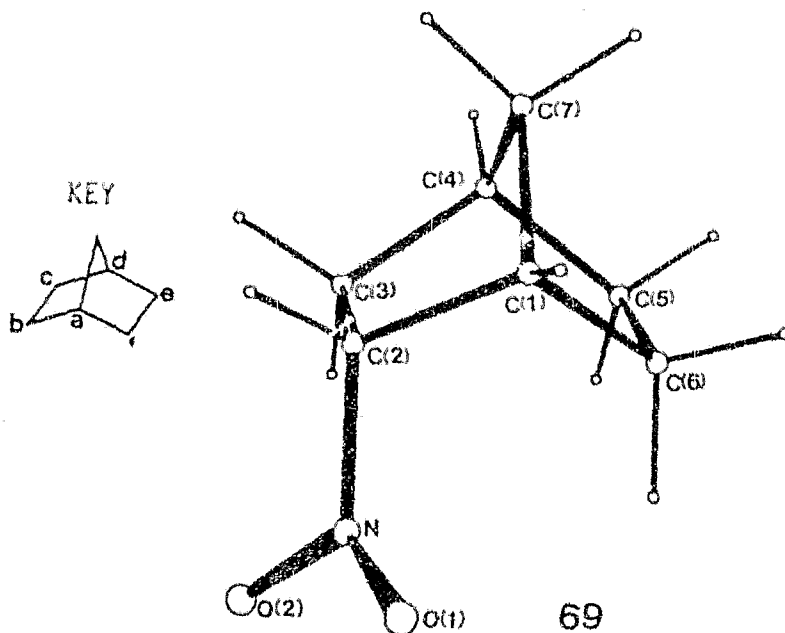
All angles in degrees and bond lengths in angstroms. Theta is the dihedral angle between the C(1,2,3,4) and C(1,6,5,4) planes.



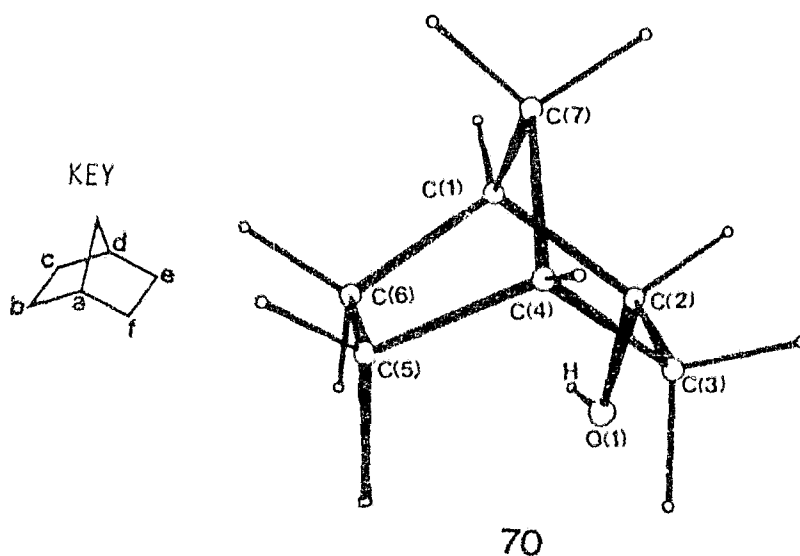
Scheme 14

The order in which functional groups have been added to this basic model is shown in the flowsheet in Scheme 14. A different numbering scheme was used for the calculated structures. This scheme is independent of the functional groups present and is shown in Scheme 13. The geometrical parameters for all the calculated structures appear in Appendix 4.

Firstly, the calculations were repeated for the simple cases in which either an isolated endo-nitro or endo-hydroxy group was introduced. The preferred orientation of an endo nitro substituent on the norbornyl skeleton is found at an angle of -46.1 degrees for C(c)-C(b)-N-O(2) as indicated in (69). The values for former angle in the crystal structure of (6) and (7) are -14.7 and -14.3 degrees respectively.

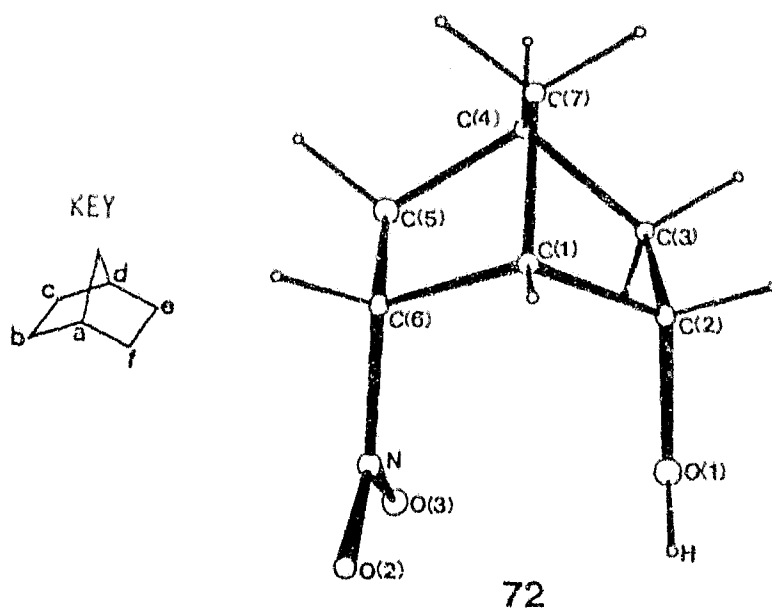


The most stable conformation for an endo hydroxyl group is at the nearly anti angle of -174.1 degrees for C(e)-C(f)-O-H as shown in (70). The hydroxyl orientation in (7) is given by an angle of -142.0 degrees for C(e)-C(f)-O-H.



Initially it was thought that the nitro group in (7) might be forced into a specific conformation by the geminal chlorine atom and that the bulkiness of this substituent actually dictates the geometry of the nitro group, but the calculations on the model (71) proved that this is not the case. A comparison between 2-endo-nitrobicyclo[2.2.1]heptane, (69), and 2-exo-chloro-2-endo-nitrobicyclo[2.2.1]heptane, (71), shows a small (1.4 degrees) difference for the dihedral angle $\angle(c)-C(b)-N-O(1)$.

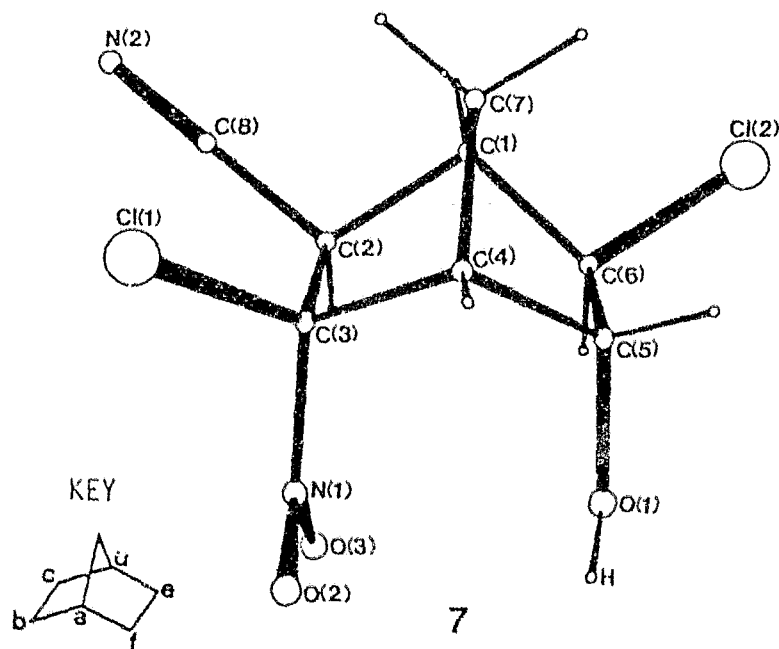
When both endo-nitro and endo-hydroxy groups are present, non-bonded interactions between these groups results in the stable conformation shown in (72). The torsion angles $\angle(e)-C(f)-O-H$ and $\angle(c)-C(b)-N-O(3)$ are -174.0 and 14.0 degrees respectively.



Moreover, a second energetic requirement needs to be satisfied by the nitro group when an α -chlorine atom is introduced to the molecule, (73). The nitro group reorientates itself to adopt the conformation with $C(c)-C(b)-N-O(3)$ equal to -42.3 degrees. This reorientation causes a subsequent change in the orientation of the hydroxyl group ($C(e)-C(f)-O-H = -38.0^\circ$).

The vicinal nitrile group does not cause a considerable change, (74), in the orientation of the nitro group ($C(c)-C(b)-N-O(3) = -41.1^\circ$). With both vicinal nitrile and geminal chlorine, (75), the dihedral angle, $C(c)-C(b)-N-O(3)$, is -41.7 . The nitro group orientation still does not change much (-42.9°) when the hydroxyl group is now introduced, (76). At this stage, it is probably still the effect of the α -chlorine atom overriding the non-bonding interaction between the nitro and hydroxyl groups, exactly as was seen as going from (71) to (73). It is only when the final substituent, the chlorine atom vicinal to the hydroxy group (7) is introduced, that one can in some measure counteract the geminal chlorine effect, and see the effect of non-bonded attraction between the nitro and hydroxy groups in a $C(c)-C(b)-N-O(3)$ torsion angle of 7.3 degrees.

The presence of the chlorine atom vicinal to the hydroxyl function appears to be very crucial for the orientation of the latter. A comparison between (70), (72) and (77) shows a major difference in the torsional angle (-41.5°) of (77) compared to that of (72) (-174.0°) and (70) (-174.1°). In going to the structure of (7) where the nitro group is in the presence of both the nitrile and the α -chlorine group, the non-bonded interaction of the nitro group with the hydroxyl group seems to be much more favoured, and the hydroxyl group is swung through a rather large angle ($C(e)-C(f)-O-H = -167.8^\circ$) to adopt the conformation shown in below.



The calculated structures provided a useful catalogue of possible orientations. Convergence was generally reached at energy minima corresponding to two different orientations of the nitro group. Table 20 shows the values for the dihedral angle C(c)-C(b)-N-O(3) for all the computed structures containing this fragment.

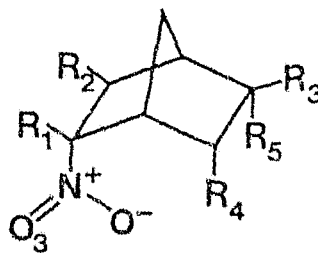
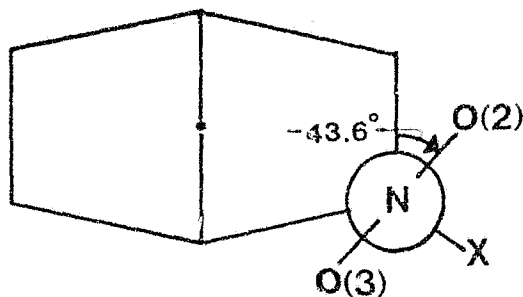


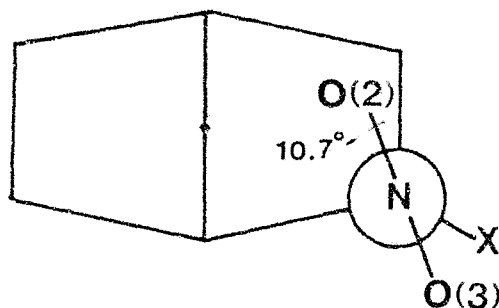
Table 20. Conformations of the nitro group.

Angle (°)	R(1)	R(2)	R(3)	R(4)	R(5)	Compound
-46.1	H	H	H	H	H	69
-44.7	Cl	H	H	H	H	71
-42.3	Cl	H	H	OH	H	73
14.0	H	H	H	OH	H	72
-41.1	H	CN	H	H	H	74
-41.7	Cl	CN	H	H	H	75
-43.5	H	H	Cl	OH	H	77
-42.9	Cl	CN	H	OH	H	76
-46.4	H	H	H	H	OH	83
7.3	Cl	CN	Cl	OH	H	7
crystal:						
-14.3	Cl	CN	Cl	OH	H	7
-14.7	Br	CN	Br	OH	H	6

The one minimum for the potential energy is found at a mean dihedral angle of -43.6 degrees. This conformation is shown in the following Newman projection.



The other minimum for the conformational potential energy of the nitro group is at an angle of 10.7 degrees. The nitro group is rotated through an angle of 54.3 degrees and O(3) lies between the bridgehead carbon and C(c) which is indicated in the next Newman projection.



According to Durig *et al.*¹¹⁸ the energy required to rotate about a C-NO₂ bond is of the order of 1 kcal/mol in aliphatic systems, which explains the existence of different conformations for the nitro group. It is interesting to note that each of these conformations brings an alternative oxygen atom in closer contact with the hydroxyl group. The value of the corresponding torsion angle, in the crystal structure of compound (7), is -14.3 degrees. This position is possible due to the formation of the intramolecular hydrogen bond.

A corresponding change in the position of the hydroxyl proton is

also observed. Table 21 contains the values for the torsion angle C(3)-C(2)-O(1)-H for all the calculated structures having this fragment.

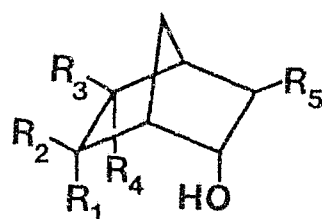
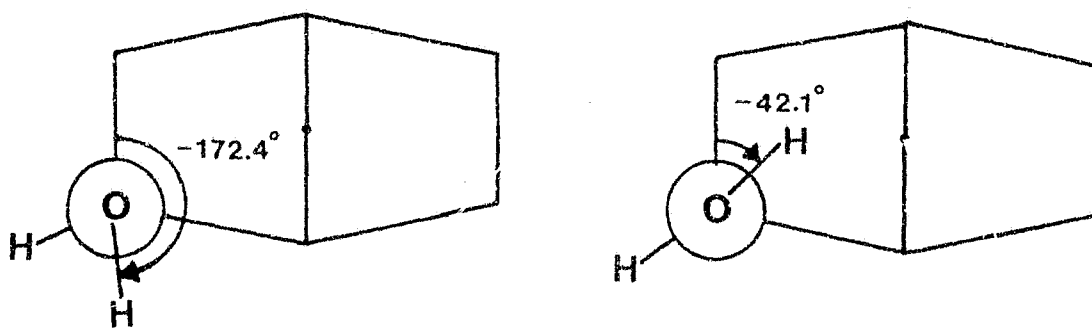


Table 21. Conformations of the hydroxyl group.

Angle (°)	R1	R2	R3	R4	R5	Compound
-174.1	H	H	H	H	H	70
-38.0	NO ₂	Cl	H	H	H	73
-174.0	NO ₂	H	H	H	H	72
-41.5	NO ₂	H	H	H	Cl	77
-46.8	NO ₂	Cl	CN	H	H	76
-173.7	H	H	H	NO ₂	H	83
-167.8	NO ₂	Cl	CN	H ²	Cl	7
Crystal:						
-142.0	NO ₂	Cl	CN	H	Cl	7

These values correspond to potential energy minima in the absence of hydrogen bonding for two orientations of the hydroxyl proton, namely at mean angles of -172.4 and -42.1 degrees with respect to the dihedral angle as defined for Table 20. The value found for the crystal structure is -142.0 degrees. The following two Newman projections show the energy minima.



The calculations have shown that hydrogen bonding to the nitro group can take place to either O(2) or O(3) of the nitro group but

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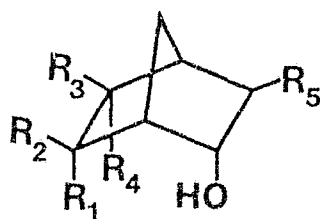
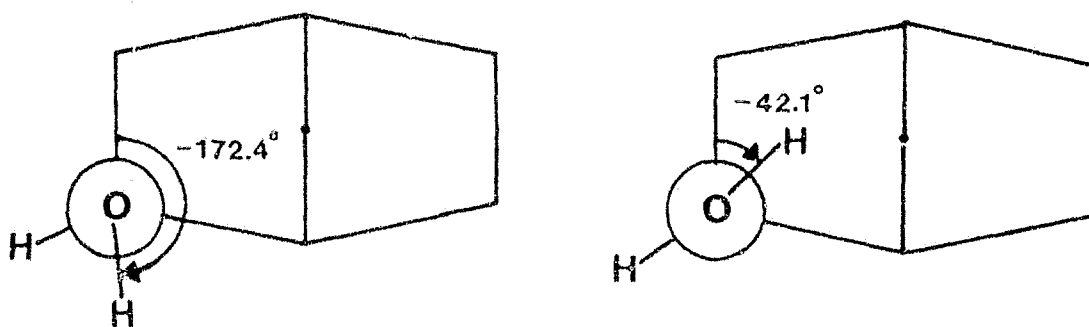


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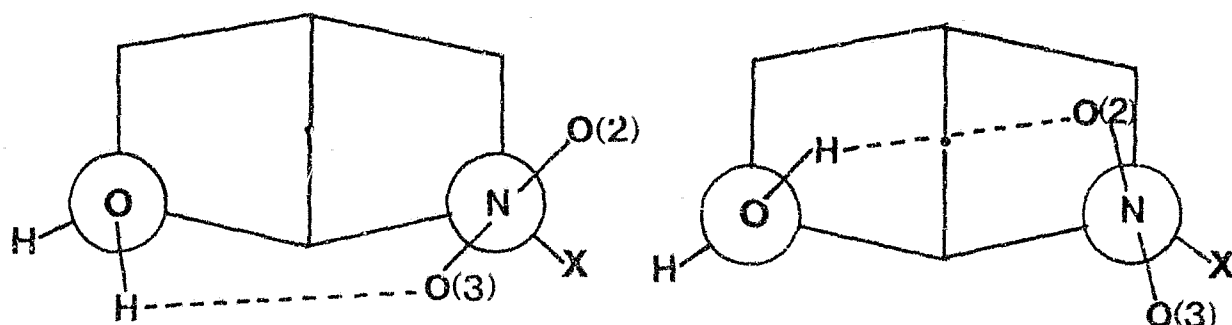
Angle (°)	R1	R2	R3	R4	R5	Compound
-174.1	H	H	H	H	H	70
-38.0	NO ₂	Cl	H	H	H	73
-174.0	NO ₂	H	H	H	H	72
-41.5	NO ₂	H	H	H	Cl	77
-46.8	NO ₂	Cl	CN	H	H	76
-173.7	H	H	H	NO ₂	H	83
-167.8	NO ₂	Cl	CN	H	Cl	7
Crystal:						
-142.0	NO ₂	Cl	CN	H	Cl	7

These values correspond to potential energy minima in the absence of hydrogen bonding for two orientations of the hydroxyl proton, namely at mean angles of -172.4 and -42.1 degrees with respect to the dihedral angle as defined for Table 20. The value found for the crystal structure is -142.0 degrees. The following two Newman projections show the energy minima.



The calculations have shown that hydrogen bonding to the nitro group can take place to either O(2) or O(3) of the nitro group but

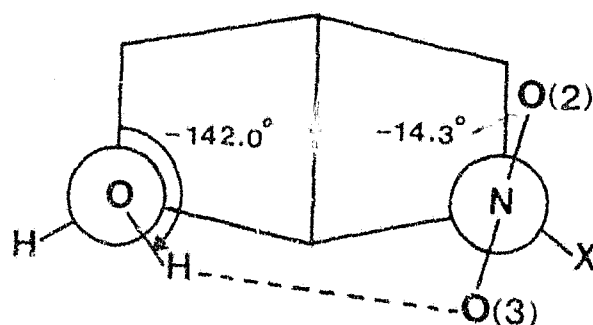
never to both oxygens atoms simultaneously as depicted below.



case 1

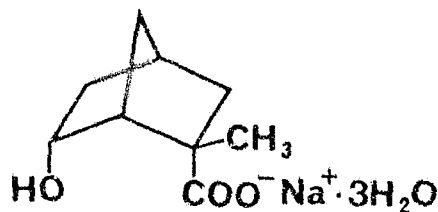
case 2

The most stable position for the hydroxyl proton is the position anti to the C(e)-C(f) bond, but due to the hydrogen bonding interaction it is positioned at torsion angle of -142.0 degrees. A bifurcated hydrogen bond would imply that the hydroxyl proton has to overcome the torsional barrier to adopt a nearly-eclipsed position with respect to the C(f)-C(a) bond, which is not favoured energetically.



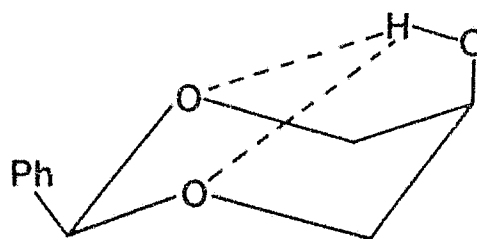
crystal structure

Proof that the most stable conformation of the hydroxyl proton is in fact the anti position is found in the crystal structure of sodium 2-exo-methyl-6-endo-carboxylate.3H₂O,²¹² (78), as well as in the calculated structure of bicyclo[2.2.1]heptan-2-endo-ol, (70). In these examples the hydroxyl group is featured in a non-hydrogen bonded environment.



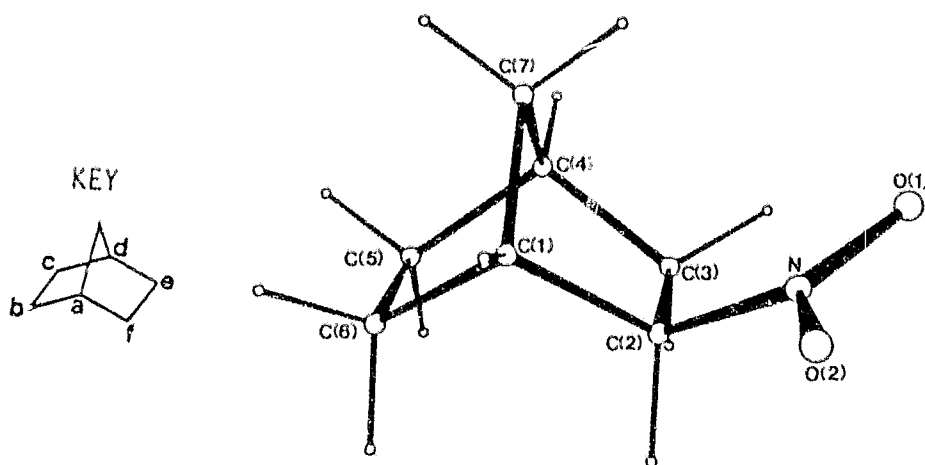
78

The inverse situation is found with the hydrogen bonds in (*Z*)-2-phenyl-1,3-dioxan-5-ol,²¹³ (79), and related substances²¹⁴ which are of the bifurcated type. The hydroxyl groups bisects the regions between the acceptor groups, and hydrogen bonding to just one of the acceptors is not energetically favoured because the hydroxyl groups would have to adopt eclipsed conformations.



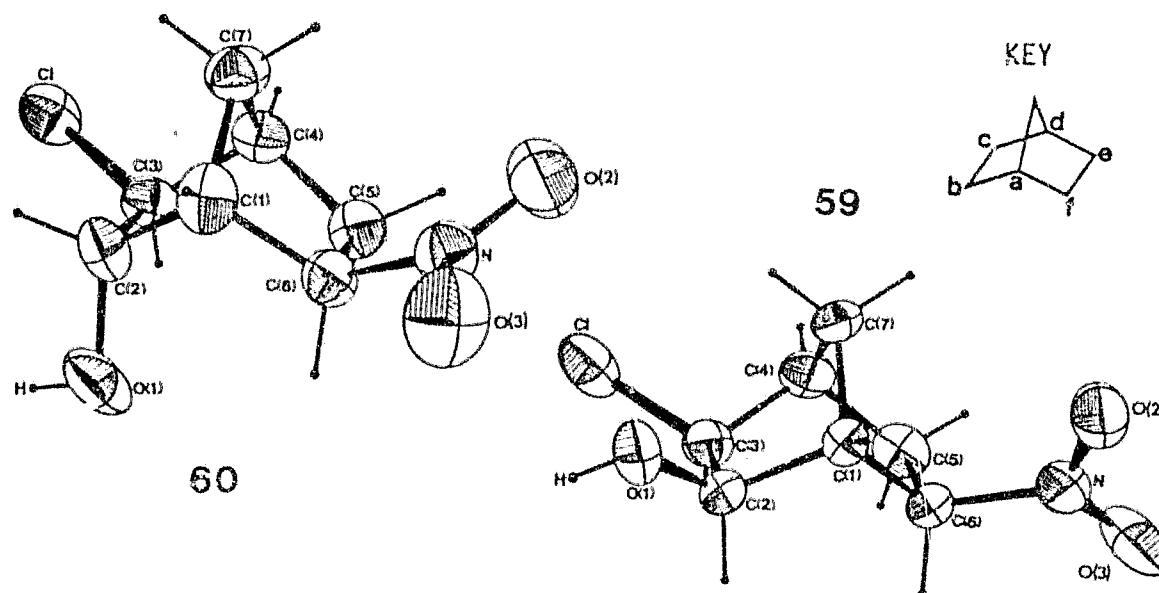
79

The discrepancy between the orientations of the *exo* nitro groups in the crystal structures of (59) and (60) prompted the further investigation reported here. The geometries of the different conformers of (59) and (60) were calculated. The computed structure for 2-*exo*-nitrobicyclo[2.2.1]heptane, (80), has a torsion angle of -1.8 degrees for C(c)-C(b)-N-O(1).

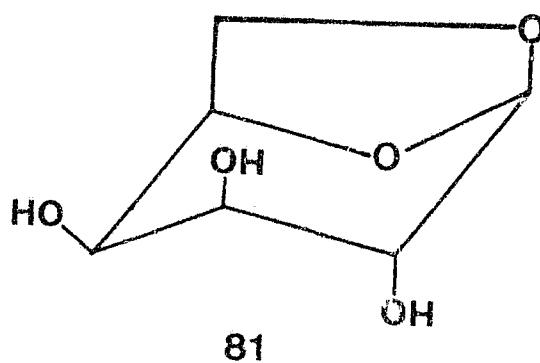


80

The dihedral angles in the two crystal structures of 3-exo-chloro-6-exo-nitrobicyclo[2.2.1]heptan-2-exo-ol, (60), and 3-exo-chloro-5-exo-nitrobicyclo[2.2.1]heptan-2-endo-ol, (59), are -70.6 and 10.4 degrees respectively, but both these structures show evidence of intermolecular hydrogen bonding to hydroxyl groups. This is most probably the major reason for the deviation of these angles from the computed value.²¹⁵ The pronounced difference between (59) and (60) is a net effect arising from hydrogen bonding and steric interactions as was discussed in Chapter 3.



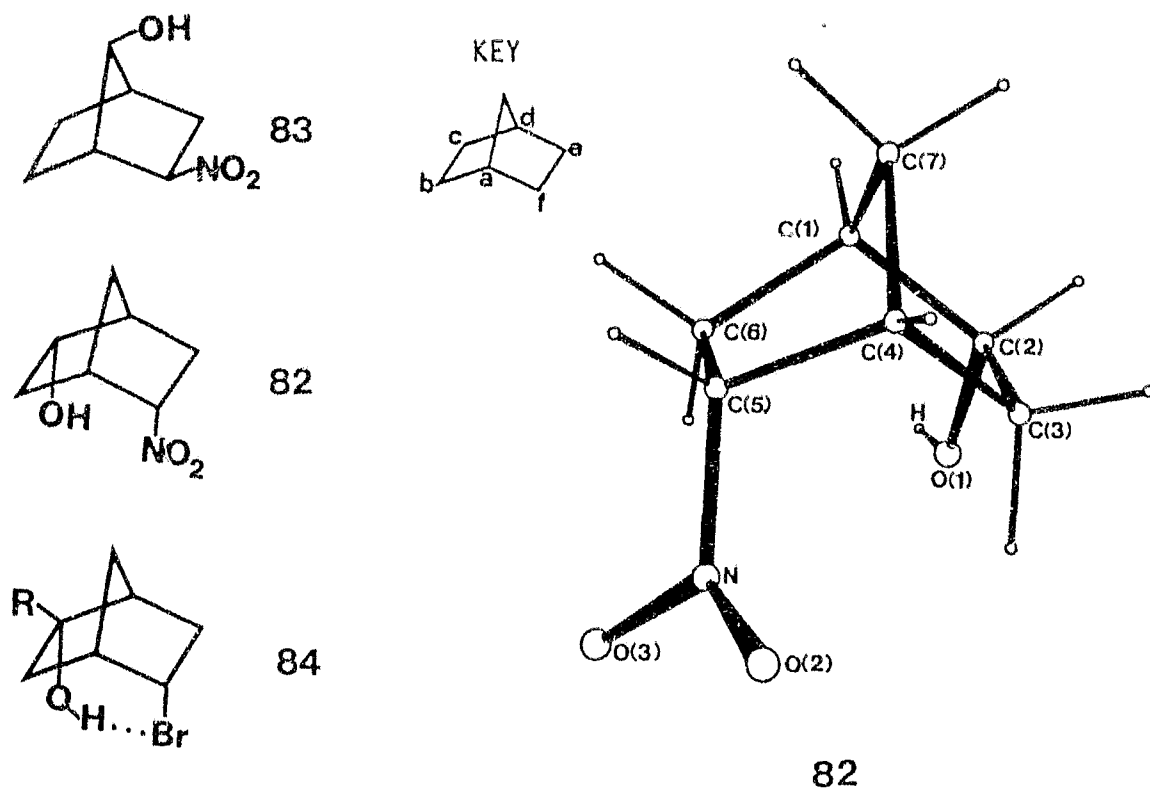
Ruble and co-workers²¹⁶ reported the crystal structure and molecular mechanics calculations of 1,6-anhydro- β -D-galactopyranose, (81), and concluded that the major difference in the conformations of the crystal structure and calculated structure is in the orientations of the hydroxyl groups. The orientation of these hydroxyl groups depends on intermolecular hydrogen bonding, which was not accounted for in this molecular mechanics model. The large discrepancies between values of these torsion angles are therefore not unexpected.

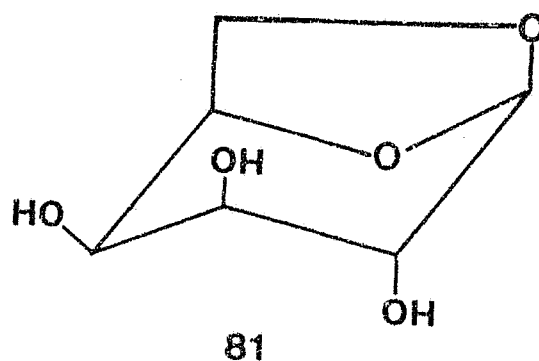


Like other theoretical methods, molecular mechanics can also be used to predict properties of unknown molecules. The molecular structures of 5-endo-nitrobicyclo[2.2.1]heptan-2-endo-ol, (82), and 2-exo-nitrobicyclo[2.2.1]heptan-7-syn-ol, (83), were calculated to investigate the possibility of hydrogen bonding before attempts were made to synthesise these systems.

Newton and Roberts²¹⁷ have studied the bicyclic intermediate (84) and they have reported that an endo substituent at C(5) is capable of forming a hydrogen bond. In our case, (82), it was shown from the calculations that hydrogen bonding is not favoured, as indicated by the very large oxygen-oxygen distances below:

$$\begin{aligned} \text{O}(1) \dots \text{O}(2) &= 4.538 \text{ \AA}, \\ \text{O}(1) \dots \text{O}(3) &= 4.121 \text{ \AA}. \end{aligned}$$

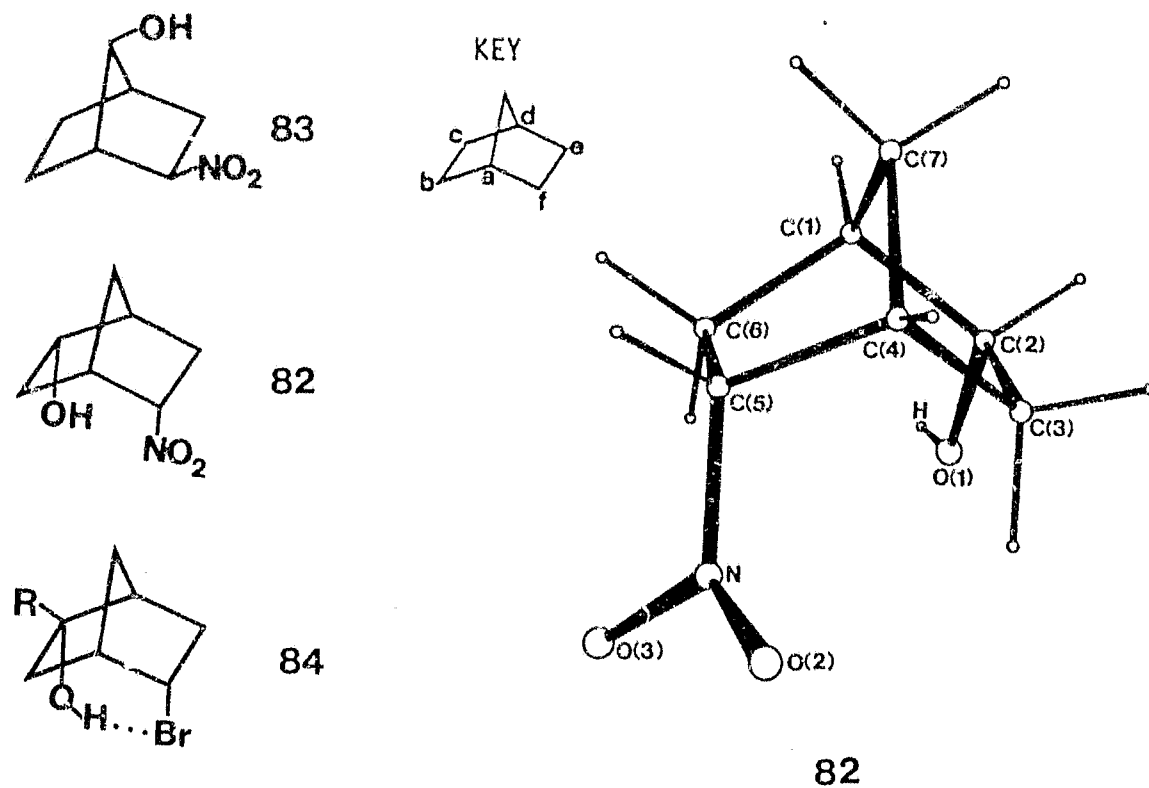




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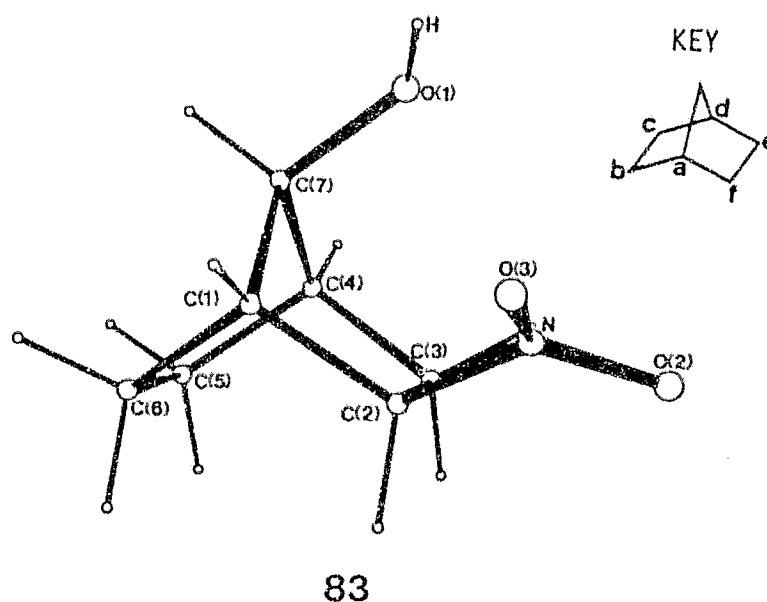


It can thus be concluded that intramolecular hydrogen bonding is not probable in these conformally restricted 1,4-nitroalcohols. However, in the 1,3-nitroalcohol, (83), it can occur if the nitro group rotates in the usual way to favour the interaction. The non-bonded distances listed below were calculated without taking any hydrogen bonding into account.

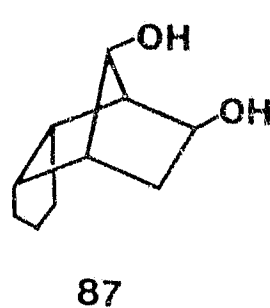
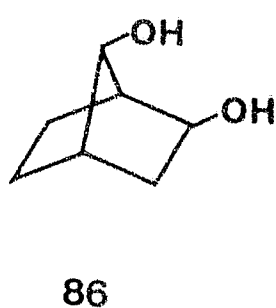
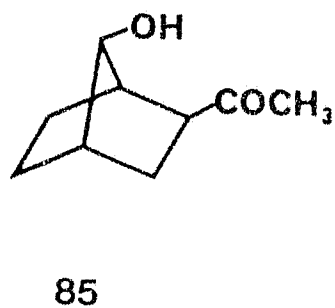
$$O(1) \dots O(2) = 3.627 \text{ \AA},$$

$$O(1) \dots O(3) = 3.293 \text{ \AA},$$

$$O(3) \dots H = 3.008 \text{ \AA}.$$

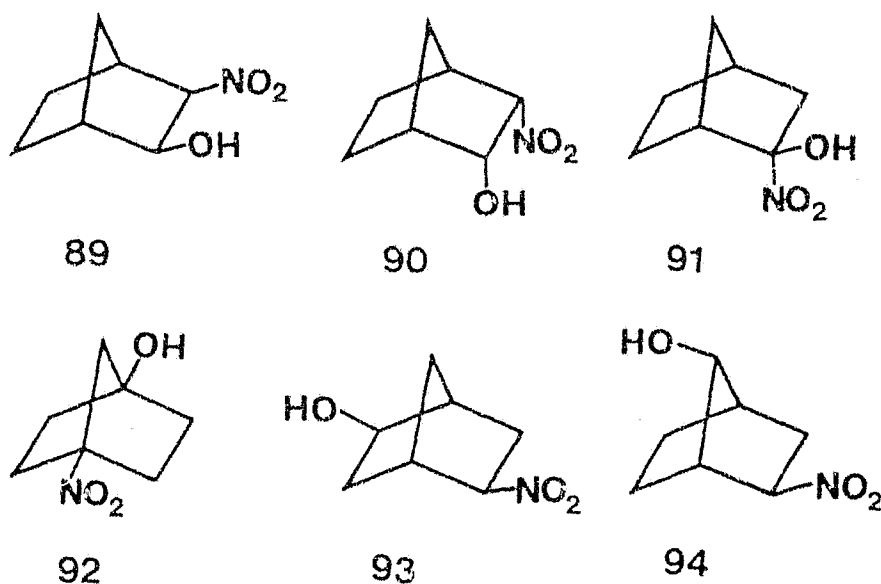


Intramolecular hydrogen bonding in 2,7-functionalised norbornanes like (85), (86) and (87) have been reported. 218-220

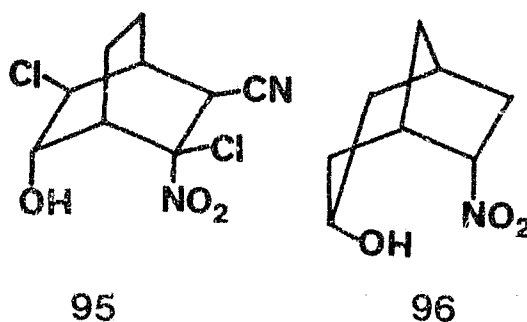


FUTURE DIRECTION

A noteworthy feature to emerge from this project is that, no matter where nitro and hydroxy groups are positioned on a norbornyl skeleton, hydrogen bonding between them (whether intra- or intermolecular) appears to exist. In structural terms, the types of compounds which might then show such hydrogen bonding are obviously much more diverse than have been investigated so far. For example, systems (89), (90) and (91) might possess intramolecular hydrogen bonds, while those like (92), (93) and (94) (and even tricyclic compounds like (56) and (65) described in this project) might show interesting intermolecular hydrogen bonding. A very fruitful extension of this project might well be the synthesis and crystallographic investigation of these and similar systems

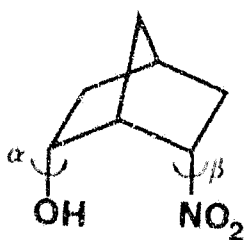


The rigid norbornane skeleton is obviously immobile, but the conformation of the substituents attached to it are conformationally freer. In this regard it would be interesting to examine the conformation of substituents in less rigid systems (like (95) and (96)), and the consequent effects on hydrogen bonding.



In general, hydrogen bonding can be studied for different donors XH (X = N and S) and acceptor groups with a similar demand to the nitro group (carboxylate and sulphone), thus providing yet another possible extension of the project.

The molecular mechanics approach can be improved by introducing a potential for hydrogen bonding to the program which must be able to account for the strength as well as the directional effect of this interaction. The ability to simulate packing forces would add to the advantages of this method. A routine that would allow a rigid body calculation, with the exception of a few parameters (like the angles α and β shown below), could be useful in the determination of energy surfaces.



CHAPTER 5

EXPERIMENTAL

GENERAL NOTES

Infrared spectra were recorded as neat liquids or potassium bromide disks using a Pye Unicam SP3-300 or a Perkin-Elmer 580B spectrometer. High resolution spectra, for the hydrogen bonding studies, were recorded in solution cells (0.5 mm pathlength) fitted with sodium chloride windows on the latter instrument. Absorption bands are listed in cm^{-1} . The following abbreviations are used: s=strong; m=medium; w=weak and br=broad.

Nuclear magnetic resonance spectra were determined on either a Bruker WP80 (80 MHz) or a Varian EM360A (60 MHz) spectrometer and the chemical shifts are reported in delta units downfield from tetramethylsilane. The variable temperature work was recorded on a Bruker WM500 spectrometer. The solvents were dried when necessary with activated 4Å molecular sieves. The chemical shifts are quoted in the following way: delta value (number of protons, nature of the resonance, coupling constants, assignment). Coupling constants were obtained from a first-order analysis of observed splitting patterns which are abbreviated as follows: s=singlet; d=doublet; t=triplet; m=multiplet; and br=broad.

Mass spectra were recorded on a Varian LH-7 mass spectrometer. All the peaks in the higher mass regions with relative abundance greater than 10% have been quoted unless otherwise stated. The sequence in which data are tabulated is: m/e value (per cent relative abundance, assignment if unambiguous).

All melting points were performed on a Reichert hot-stage

microscope melting point apparatus and are uncorrected. All organic extracts from aqueous media were dried over anhydrous magnesium sulphate before concentration. A Buchi Rotavapor was used for removal of solvent from solutions under reduced pressure of ca. 25 mm Hg. Organic solvents used for preparations were purified and dried according to standard procedures.²²¹ Reactions were monitored, wherever possible, by thin-layer chromatography.

Merck DC-Fertigplatten Kieselgel 60F-254 (0.25 mm) plates were used for thin layer chromatography. The spots were detected with one of the following techniques: ultra-violet radiation; iodine vapour or chromic acid spray.²¹⁹ The stationary phase for column chromatography was Merck Kieselgel 60 (particle size 0.063 to 0.2 mm).

Preparative medium pressure chromatography was used for difficult separations. The apparatus consisted of two Chromatronix LC columns. The compound was applied onto a scrubber column (12.7x265 mm) and then transferred, with a suitable solvent mixture, onto the main column (12.7x960 mm) using a pressure of 40-60 p.s.i. These columns were packed with ICN Kieselgel Woelm (particle size 0.063 to 0.032).

5.1. Preparation of 2-nitroethanol.

2-Nitroethanol was prepared by condensation of formaldehyde, employed in the solid state as paraformaldehyde, with a large excess of nitromethane in the presence of an alkali catalyst as outlined in the paper by Noland.¹²⁷

¹H NMR (CDCl₃) 4.55 (2H, t, J=6 Hz, H3 and H4),
 4.15 (2H, dt, J=4.4 and J=6.2 Hz, H2 and H3),
 3.35 (1H, t, J=6 Hz, hydroxyl).

IR (thin film) 3560(m, br, OH), 2960(w), 2905(w, shoulder),
1555(s, NO₂), 1375(s, NO₂), 1175(s, C-O).

5.2. Preparation of nitroethylene.

The nitro olefin was prepared according to the method of Buckley and Scaife.¹²⁸ which involves the phthalic anhydride dehydration of 2-nitroethanol.

¹H NMR (CDCl₃) 7.16 (1H, dd, J=7 Hz and J=15 Hz),
6.63 (1H, dd, J=15 Hz and J=2 Hz),
5.95 (1H, br d, J=7 Hz).

IR (thin film) 3130(w, CH=CH₂), 3110(w, shoulder),
2865(w), 1638(w, C=C), 1523(s, NO₂),
1375(s, NO₂), 1355(s).

5.3. Diels-Alder reaction of nitroethylene with cyclopentadiene.¹²⁹

Nitroethylene (2.03 g; 27.71 mmol) was dissolved in dry diethyl ether (20 ml). The solution was cooled to 0°C in an ice bath, and freshly cracked cyclopentadiene (2.64 g; 40.30 mmol) was added dropwise to the solution with stirring. The reaction mixture temperature was maintained at 0°C for 20 minutes and then allowed to reach room temperature with stirring being continued for another hour. Thin-layer chromatography showed only one spot, R_f 0.68 (ethyl acetate-hexane; 1:3). The solvent and excess cyclopentadiene were removed at reduced pressure to give the product as a pale yellow semi-solid (3.81g, 98%). The product was vacuum distilled to afford a colourless solid (2.86 g; 75% recovery) b.p. 55-60°C/0.7 mm Hg (literature 60-65°C/1.8 mm Hg),¹²⁹ m.p. 37-40°C.

¹H NMR (CDCl₃) 6.40 (1H, dd, J=3 Hz, J=6 Hz, H2),
5.93 (1H, dd, J=3 Hz, J=6 Hz, H3),
5.03 (1H, m, J=4 Hz, H5x),

3.58 (1H, m, bridgehead),
3.00 (1H, m, bridgehead),
2.50-1.30 (4H, m, H7a, H7s, H6n and H6x).

IR (thin film) 3150(w), 3075(w), 2990(m), 2955(m),
2910(w), 2880(w), 1535(s, NO₂), 1462(w),
1445(m), 1375(s, NO₂), 710(s).

MS 93(39, M-NO₂), 91(57), 81(18), 79(76),
78(15), 77(70), 67(15), 66(100, M-(NO₂,
C₅H₆)).

5.4. Reaction of 5-endo-nitrobicyclo[2.2.1]hept-2-ene, (48), with
chromyl chloride.¹⁴⁰

A solution of 5-endo-nitrobicyclo[2.2.1]hept-2-ene (3.80 g;
27.31 mmol) in acetone (60 ml) was cooled in a dry ice-acetone bath
to -78°C and then treated with chromyl chloride¹⁷⁵ (8.68 g; 48.06
mmol) which was added via a dropping funnel with vigorous stirring
of the solution. Addition was controlled so that a temperature of
-70°C was not exceeded. After the addition (30 minutes) had been
completed, the mixture was stirred at -75°C for 65 minutes, then
allowed to warm up to room temperature and stirred for an
additional 6 hours. Thin-layer chromatography showed that all the
starting material had been consumed. The dark red-brown mixture was
then quenched by slowly pouring it into an ice-cold aqueous
solution of sodium bisulphite (0.3 mol/30 ml). The green mixture
was stirred for 45 minutes in an ice bath. It was then concentrated
and extracted with diethyl ether (3x25 ml portions). The combined
organic extracts were washed with water (2x20 ml portions) and
sodium chloride (50 ml, saturated, aqueous). The ether was
evaporated to give a viscous oil (3.00 g; 58% crude yield).
Thin-layer chromatography showed two major spots, R_f 0.86 and
0.57 (ethyl acetate-hexane; 1:1). This mixture of products was used

for most purposes.

Samples of the two major products were separated from the mixture by column chromatography (80 g; 2.8x30 cm) eluting with ethyl acetate-hexane mixtures (1:20 to 1:5). Very small quantities of the pure components were obtained, and these were tentatively assigned as 3-exo-chloro-6-exo-nitrobicyclo[2.2.1]heptan-2-one, (50), (211 mg; ca. 5% yield), R_f 0.86, m.p. 78-79°C, recrystallised from diisopropyl ether and ethyl acetate and 3-exo-chloro-6-endo-nitrobicyclo[2.2.1]heptan-2-one, (49), (256 mg; ca. 6%), R_f 0.57, m.p. 86-87°C, recrystallised from ethyl acetate. The total recovery from the column was 2.45 g, of which 1.78 g was still a mixture of the two major isomers. The rest comprised a mixture of the isomers with other minor products.

Analyses of endo nitro isomer:

^1H NMR (CDCl_3) 5.09 (1H, 5-line m, J ca. 4.5 Hz, H6),
4.15 (1H, d, J = 3.42 Hz, H3),
3.25 (1H, m, H1),
2.92 (1H, m, H4),
2.75-1.95 (3H, m, H5x, H5n and H7a),
1.79 (1H, d (with fine coupling), J = 12 Hz, H7s).

IR (KBr) 3010(w), 2970(m), 2900(w), 1762(s, C=O),
1550(s, NO_2), 1368(s, NO_2).

MS 189/191(0.3/0.6, M^+), 143/145 (2/0.8,
M- NO_2), 115(7, M-(C=O, NO_2)), 107(3),
80(34, M-(C=O, Cl, NO_2)), 79(100), 78(16),
77(98), 75(23), 67(28), 66(18), 65(14), 63(7).

C, H and N microanalysis

Found: C, 44.31; H, 4.06; N 7.33.

$C_7H_8NO_3Cl$ requires C, 44.35; H 4.25;
N, 7.39%.

Analyses of exo nitro isomer:

^1H NMR ($CDCl_3$) 4.66 (1H, 4-line m, J ca. 3.9 Hz, H6),
3.76 (1H, d, J = 2.69 Hz, H3),
3.39 (1H, br s, H1),
2.86 (1H, m, H4),
2.60-2.90 (2H, m, H5x and H5n),
2.31 (1H, d (with fine coupling), J = 11 Hz, H7a),
2.00 (1H, d (with fine coupling), J = 11 Hz, H7s).

IR (KBr) 3010(w), 2998(w), 2970(w), 2910(w),
1762(s, C=O), 1550(s, NO_2), 1367(s, NO_2).

MS 189/191(6/2, N^+), 142/144(6/2, M- NO_2),
122(3), 115(6), 107(8, M-(NO_2 , Cl)), 88(3),
86(5), 81(6), 80(11), 79(100), 78(10), 77(39),
75(16), 67(16), 66(11), 65(8).

C, H and N microanalysis

Found C, 44.13; H, 4.10; N, 7.39.

$C_7H_8NO_3Cl$ requires C, 44.35; H, 4.25;
N, 7.39%.

5.5. Attempted hydrodehalogenation of α -chloroketones.

(a) With iodotrimethylsilane.¹⁴⁴

Chlorotrimethylsilane (133.6 mg; 1.23 mmol), and after 5 minutes,
sodium iodide (184.4 mg; 1.23 mmol) were added to a stirred mixture of
unseparated isomers (152 mg; 0.81 mmol) in dry acetonitrile (4 ml).
The mixture was stirred at room temperature for 48 hours after which

C, H and N microanalysis

Found: C, 44.31; H, 4.06; N 7.33.

$C_7H_8NO_3Cl$ requires C, 44.35; H 4.25;
N, 7.39%.

Analyses of exo nitro isomer:

^1H NMR ($CDCl_3$) 4.66 (1H, 4-line m, J ca. 3.9 Hz, H6),
3.76 (1H, d, J = 2.69 Hz, H3),
3.39 (1H, br s, H1),
2.86 (1H, m, H4),
2.60-2.90 (2H, m, H5x and H5n),
2.31 (1H, d (with fine coupling), J = 11 Hz, H7a),
2.00 (1H, d (with fine coupling), J = 11 Hz, H7s).

IR (KBr) 3010(w), 2998(w), 2970(w), 2910(w),
1762(s, C=O), 1550(s, NO_2), 1367(s, NO_2).

MS 189/191(6/2, M^+), 142/144(6/2, M- NO_2),
122(3), 115(6), 107(8, M-(NO_2 , Cl)), 98(3),
86(5), 81(6), 80(11), 79(100), 78(10), 77(39),
75(16), 67(16), 66(11), 65(8).

C, H and N microanalysis

Found C, 44.13; H, 4.10; N, 7.39.

$C_7H_8NO_3Cl$ requires C, 44.35; H, 4.25;
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(a) With iodotrimethylsilane.¹⁴⁴

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sodium iodide (184.4 mg; 1.23 mmol) were added to a stirred mixture of
unseparated isomers (152 mg; 0.81 mmol) in dry acetonitrile (4 ml).
The mixture was stirred at room temperature for 48 hours after which

no change was apparent when monitored with thin-layer chromatography. The mixture was then refluxed for 26 hours under a nitrogen atmosphere after which thin-layer chromatography showed that no starting material had been consumed. The organic extracts were poured into a 10% aqueous solution of sodium thiosulphate. The starting material was recovered in approximately quantitative yield.

IR (thin film) 2995(m), 2980(m), 2940(w), 1765(s, C=O),
1555(s, NO₂), 1375(s, NO₂).

(b) With cerium(III) iodide.¹⁴⁸

To a stirred, slightly cloudy solution of cerium(III) sulphate heptahydrate (0.99 g; 1.5 mmol) in water (5 ml) was added sequentially sodium iodide (1.35 g; 9.00 mmol) and a solution of the abovementioned unseparated α -chloroketones (380 mg; 2.00 mmol) in tetrahydrofuran (5 ml). The mixture immediately assumed a brown colour. After 30 minutes it was quenched with aqueous thiosulphate and extracted with diethyl ether (3x10 ml portions). It was shown by thin-layer chromatography that no change had occurred and removal of the solvent led to recovery of the starting material in 82% yield (310 mg).

IR (thin film) 2980(w), 2950(m), 2910(w), 1763(s, C=O),
1543(s, NO₂), 1368(s, NO₂).

(c) With vanadium(II) chloride.¹⁴⁷

A solution of the α -chloroketones (0.91 g; 4.78 mmol) in tetrahydrofuran was mixed with ca. 1M aqueous vanadium(II) chloride^{16b} (25 ml). It was refluxed under nitrogen for for 3.5 minutes and then extracted with dichloromethane (3x10 ml portions). The extracts were washed with water (10 ml) and a solution of ca. 1M sodium bicarbonate (2 ml), but evaporation of the solvent led to the recovery of the starting material in a quantitative yield.

IR (thin film) 2980(m), 2955(m), 2905(w), 1755(s, C=O),

1550(s, NO₂), 1365(s, NO₂).

(d) With zinc/acetic acid .

The α -chloroketone mixture (200 mg; 1.05 mmol) was dissolved in acetic acid (5 ml). Zinc dust (100 mg) was added to the solution and it was stirred for 3 hours at room temperature when thin-layer chromatography indicated that no change had occurred. The mixture was then heated at 60-65°C for 2 hours. Thin-layer chromatography showed that many products had been formed and no work-up was attempted.

5.6. Preparation of 3-exo-chloro-6-exo-nitrobicyclo[2.2.1]heptan-2-endo-ol, (59), and 3-exo-chloro-6-exo-nitrobicyclo[2.2.1]heptan-2-exo-ol, (60).

A mixture of the unseparated chloroketones (1.41 g; 7.42 mmol) was dissolved in dry methanol (25 ml). Sodium borohydride (188 mg; 4.97 mmol) was added to the flask with good stirring. The solution was stirred at room temperature for 6.5 hours. After this time it was shown by thin-layer chromatography that no starting material was present. The excess hydride was destroyed with water (5 ml) and the solution was neutralised with 2M hydrochloric acid with stirring being continued for a further 2 hours. The contents of the flask were then concentrated and extracted with diethyl ether (3x25 ml portions). After the removal of the solvent, the residue (1.21 g; 92% crude yield) was separated using column chromatography (48 g; 2.2x24 cm). The elution mixture was ethyl acetate-hexane (1:20 to 1:1). The first set of combined fractions gave a white solid (412.3 mg; 31%) which was recrystallised from diisopropyl ether. This compound was characterised as being 3-exo-chloro-6-exo-nitrobicyclo[2.2.1]heptan-2-endo-ol, (59), m.p. 117-119°C, R_f 0.52 (ethyl acetate-hexane; 1:1). The second set of combined fractions gave a white solid as well, (226.6 mg; 17%) and was identified as 3-exo-chloro-6-exo-nitrobicyclo[2.2.1]heptan-2-exo-ol, (60), m.p. 94-95°C, R_f 0.37. The third fraction contained the bulk of the unseparated isomers (484.8 mg) and was

not purified further. Compounds (59) and (60) were analysed by X-ray crystallography.

Analyses of endo hydroxy isomer:

^1H NMR (acetone- d_6) 5.00 (1H, 4-line m, J ca. 4.2 Hz, H6),
4.31 (1H, m, H2),
3.53 (1H, t (dd), J = 2.32 and 2.09 Hz, H3),
2.96 (1H, m, H1),
2.78 (1H, br. s, OH, D_2O -exchangeable),
2.58-2.03 (3H, m, H5x, H5n and H4),
1.93 (1H, d (with fine coupling), J = 11 Hz, H7s),
1.65 (1H, d (with fine coupling), J = 11 Hz, H7a).

IR (KBr) 3480(m, OH, br), 2995(w), 2970(w), 2905(w),
1533(s, NO_2), 1465(w), 1370(s, NO_2),
1330(w), 1305(w), 1288(w), 1273(w), 1255(w),
1240(m), 1225(m), 1198(w), 1190(w), 1145(w),
1125(w), 1080(m), 1060(s, C-O), 1015(w),
975(w), 950(m), 940(w), 925(w), 890(w), 850(w),
815(s), 770(w), 710(w), 585(w), 525(w), 490(w).

MS 145(4, M- NO_2), 143(9), 108(27), 90(19),
80(46), 78(54), 76(19), 74(9), 66(100), 65(22),
64(25).

C, H and N microanalysis

Found: C, 44.08; H, 5.30; N, 7.54.

$\text{C}_7\text{H}_{10}\text{NO}_3\text{Cl}$ requires C, 43.88; H,
5.26; N, 7.31%.

Analyses of exo hydroxy isomer:

^1H NMR (acetone- d_6) 4.56 (4-line m, J ca. 4.2 Hz, H6),
4.08 (1H, dd, J = 5.6 and 3.0 Hz, H3),
4.00 (1H, m, H2),

2.78 (1H, br. s, OH, D₂O-exchangeable),
2.46 (1H, m, H1),
2.30-2.05 (3H, m, H4, H5x and H5n),
1.90 (1H, d (with fine coupling), J = 11.4 Hz, H7s),
1.50 (1H, d (with fine coupling), J = 11.4 Hz, H7a).

IR (KBr) 3490(m, OH, br), 3000(w), 2980(w), 2955(w),
2920(w), 1540(s, NO₂), 1480(w), 1465(w),
1448(w), 1386(s, NO₂), 1335(w), 1320(m),
1290(w), 1280(w, shoulder), 1260(m), 1240(w),
1220(w), 1200(w), 1176(m), 1123(m), 1099(s,
C-O), 1060(w), 1045(w), 1015(w), 975(w),
950(w), 940(w), 930(w), 915(m), 885(m), 865(m),
793(m), 770(m), 760(m), 730(w), 685(w), 640(w),
525(s), 475(m), 425(w), 375(w).

MS 145(2, M-NO₂), 144(23), 143(4), 108(30),
90(15), 80(45), 78(49), 76(17), 74(10),
66(100), 65(24), 64(20).

C, H and N microanalysis

Found: C, 44.23; H, 5.34; N, 7.34.

C₇H₁₀NO₂Cl requires C, 43.88; H,
5.26; N, 7.31%.

5.7. Preparation of 2,3-exo-epoxy-5-endo-nitrobicyclo[2.2.1]heptane, (54).

5-endo-Nitrobicyclo[2.2.1]hept-2-ene (500 mg; 3.59 mmol) was dissolved in dichloromethane (10 ml). m-Chloroperoxybenzoic acid (85% pure; 1.05; 6.10 mmol) in dichloromethane (30 ml) was added to the stirred solution containing the olefin. The reaction mixture was stirred for 26 hours at room temperature. Thin-layer chromatography showed no evidence of unreacted starting material. A

sodium sulphite solution (2g) in water (50 ml) was added dropwise to the reaction mixture. The solution was neutralised with a small amount of 2M sodium bicarbonate solution. The contents of the flask were concentrated under reduced pressure and then extracted with dichloromethane (3x15 ml portions). Evaporation of the solvent led to the isolation of the product as a white solid (512 mg; 94% crude yield) which was recrystallised from diisopropyl ether to give 2,3-exo-epoxy-5-endo-nitrobicyclo[2.2.1]heptane, (54), (453 mg; 87%), R_f 0.45 (ethyl acetate-hexane; 1:3), m.p. 105-107°C. This epoxide is unstable and decomposes on standing at room temperature.

^1H NMR (CDCl_3) 4.83 (1H, 6-line m, H5),
 3.20 (3H, m, H2, H3 and H4),
 2.65 (1H, m, H1),
 2.14 (1H, m, H6x),
 2.05 (1H, m, H6n),
 1.53 (1H, d, $J=11$ Hz, H7s),
 0.88 (1H, d, $J=11$ Hz, H7a).

IR (KBr) 2980(w), 1540(s, NO_2), 1460(w),
 1445(w), 1375(s, NO_2), 1330(w), 1250(w,
 epoxide), 850(s, epoxide).

MS 156(19, M^+), 149(10), 141(32),
 140(10), 139(100, M-OH), 113(16), 111(45),
 91(10), 83(16), 82(13), 81(19), 79(48), 77(35),
 76(19), 75(52), 74(19), 73(10), 71(19), 70(10),
 69(16), 67(42), 66(16), 65(23).

5.8. Attempted rearrangement of 2,3-exo-epoxy-5-endo-nitro-
bicyclo[2.2.1]heptane, (54), with a Lewis acid.¹³⁷

2,3-exo-Epoxy-5-endo-nitrobicyclo[2.2.1]heptane (100 mg;

0.64 mmol) was dissolved in dry tetrahydrofuran (5 ml). Anhydrous magnesium bromide tri-etherate (184 mg; 0.45 mmol) was added to the solution with good stirring. The mixture was stirred for 35 hours at room temperature after which thin-layer chromatography showed that all the starting material had been consumed. The plate showed a spot with an R_f of 0.17 (ethyl acetate-hexane; 1:3). The solid was filtered and washed with diethyl ether (25 ml) and the solvent was evaporated to leave a white crystalline solid (86 mg; 89% crude yield) which was recrystallised from cyclohexane and ethyl acetate to give white prismatic crystals (852 mg; 54% overall yield). The product was found to be 5-nitrotricyclo-[2.2.1.0^{3,5}]heptan-2-R*-ol, (56), m.p. 77-78°C.

¹H NMR (CDCl₃) 4.13 (1H, s, H2),
 2.60 (2H, s, H6x and H6n),
 2.14 (1H, m, H1),
 2.01 (2H, m, H7a and H7s),
 1.77 (1H, s, H3),
 1.65 (2H, s, H4 and hydroxyl, the latter is
 D₂O-exchangeable).

IR (KBr, 3260(m, br, OH), 3016(w), 2990(w),
 2960(w), 2880(w), 1510(s, NO₂), 1374(s,
 NO₂), 1090(s, C-O).

MS 157(M⁺), 139(5, M-H₂O), 128(12),
 112(15), 111(16, M-NO₂), 110(12), 109(21),
 108(19), 99(17), 96(11), 93(10,
 M-(NO₂-H₂O), 92(24), 85(11), 84(12),
 82(40), 81(32), 80(100), 79(23), 78(68),
 70(17), and many peaks of intensity >10% below
 m/e 70.

C, H and N microanalysis

Found: C, 54.02; H, 5.96; N, 9.00.

$C_7H_9NO_3$ requires C, 54.18; H, 5.85;

N, 9.03%.

5.9. Preparation of 3-endo-nitrobicyclo[2.2.1]hept-5-ene-2-exo-carbonitrile, (5).¹⁰²

(E)-3-Nitropropenenitrile¹⁰³ (1.23 g; 12.54 mmol) was dissolved in dry diethyl ether (60 ml), the solution was cooled to 0°C in an ice bath and cyclopentadiene (1.06 g; 15.90 mmol) was introduced to the stirred solution over a period of 20 minutes. The mixture was stirred for 2.5 hours at 5°C and another 3 hours at room temperature. Thin-layer chromatography showed one major spot, R_f 0.31 (ethyl acetate-hexane; 1:3). The product was obtained as a white solid after removal of the solvent and was recrystallised from methanol to give the desired product (1.28 g) in 62% overall yield. m.p. 123-125°C.

¹H NMR (CDCl₃) 6.50 (1H, dd, J=5.4 and 3.0 Hz, H6),
 6.10 (1H, dd, J=5.4 and 3.0 Hz, H5),
 5.39 (1H, t (dd), J=3.8 and 3.8 Hz, H3x),
 3.62 (1H, br s, H4),
 3.32 (1H, br s, H1),
 3.09 (1H, m, H2n),
 1.68 (2H, s, H7a and H7s).

IR (KBr) 3070(w), 2980(w), 2880(w), 2240(w, CN),
 1545(s, NO₂), 1367(m, NO₂).

C, H and N microanalysis

Found: C, 42.09; H, 3.15; N, 6.91.

$C_8H_8N_2O_2$ requires C, 42.02; H,

3.27; N, 7.00%.

5.10. Preparation of 3-exo,6-exo-dichloro-5-endo-hydroxy-3-endo-nitrobicyclo[2.2.1]heptane-2-exo-carbonitrile, (7).¹⁰²

N-Chlorosuccinimide (3.75 g; 28.08 mmol) and ammonium hexafluorophosphate (16.50 mg; 0.10 mmol) were added to 3-endo-nitrobicyclo[2.2.1]hept-5-ene-2-exo-carbonitrile, (8), (2.14 g; 12.82 mmol) in dry methanol (50 ml) and the mixture was heated at 55-63°C for 6 hours. Thin-layer chromatography showed that no starting material remained. The solvent was removed under reduced pressure, water (25 ml) was added and the organic matter was extracted with diethyl ether (4x10 ml portions). The solvent was removed and the white residue was recrystallised from methanol to give white crystals of 3-exo,6-exo-dichloro-5-^{endo-}hydroxy-3-endo-nitrobicyclo[2.2.1]heptane-2-exo-carbonitrile, (7), (1.93 g; 60% yield) m.p. 194-195°C, R_f 0.50 (ethyl acetate-hexane; 1:3). This compound was analysed by X-ray crystallography.

^1H NMR (acetone- d_6) 5.30 (1H, d, $J = 4.6$ Hz, OH),
4.57 (2H, m, H5 and H2),
4.02 (1H, m, H6),
3.40 (1H, m, H4),
2.96 (1H, m, H1),
2.40 (2H, t with additional fine coupling, $J = 1.3$ Hz, H7s and H7a).

IR (KBr) 3435(s, OH), 3025(w), 2950(w), 2288(m, CN),
1578(s, NO_2), 1480(w), 1425(w), 1395(w),
1360(s, NO_2), 1341(m), 1303(s), 1285(m),
1265(w), 1250(w), 1240(w), 1200(m), 1163(s),
1115(w), 1100(s), 1075(m), 1037(w), 1022(w),
1010(m), 963(w), 943(w), 930(m), 912(w),
878(w), 830(s), 800(s), 780(w), 705(w), 660(m),
598(m), 550(m), 534(m), 465(w), 443(w), 402(w),
380(w), 340(w).

MS 204/206(6/4, M-NO₂), 178(10, M-NO₂, CN),
143(18, M-NO₂, Cl, CN), 142(12), 141(57),
140(19), 138(45), 128(19), 126(57), 125(9),
115(16), 113(45), 111(11), 105(10), 104(32),
103(17), 102(60), 101(21), 100(10), 99(13),
92(14), 91(16), 90(37), 80(10), 79(14), 78(36),
77(100), 76(42), 75(53), 73(13), 67(12),
66(26), 65(39), 64(28), 63(27).

C, H and N microanalysis

Found: C, 38.08; H, 3.17; N, 11.07.

C₈H₈N₂O₃Cl₂ requires C,
38.27; H, 3.21; N, 11.16%.

5.11. Hydroboration-oxidation of 5-endo-nitrobicyclo[2.2.1]-
hept-2-ene, (48).¹³¹

A dry flask equipped with a stirrer bar and two rubber septa was flushed with dry nitrogen and maintained under a positive nitrogen pressure. The flask was charged with 5-endo-nitrobicyclo-[2.2.1]hept-2-ene (5.0 g; 35.9 mmol) and dry dichloromethane (50 ml) and cooled to 0°C with an ice bath. Hydroboration was achieved by the dropwise addition of borane-dimethyl sulphide (1.37 g; 18.0 mmol) with a syringe over a period of 7 minutes. Following the addition of the borane, the cooling bath was removed and the solution allowed to stir at room temperature for 3.75 hours. The reaction mixture was then heated to reflux for 1 hour to ensure complete hydroboration at which stage thin-layer chromatography showed no starting material. The resulting organoborane was then cooled to 0°C. Pyridinium chlorochromate¹³² (23.2 g; 107.7 mmol) was added slowly and the mixture was allowed to reach room temperature and then stirred for 10 hours at this temperature. The liquid in the flask was decanted and the black residue washed with

MS 204/206(6/4, M-NO₂), 178(10, M-NO₂, CN),
143(18, M-NO₂, Cl, CN), 142(12), 141(57),
140(19), 138(45), 128(19), 126(57), 125(9),
115(16), 113(45), 111(11), 105(10), 104(32),
103(17), 102(60), 101(21), 100(10), 99(13),
92(14), 91(16), 90(37), 80(10), 79(14), 78(36),
77(100), 76(42), 75(53), 73(13), 67(12),
66(26), 65(39), 64(28), 63(27).

C, H and N microanalysis

Found: C, 38.08; H, 3.17; N, 11.07.

C₈H₈N₂O₃Cl₂ requires C,
38.27; H, 3.21; N, 11.16%.

5.11. Hydroboration-oxidation of 5-endo-nitrobicyclo[2.2.1]-
hept-2-ene, (48).¹³¹

A dry flask equipped with a stirrer bar and two rubber septa was flushed with dry nitrogen and maintained under a positive nitrogen pressure. The flask was charged with 5-endo-nitrobicyclo-[2.2.1]hept-2-ene (5.0 g; 35.9 mmol) and dry dichloromethane (50 ml) and cooled to 0°C with an ice bath. Hydroboration was achieved by the dropwise addition of borane-dimethyl sulphide (1.37 g; 18.0 mmol) with a syringe over a period of 7 minutes. Following the addition of the borane, the cooling bath was removed and the solution allowed to stir at room temperature for 3.75 hours. The reaction mixture was then heated to reflux for 1 hour to ensure complete hydroboration at which stage thin-layer chromatography showed no starting material. The resulting organoborane was then cooled to 0°C. Pyridinium chlorochromate¹³² (23.2 g; 107.7 mmol) was added slowly and the mixture was allowed to reach room temperature and then stirred for 10 hours at this temperature. The liquid in the flask was decanted and the black residue washed with

dry diethyl ether (5x20 ml portions). The combined organic extracts were filtered through a pad of anhydrous magnesium sulphate and neutral alumina. The filtrate was evaporated to furnish the products as a yellow oil (2.55 g; 46% crude yield). Thin-layer chromatography showed that the mixture consisted of three compounds, R_f 0.69, 0.58 and 0.44 (ethyl acetate-hexane; 1:1). Column chromatography was used to separate the mixture. Ethyl acetate-hexane mixtures (1:10 to 1:1) were used for the elution but incomplete separation of the isomers was achieved. A small amount of material was obtained in a pure form and was recrystallised from diisopropyl ether. This compound was assigned tentatively as either 6-endo-nitrobicyclo[2.2.1]heptan-2-one, (57), or 5-endo-nitrobicyclo[2.2.1]heptan-2-one, (58), (43 mg; R_f = 0.44; m.p. 126-128°C).

^1H NMR (CDCl_3) 5.01 (1H, 5-line m, J ca. 4.5 Hz, H6),
 3.08 (1H, m, H1),
 2.78 (1H, m, H4),
 2.25 (4H, m, H3x, H3n, H5x and H5n),
 1.83 (2H, s, H7s and H7a).

IR (KBr) 2990(w), 2920(w), 2690(w), 1755(s, C=O),
 1550(s, NO_2), 1375(s, NO_2), 1075(s).

C, H and N microanalysis

Found: C, 53.99; H, 9.75; N, 8.98.

$\text{C}_7\text{H}_9\text{NO}_3$ requires C, 54.19; H, 9.85; N, 9.03%.

5.12. Attempted preparation of 6-endo-nitrobicyclo[2.2.1]heptan-2-endo-ol, (8), (or 5-endo-nitrobicyclo[2.2.1]heptan-2-endo-ol).

An isomer mixture of the corresponding ketones from the above

preparation (1.70 g; 10.97 mmol) was dissolved in dry methanol (20 ml). The contents of the flask were cooled to 0°C with an ice bath. Sodium borohydride (0.249 g; 6.58 mmol) was added to the solution with good stirring. The solution was allowed to stir for 15 minutes at 0-5°C. The ice bath was removed and the solution was stirred for 55 minutes at room temperature. Thin-layer chromatography indicated that no starting material remained after this period. Two spots were present on the plate, R_f 0.44 and R_f 0.33 (ethyl acetate-hexane; 3:5). The excess hydride was destroyed by dropwise addition of water (10 ml) and 2M hydrochloric acid (5 ml), with stirring being continued for a further 20 minutes. The methanol was evaporated and the aqueous phase extracted with diethyl ether (3x15 ml portions). Evaporation of the solvent gave a yellow oil (1.40 g; 81% crude yield). Medium pressure chromatography failed to separate the mixture into the different components (elution mixture: ethyl acetate-petroleum ether(60-80°C); 1:3)

5.13. Preparation of β -nitrostyrene.

The method of Worrall¹⁷¹ which uses the condensation of benzaldehyde and nitromethane was used for the preparation of nitrostyrene.

^1H NMR (CDCl_3) 8.05 (1H, d, $J=12$ Hz, $=\text{CHNO}_2$),
7.57 (1H, d, $J=12$ Hz, Ph-CH=),
7.53 (5H, s, aromatic).

IR (KBr) 3010(w), 1632(m), 1602(w), 1578(w),
1550(m), 1515(s, NO_2), 1490(m), 1450(m),
1342(s, NO_2).

5.14. Preparation of 5-endo-nitro-6-phenylbicyclo[2.2.1]hept-2-ene, (61).

This compound was prepared by the reaction of cyclopentadiene and

nitrostyrene as described by Poos et al.¹⁷²

¹ H NMR (CDCl ₃)	7.27 (5H, s, aromatic),
	6.56 (1H, dd, J=2.6 Hz and J=5.6 Hz, H2),
	6.11 (1H, dd, J=5.6 Hz and J=2.4 Hz, H3),
	4.98 (1H, t, J=3.6 Hz, H5),
	3.57 (1H, br s, H6),
	3.43 (1H, m, H4),
	3.15 (1H, m, H1),
	1.78 (2H, m, H7s and H7a).
IR (thin film)	3060(w), 3030(w), 2980(m), 2940(w),
	2875(w), 1598(w, C=C), 1560(m), 1530(s, NO ₂), 1493(m), 1445(w), 1365(s, NO ₂).
MS	215(12, M ⁺), 185(53, M-NO), 170(20),
	169(11, M-NO ₂), 168(25), 166(16), 155(21),
	154(15), 153(22), 150(42), 141(34), 129(16),
	128(31), 117(37), 115(42), 107(16), 103(21),
	102(18), 92(18, M-Ph, NO), 91(100), 89(13),
	83(12), 79(13), 78(15), 77(46), 76(16),
	67(45), 66(77, M-Ph, NO ₂ ,
	H ₂ C=CH ₂), 65(56), 63(21).

5.15. Preparation of 3-exo-chloro-6-endo-nitro-5-exo-phenylbicyclo[2.2.1]heptan-2-one, (63), and 3-exo-chloro-5-endo-nitro-6-exo-phenylbicyclo[2.2.1]heptan-2-one, (64).¹⁴⁰

A solution of 5-nitro-6-phenylbicyclo[2.2.1]hept-2-ene, (48), (10 g; 46.6 mmol, 90% endo-nitro adduct) in acetone (80 ml) was cooled in an ice-salt bath to -5°C. Chromyl chloride¹⁷⁵ (14.4 g; 93.2 mmol) was added slowly via a dropping funnel with vigorous stirring of the solution. Addition was controlled so that a temperature of 1°C was not exceeded. After addition was complete

nitrostyrene as described by Poos et al.¹⁷²

¹ H NMR (CDCl ₃)	7.27 (5H, s, aromatic),
	6.56 (1H, dd, J=2.6 Hz and J=5.6 Hz, H2),
	6.11 (1H, dd, J=5.6 Hz and J=2.4 Hz, H3),
	4.98 (1H, t, J=3.6 Hz, H5),
	3.57 (1H, br s, H6),
	3.43 (1H, m, H4),
	3.15 (1H, m, H1),
	1.78 (2H, m, H7s and H7a).
IR (thin film)	3060(w), 3030(w), 2980(m), 2940(w),
	2875(w), 1598(w, C=C), 1560(m), 1530(s, NO ₂), 1493(m), 1445(w), 1365(s, NO ₂).
MS	215(12, M ⁺), 185(53, M-NO), 170(20),
	169(11, M-NO ₂), 168(25), 166(16), 155(21),
	154(15), 153(22), 150(42), 141(34), 129(16),
	128(31), 117(37), 115(42), 107(16), 103(21),
	102(18), 92(18, M-Ph, NO), 91(100), 89(13),
	83(12), 79(13), 78(15), 77(46), 76(16),
	67(45), 66(77, M-Ph, NO ₂ ,
	H ₂ C=CH ₂), 65(56), 63(21).

5.15. Preparation of 3-exo-chloro-6-endo-nitro-5-exo-phenylbicyclo[2.2.1]heptan-2-one, (63), and 3-exo-chloro-5-endo-nitro-6-exo-phenylbicyclo[2.2.1]heptan-2-one, (64).¹⁴⁰

A solution of 5-nitro-6-phenylbicyclo[2.2.1]hept-2-ene, (48), (10 g; 46.6 mmol, 90% endo-nitro adduct) in acetone (80 ml) was cooled in an ice-salt bath to -5°C. Chromyl chloride¹⁷⁵ (14.4 g; 93.2 mmol) was added slowly via a dropping funnel with vigorous stirring of the solution. Addition was controlled so that a temperature of 1°C was not exceeded. After addition was complete

(ca. 45 minutes), the mixture was stirred at -5°C for an hour, then allowed to warm to room temperature, and stirred at $20-21^{\circ}\text{C}$ for six hours. The homogeneous dark red-brown mixture was quenched by slowly pouring it into an ice-cold aqueous solution of sodium bisulphite (14 g/500 ml water). The green mixture was stirred for 45 minutes in an ice-bath and then extracted with diethyl ether (4x50 ml portions). The combined organic phases were washed with water (200 ml) and sodium chloride solution (100 ml). It was then concentrated to give a greenish yellow oil weighing 9.55 g (78%). Thin-layer chromatography indicated three major spots with R_f -values of 0.69, 0.64 and 0.51 (ethyl acetate-hexane; 1:2). An attempt to distil some of the product led to extensive decomposition. It was decided to separate the mixture with column chromatography, but this resulted in very poor separation of the components. The recovered product (8.37 g) was then separated with low pressure chromatography (elution mixture: ethyl acetate-hexane; 1:2) which gave better, but not complete, separation of the mixture of isomers. The first set of fractions ($R_f=0.52$, ethyl acetate-hexane; 1:3) gave a white solid (0.277 g) which was recrystallised from diisopropyl ether to give needle-shaped crystals, m.p. $125-126^{\circ}\text{C}$. This compound was tentatively assigned as 3-exo-chloro-6-endo-nitro-5-exo-phenylbicyclo[2.2.1]heptan-2-one, (63). The second set of fractions ($R_f=0.42$) gave a yellow oil (0.537 g), which crystallised after standing for four weeks at room temperature. This solid was identified tentatively as being 3-exo-chloro-5-endo-nitro-6-exo-phenylbicyclo[2.2.1]heptan-2-one, (64), m.p. $79-80.5^{\circ}\text{C}$. The third set of fractions ($R_f=0.34$) produced also a yellow oil (0.392 g). This product was probably derived from the minor isomer in the starting material and it was not fully characterised.

Analyses of compound (63).

^1H NMR (CDCl_3) 7.25 (5H, m, aromatic protons),
5.15 (1H, t (dd), $J = 5.13$ and 4.88 Hz, H6),
4.05 (1H, d, $J = 2.93$ Hz, H3),
3.87 (1H, m, H4),
3.45 (1H, m, H1),
3.06 (1H, m, H5),
2.52 (1H, d (with fine coupling), $J = 12$ Hz, H7a),
2.20 (1H, d (with fine coupling), $J = 12$ Hz, H7s).

IR (KBr) 3080(w), 3030(w), 3010(w), 2985(w),
1762(s, C=O), 1600(w), 1585(w), 1540(s,
 NO_2), 1495(m, C=C), 1460(w), 1454(w),
1382(m, NO_2), 1370(w), 1323(w), 1280(w),
1268(w), 1240(w), 1218(w), 1200(w), 1155(m),
1110(w), 1090(w), 1070(w), 1030(w), 1015(w),
988(w), 955(w), 948(w), 925(w), 895(w),
820(w), 805(w), 778(w), 765(w), 742(s),
705(m), 695(m), 663(m), 630(w), 580(w),
533(w), 478(w), 460(w).

MS 265(0.5, M^+), 230(9, M-Cl), 229(61, M-HCl),
183(12), 156(15), 155(82), 154(34), 153(46),
152(20), 144(15), 143(100), 142(27), 141(24),
129(43), 128(80), 127(31), 125(18), 117(30),
116(19), 115(81), 105(35), 103(15), 102(16),
101(12), 91(68), 89(12), 81(24), 78(20),
77(61), 76(24), 75(15), 65(22), 64(12),
63(19).

C, H and N microanalysis

Found: C, 58.49; H, 4.71; N, 5.28.

$\text{C}_{13}\text{H}_{12}\text{NO}_3\text{Cl}$ requires C, 58.77; H,
4.55; N, 5.27%.

Analyses of compound (64).

^1H NMR (CDCl_3) 7.35 (5H, m, aromatic protons),
5.13 (1H, t (dd), $J = 4.4$ and 4.8 Hz, H5),
4.25 (1H, d, $J = 2.4$ Hz, H3),
3.65 (1H, m, H4),
3.32 (1H, m, H1),
3.10 (1H, br. s, H6),
2.43 (1H, d (with fine coupling), $J = 12$ Hz, H7a),
2.13 (1H, d (with fine coupling), $J = 12$ Hz, H7s).

IR (KBr) 3050(w), 3055(w), 3018(w), 2990(w), 2970(w),
2900(w), 1765(s, C=O), 1600(w, C=C), 1550(s,
 NO_2), 1495(m, C=C), 1468(m), 1362(m, br,
 NO_2), 1322(m), 1305(w), 1278(w), 1255(w),
1218(w), 1190(w), 1160(w), 1145(m), 1090(w),
1060(w), 1018(w), 1015(m), 952(w), 937(m),
928(m), 908(w), 895(w), 885(w), 804(w),
802(w), 712(m), 752(m), 740(s), 718(w),
700(s), 680(w), 660(w), 598(w), 530(w),
520(m), 490(w), 445(w), 310(w), 315(w).

C, H and N microanalysis

Found: C, 58.81; H, 4.43; N, 5.33.

$\text{C}_{13}\text{H}_{12}\text{NO}_3\text{Cl}$ requires C, 58.77; H,
4.55; N, 5.27%.

5.16. Reduction of 3-exo-chloro-5-endo-nitro-6-exo-phenylbicyclo[2.2.1]heptan-2-one, (63).¹⁵⁶

The title compound (500 mg; 1.88 mmol) was dissolved in dry tetrahydrofuran (30 ml) under a nitrogen atmosphere. The solution was cooled in an ice bath before the potassium tri-sec-butylborohydride (4.70 ml; 2.35 mmol; 0.5 M/THF) was introduced

dropwise with a syringe. The mixture was stirred for five hours after which thin-layer chromatography indicated that no starting material had remained. The organoborane was hydrolysed with 2M hydrochloric acid (4 ml) and stirred for a further two hours at room temperature. The solvent was removed and the organic matter was extracted with diethyl ether (3x20 ml portions). Evaporation of the solvent led to the isolation of a yellow oil. Thin-layer chromatography showed two spots with R_f -values of 0.98 and 0.29 (ethyl acetate-hexane; 1:2), the former being the residue from the reducing agent. This mixture was separated easily with column chromatography (21 g; 1.8x15 cm, ethyl acetate-hexane; 1:2). The removal of the solvent gave a yellow oil (0.351 g; 81%), which crystallised on the addition of chloroform. The compound was recrystallised from mixture of ethyl acetate and diisopropyl ether to yield 6-nitro-5-phenyltricyclo[2.2.1.0^{3,5}]heptan-2-ol, (6b), (203 mg; 47%) as white prism-shaped crystals, m.p. 154-155°C.

¹H NMR (acetone-d₆) 7.22 (5H, m, aromatic protons),
4.63 (1H, m, OH, D₂O-exchangeable),
4.32 (1H, s, H6),
4.18 (1H, m, H2),
2.85 (1H, d (with fine coupling), J = 6 Hz, H7a),
2.57 (1H, d (with fine coupling), J = 6 Hz, H7s),
2.03 (1H, m, H1),
1.73 (1H, d (with fine coupling), J = 10 Hz, H3),
1.38 (1H, d (with fine coupling), J = 10 Hz, H4).

IR (KBr) 3230(br, s, OH), 3080(w), 3060(w), 3030(w),
3010(w), 2980(w), 2925(w), 1603(w, C=C),
1512(s, NO₂), 1453(m, C=C), 1372(s,
NO₂), 1355(s), 1320(m), 1290(w), 1283(w),

1275(w), 1208(w), 1158(w), 1143(m), 1095(m),
1078(m), 1058(m), 1030(w), 1020(w), 1000(w),
986(m), 969(w), 935(w), 929(w), 910(w),
861(w), 854(w), 845(w), 812(w), 795(m),
755(w), 740(m), 732(m), 702(s), 660(w),
635(w), 527(m), 502(m), 450(w), 400(w).

C, H and N microanalysis

Found: C, 67.54; H, 5.65; N, 6.13.

$C_{13}H_{13}NO_3$ requires C, 58.33; H, 5.27; N, 5.23%

APPENDIX 1

TABLE 1. Anisotropic thermal vibration parameters ($U_{ij} \times 10^3/\text{\AA}^2$) of non-hydrogen atoms for 3-exo,6-exo-dichloro-5-endo-hydroxy-3-endo-nitrobicyclo[2.2.1]heptane-2-exo-carbonitrile, (7).

	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Cl(1)	71(2)	59(1)	82(2)	-20(1)	13(1)	-21(1)
Cl(2)	56(1)	44(1)	62(1)	5(1)	17(1)	-9(1)
O(1)	77(5)	44(3)	48(3)	10(3)	12(3)	20(3)
O(2)	41(4)	101(6)	66(5)	10(4)	7(3)	29(4)
O(3)	71(4)	85(5)	34(4)	-9(3)	6(3)	9(4)
N(1)	78(6)	47(5)	58(5)	-6(4)	23(4)	16(4)
N(2)	55(5)	46(4)	46(5)	0(3)	1(4)	4(4)
C(1)	35(5)	44(5)	38(5)	0(4)	13(4)	9(4)
C(2)	39(5)	34(4)	32(4)	2(4)	11(3)	8(4)
C(3)	32(4)	29(4)	40(5)	2(3)	8(3)	9(3)
C(4)	36(4)	35(4)	36(5)	2(4)	14(3)	3(4)
C(5)	52(5)	31(4)	45(5)	-7(4)	13(4)	18(4)
C(6)	50(6)	39(5)	44(5)	1(4)	15(4)	-4(4)
C(7)	46(5)	40(5)	33(4)	-1(4)	10(4)	8(4)
C(8)	49(5)	45(5)	38(5)	-4(4)	15(4)	15(4)

TABLE 2. Isotropic thermal vibration parameters ($U_{iso} \times 10^3/\text{\AA}^2$) of the hydrogen atoms for 3-exo,6-exo-dichloro-5-endo-hydroxy-3-endo-nitrobicyclo[2.2.1]heptane-2-exo-carbonitrile, (7).

	U(iso)
H(1)	39(22)
H(2)	30(19)
H(4)	54(26)
H(5)	48(26)
H(6)	51(26)
H(7s)	28(18)
H(7a)	43(23)
H(hydroxyl)	339(107)

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 3,6-EXO,EXO-DICHLORO-5-ENDO-HYDROXY-3-ENDO-NITRO-BICYCLO[2.2.1]HEPTANE-2-EXO-CARBONITRILE.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	0	0	92	97	4	14	0	2	4	6	6	1	11	12	1	17	1	6	6	-3	7	2	26	25
4	0	0	12	13	1	15	0	5	5	-3	7	1	10	10	-4	0	2	41	41	-1	7	2	34	34
6	0	0	27	29	3	15	0	11	12	-3	7	1	31	31	-2	0	2	126	119	1	7	2	45	46
1	1	0	38	40	0	16	0	9	8	-1	7	1	55	53	0	0	2	174	115	3	7	2	33	34
3	1	0	19	19	2	16	0	13	13	1	7	1	27	26	2	0	2	23	24	5	7	2	1	1
5	1	0	11	13	1	17	0	4	5	3	7	1	11	10	4	0	2	31	31	-6	8	2	5	4
7	1	0	6	5	-7	1	1	16	17	-4	8	1	24	23	6	0	2	21	20	-4	8	2	23	21
2	2	0	97	100	-5	1	1	19	18	-2	8	1	3	3	-7	1	2	10	11	-2	8	2	33	31
4	2	0	39	41	-3	1	1	37	39	0	8	1	57	58	-5	1	2	11	10	0	8	2	25	23
6	2	0	18	19	-1	1	1	94	90	2	8	1	46	48	-3	1	2	70	65	2	8	2	16	15
1	3	0	76	80	1	1	1	33	36	4	8	1	30	32	-1	1	2	135	130	6	8	2	8	7
3	3	0	40	40	3	1	1	56	59	6	8	1	8	8	3	1	2	22	22	-3	9	2	23	22
5	3	0	26	28	5	1	1	22	22	-5	9	1	23	23	3	1	2	49	51	-1	9	2	20	21
7	3	0	8	8	7	1	1	8	8	-3	9	1	3	3	5	1	2	16	16	-1	9	2	17	17
0	4	0	33	34	-6	2	1	10	11	-1	9	1	32	32	7	1	2	22	22	3	9	2	13	13
2	4	0	62	62	-4	2	1	32	32	3	9	1	15	15	-6	2	2	17	16	5	9	2	11	10
4	4	0	12	13	-2	2	1	37	34	3	9	1	9	9	-4	2	2	43	39	-4	10	2	22	20
6	4	0	6	8	0	2	1	85	91	5	9	1	5	5	-2	2	2	65	67	-2	10	2	9	9
1	5	0	38	39	4	2	1	21	21	-4	10	1	9	10	0	2	2	46	49	0	10	2	28	28
3	5	0	28	28	2	2	1	7	9	2	10	1	22	25	4	2	2	26	26	2	10	2	11	12
5	5	0	5	5	6	2	1	18	18	2	10	1	6	7	-7	3	2	8	10	4	10	2	26	24
0	6	0	113	115	-7	3	1	4	5	-5	11	1	6	5	-3	3	2	22	20	-3	11	2	9	9
2	6	0	44	45	-5	3	1	28	28	-3	11	1	12	12	-3	3	2	42	39	-1	11	2	2	2
4	6	0	29	30	-3	3	1	51	47	-1	11	1	25	23	-3	3	2	40	39	1	11	2	61	61
6	6	0	14	16	-1	3	1	63	67	-1	11	1	33	33	-1	3	2	106	109	3	11	2	35	35
1	7	0	38	39	3	3	1	59	60	3	11	1	17	18	1	3	2	59	61	5	11	2	7	7
3	7	0	26	28	3	3	1	15	15	-2	12	1	8	7	3	3	2	40	40	-4	12	2	7	9
5	7	0	27	27	5	3	1	15	15	0	12	1	10	9	5	3	2	40	40	-2	12	2	13	12
0	8	0	60	61	7	3	1	6	6	0	12	1	16	16	-6	4	2	10	10	0	12	2	8	8
2	8	0	25	25	-6	4	1	4	4	2	12	1	23	23	-4	4	2	37	34	2	12	2	12	11
4	8	0	5	4	-4	4	1	40	33	2	12	1	10	10	-2	4	2	15	16	-3	13	2	21	20
6	8	0	12	14	-2	4	1	48	45	4	12	1	19	10	2	4	2	14	14	-1	13	2	29	29
1	9	0	40	41	0	4	1	26	26	-3	13	1	5	5	0	4	2	57	54	1	13	2	14	13
3	9	0	38	39	2	4	1	21	23	-1	13	1	23	23	4	4	2	50	50	-3	13	2	12	12
5	9	0	9	10	4	4	1	21	22	-4	14	1	9	8	-3	5	2	27	27	-4	14	2	11	11
0	10	0	11	10	-5	5	1	9	10	-4	14	1	38	37	3	5	2	10	10	0	14	2	5	6
2	10	0	43	43	-3	5	1	21	48	0	14	1	33	32	3	5	2	27	29	0	14	2	11	11
4	10	0	34	35	-1	5	1	51	51	2	14	1	10	10	5	5	2	17	14	2	14	2	11	11
1	11	0	24	25	-1	5	1	71	75	2	14	1	7	7	-6	6	2	10	9	4	14	2	4	3
3	11	0	26	27	1	5	1	1	1	-3	15	1	14	12	-4	6	2	10	9	-3	15	2	11	10
5	11	0	17	18	5	5	1	14	15	-1	15	1	6	6	-2	6	2	25	23	-1	15	2	17	17
0	12	0	23	24	-6	6	1	5	5	3	15	1	1	1	0	6	2	33	34	-1	15	2	17	17
2	12	0	7	8	-4	6	1	21	22	-2	16	1	10	10	2	6	2	46	48	3	15	2	22	22
4	12	0	14	15	-2	6	1	49	48	-2	16	1	6	6	4	6	2	33	32	-2	16	2	9	9
1	13	0	11	11	0	6	1	46	47	2	16	1	18	18	-5	7	2	13	13	0	16	2	5	5
3	13	0	11	11	0	6	1	20	19	-1	17	1	3	3	-1	17	1	25	24	0	16	2	5	5
0	14	0	16	15	4	6	1	6	7	-1	17	1	1	2	-5	7	2	25	24	-5	7	2	5	5
2	14	0	7	7	-1	17	1	6	6	-1	17	1	1	3	-1	17	1	3	3	-1	17	1	5	5

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 3,6-EXO,EXO-DICHLORO-5-ENDO-HYDROXY-3-ENDO-NITRO-BICYCLO[2.2.1]HEPTANE-2-EXO-CARBONITRILE.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	0	0	95	97	4	14	0	2	4	6	6	1	11	12	1	17	1	6	6	-3	7	2	26	25
4	0	0	12	13	1	15	0	5	5	-5	7	1	10	10	-4	0	2	41	41	-1	7	2	54	54
6	0	0	27	29	3	15	0	11	12	-3	7	1	31	31	-2	0	2	126	119	1	7	2	43	46
1	1	0	38	40	0	16	0	9	8	-1	7	1	55	53	0	0	2	114	115	3	7	2	33	34
3	1	0	19	19	2	16	0	13	13	1	7	1	27	26	2	0	2	23	24	5	7	2	1	1
5	1	0	11	13	1	17	0	4	5	3	7	1	11	10	4	0	2	31	31	-6	8	2	5	4
7	1	0	6	5	-7	1	1	16	17	-4	8	1	24	23	6	0	2	21	20	-4	8	2	23	21
2	2	0	97	100	-5	1	1	19	18	-2	8	1	3	3	-7	1	2	13	11	-2	8	2	33	31
4	2	0	39	41	-3	1	1	37	35	0	8	1	57	58	-5	1	2	11	10	0	8	2	25	23
6	2	0	18	19	-1	1	1	94	90	2	8	1	46	48	-3	1	2	70	65	2	8	2	16	15
1	3	0	76	80	1	1	1	33	36	4	8	1	30	32	-1	1	2	135	130	6	8	2	8	7
3	3	0	40	40	3	1	1	56	59	6	8	1	8	8	1	1	2	49	51	-5	9	2	23	22
5	3	0	26	28	5	1	1	22	22	-5	9	1	23	23	3	1	2	22	22	-3	9	2	33	32
7	3	0	8	8	7	1	1	8	8	-3	9	1	5	5	5	1	2	16	16	-1	9	2	20	21
0	4	0	33	34	-6	2	1	10	11	-1	9	1	32	32	7	1	2	15	9	1	9	2	17	17
2	4	0	62	62	-4	2	1	32	32	1	9	1	9	9	-6	2	2	22	22	3	9	2	13	13
4	4	0	12	13	-2	2	1	37	34	3	9	1	15	15	-4	2	2	17	16	5	9	2	11	10
6	4	0	6	8	0	2	1	85	91	5	9	1	5	5	-2	2	2	43	39	-4	10	2	22	20
1	5	0	38	39	2	2	1	21	21	-4	10	1	9	10	0	2	2	65	67	-2	10	2	3	3
3	5	0	28	28	4	2	1	7	9	-2	10	1	39	38	2	2	2	46	49	0	10	2	9	9
5	5	0	5	5	6	2	1	18	18	2	10	1	22	25	4	2	2	26	26	2	10	2	28	28
0	6	0	113	115	-7	3	1	4	5	4	10	1	6	7	6	2	2	8	10	4	10	2	11	12
2	6	0	44	45	-5	3	1	28	28	-5	11	1	6	5	-7	3	2	7	7	-5	11	2	26	24
4	6	0	29	30	-3	3	1	51	47	-3	11	1	12	12	-5	3	2	22	20	-3	11	2	9	9
6	6	0	14	16	-1	3	1	25	25	-1	11	1	25	25	-3	3	2	42	39	-1	11	2	2	2
1	7	0	38	39	1	3	1	65	67	1	11	1	33	33	-1	3	2	40	39	1	11	2	61	61
3	7	0	26	28	3	3	1	59	60	3	11	1	17	18	1	3	2	106	109	3	11	2	35	35
5	7	0	27	27	5	3	1	15	15	5	11	1	8	7	3	3	2	59	61	5	11	2	3	3
0	8	0	60	61	7	3	1	6	6	-2	12	1	10	9	5	3	2	40	40	-4	12	2	7	7
2	8	0	25	25	-6	4	1	6	6	0	12	1	26	27	-6	4	2	10	9	-2	12	2	9	9
4	8	0	5	4	-4	4	1	40	33	2	12	1	10	10	-4	4	2	44	42	0	12	2	13	12
6	8	0	12	14	-2	4	1	48	45	4	12	1	9	10	-2	4	2	37	34	2	12	2	8	8
1	9	0	40	41	0	4	1	26	26	-3	13	1	5	5	0	4	2	76	77	4	12	2	12	11
3	9	0	38	39	2	4	1	21	23	-1	13	1	16	16	2	4	2	15	16	-3	13	2	21	20
5	9	0	9	10	4	4	1	21	22	1	13	1	23	23	4	4	2	14	14	-1	13	2	29	29
0	10	0	11	10	6	4	1	9	10	3	13	1	10	10	-5	5	2	28	27	1	13	2	38	38
2	10	0	43	43	-5	5	1	21	19	-4	14	1	9	8	-3	5	2	57	54	3	13	2	14	13
4	10	0	34	35	-3	5	1	48	46	-2	14	1	38	37	1	5	2	50	50	-4	14	2	12	12
1	11	0	24	25	-1	5	1	51	49	0	14	1	33	32	3	5	2	10	10	-2	14	2	11	11
3	11	0	26	27	1	5	1	71	75	2	14	1	10	10	5	5	2	27	29	0	14	2	5	6
5	11	0	1	14	3	5	1	1	1	-3	15	1	7	7	-6	6	2	17	14	2	14	2	11	11
0	12	0	17	18	5	5	1	14	15	-1	15	1	14	12	-4	6	2	10	9	4	14	2	4	3
2	12	0	23	24	-6	6	1	5	5	1	15	1	6	6	-2	6	2	25	23	-3	15	2	11	10
4	12	0	7	8	-4	6	1	21	22	3	15	1	6	6	0	6	2	33	34	-1	15	2	3	3
1	13	0	14	15	-2	6	1	49	48	-2	16	1	10	10	2	6	2	46	48	1	15	2	17	17
3	13	0	11	11	0	6	1	46	47	0	16	1	6	6	4	6	2	33	32	3	15	2	22	22
0	14	0	16	15	2	6	1	20	19	2	16	1	18	18	6	6	2	13	13	-2	16	2	9	9
2	14	0	7	7	4	6	1	6	7	-1	17	1	3	2	-5	7	2	25	24	0	16	2	5	5

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 3,6-EXO,EXO-DICHLORO-5-ENDO-HYDROXY-3-ENDO-NITRO-BICYCLO[2.2.1]HEPTANE-2-EXO-CARBONITRILE.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	16	2	6	5	-4	8	3	28	27	6	0	4	19	18	-2	8	4	29	28	-5	3	5	7	6
-1	17	2	13	12	-2	8	3	18	17	-5	1	4	9	9	0	8	4	41	41	-3	3	5	20	19
1	17	2	6	5	0	8	3	37	37	-3	1	4	45	44	2	8	4	18	19	-1	3	5	43	44
-7	1	3	10	11	2	8	3	44	44	-1	1	4	41	40	4	8	4	15	15	1	3	5	43	43
-5	1	3	17	17	4	8	3	17	16	1	1	4	24	26	-5	9	4	16	16	3	3	5	25	24
-3	1	3	18	18	-5	9	3	14	13	3	1	4	16	15	-3	9	4	6	5	5	3	5	4	2
-1	1	3	48	45	-3	9	3	19	19	5	1	4	21	21	-1	9	4	4	4	-6	4	5	5	5
1	1	3	78	79	-1	9	3	14	13	-6	2	4	15	16	1	9	4	25	26	-4	4	5	23	24
3	1	3	24	25	1	9	3	26	26	-4	2	4	9	11	3	9	4	16	16	-2	4	5	26	27
5	1	3	1	2	3	9	3	9	10	-2	2	4	68	66	5	9	4	16	14	0	4	5	38	37
-6	2	3	20	19	5	9	3	9	9	0	2	4	64	64	-4	10	4	18	18	2	4	5	8	8
-4	2	3	41	40	-4	10	3	20	20	2	2	4	72	70	-2	10	4	14	13	4	4	5	5	5
-2	2	3	28	26	-2	10	3	36	35	4	2	4	25	24	0	10	4	26	27	6	4	5	4	4
0	2	3	40	38	0	10	3	20	21	6	2	4	7	6	2	10	4	27	27	-5	5	5	15	15
2	2	3	57	57	2	10	3	7	7	-5	3	4	10	10	4	10	4	7	8	-3	5	5	13	13
4	2	3	10	10	4	10	3	12	12	-3	3	4	26	25	-5	11	4	3	3	-1	5	5	25	24
6	2	3	9	8	-5	11	3	8	8	-1	3	4	61	60	-3	11	4	9	9	1	5	5	19	19
-5	3	3	21	20	-3	11	3	12	13	1	3	4	14	15	-1	11	4	30	30	3	5	5	17	16
-3	3	3	20	19	-1	11	3	3	4	3	3	4	18	19	1	11	4	36	36	5	5	5	10	9
-1	3	3	38	39	1	11	3	15	16	5	3	4	12	12	3	11	4	24	23	-6	6	5	11	12
1	3	3	84	85	3	11	3	22	23	-6	4	4	24	25	-4	12	4	3	2	-4	6	5	19	20
3	3	3	43	42	5	11	3	9	9	-4	4	4	55	54	-2	12	4	17	18	-2	6	5	21	20
5	3	3	10	9	-4	12	3	12	10	-2	4	4	49	47	0	12	4	20	20	0	6	5	18	18
-6	4	3	12	12	-2	12	3	18	19	0	4	4	19	19	2	12	4	12	12	2	6	5	15	16
-4	4	3	27	25	0	12	3	41	41	2	4	4	46	45	4	12	4	11	11	4	6	5	12	11
-2	4	3	18	18	2	12	3	4	4	4	4	4	29	29	-3	13	4	13	11	-5	7	5	7	8
0	4	3	43	44	4	12	3	22	22	6	4	4	8	6	-1	13	4	20	20	-3	7	5	31	31
2	4	3	34	34	-3	13	3	13	13	-5	5	4	10	9	1	13	4	18	18	-1	7	5	35	35
4	4	3	19	19	-1	13	3	11	10	-3	5	4	38	38	3	13	4	19	19	1	7	5	18	19
6	4	3	8	8	1	13	3	10	10	-1	5	4	34	34	-2	14	4	12	12	3	7	5	8	9
-3	5	3	28	27	3	13	3	8	8	1	5	4	18	17	0	14	4	14	15	5	7	5	6	7
-1	5	3	21	20	-4	14	3	17	16	3	5	4	19	19	2	14	4	11	10	-4	8	5	21	20
1	5	3	14	13	-2	14	3	33	31	5	5	4	18	17	-1	15	4	12	12	-2	8	5	17	18
3	5	3	26	26	0	14	3	10	10	-6	6	4	18	18	1	15	4	13	12	0	8	5	39	39
5	5	3	24	24	2	14	3	3	3	-4	6	4	16	16	0	16	4	11	10	2	8	5	22	22
-6	6	3	3	3	-3	15	3	11	11	-2	6	4	40	39	-5	1	5	26	27	4	8	5	16	16
-4	6	3	18	19	-1	15	3	14	14	0	6	4	61	63	-3	1	5	26	26	-5	9	5	17	17
-2	6	3	51	49	1	15	3	5	5	2	6	4	12	13	-1	1	5	27	27	-3	9	5	20	20
2	6	3	25	25	3	15	3	5	5	4	6	4	12	13	1	1	5	56	56	-1	9	5	2	2
4	6	3	12	12	-2	16	3	2	2	6	6	4	11	10	3	1	5	28	27	1	9	5	2	2
6	6	3	12	12	0	16	3	8	8	-5	7	4	2	3	5	1	5	13	13	3	9	5	17	15
-5	7	3	10	11	2	16	3	17	16	-3	7	4	17	19	-6	2	5	12	13	5	9	5	10	9
-3	7	3	23	22	-6	0	4	6	7	-1	7	4	21	21	-4	2	5	18	18	-4	10	5	19	19
-1	7	3	32	32	-4	0	4	47	47	1	7	4	38	38	-2	2	5	26	25	-2	10	5	10	10
1	7	3	19	20	-2	0	4	46	46	3	7	4	13	13	0	2	5	16	17	0	10	5	19	20
3	7	3	21	22	0	0	4	30	29	5	7	4	9	9	2	2	5	11	11	2	10	5	22	21
5	7	3	15	15	2	0	4	29	30	-6	8	4	6	5	4	2	5	12	12	4	10	5	18	17
-6	8	3	3	3	4	0	4	46	46	-4	8	4	30	30	6	2	5	4	3	-3	11	5	7	8

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 3,6-EXO,EXO-DICHLORO-5-ENDO-HYDROXY-3-ENDO-NITRO-BICYCLO[2.2.1]HEPTANE-2-EXO-CARBONITRILE.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-1	11	5	8	8	-3	5	6	11	11	0	2	7	9	9	1	13	7	8	8	-3	1	9	18	19
1	11	5	14	14	-1	5	6	13	12	2	2	7	14	13	-4	0	8	10	12	-1	1	9	6	6
3	11	5	12	12	1	5	6	30	30	4	2	7	5	6	-2	0	8	8	9	1	1	9	10	10
-4	12	5	17	17	3	5	6	16	16	-5	3	7	13	13	0	0	8	23	22	3	1	9	7	7
-2	12	5	24	24	5	5	6	6	5	-3	3	7	20	20	2	0	8	23	23	-4	2	9	9	10
0	12	5	9	9	-4	6	6	14	14	-1	3	7	25	25	4	0	8	13	12	-2	2	9	16	15
2	12	5	12	12	-2	6	6	26	28	1	3	7	22	22	-5	1	8	11	11	0	2	9	29	29
-3	13	5	19	19	0	6	6	11	12	3	3	7	9	8	-3	1	8	13	13	2	2	9	3	3
-1	13	5	8	8	2	6	6	7	7	5	3	7	3	4	-1	1	8	7	5	-3	3	9	12	13
1	13	5	11	10	4	6	6	9	9	-4	4	7	6	6	1	1	8	23	22	-1	3	9	12	12
3	13	5	12	11	-5	7	6	8	8	-2	4	7	21	21	3	1	8	10	9	1	3	9	10	9
-2	14	5	10	9	-3	7	6	39	39	0	4	7	24	24	-4	2	8	18	19	3	3	9	4	4
0	14	5	2	2	-1	7	6	41	42	2	4	7	4	5	-2	2	8	19	20	-4	4	9	5	5
2	14	5	10	10	1	7	6	18	18	4	4	7	8	7	0	2	8	16	16	-2	4	9	14	15
-1	15	5	5	4	3	7	6	13	13	-5	5	7	13	14	2	2	8	19	19	0	4	9	24	24
1	15	5	7	7	5	7	6	7	7	-3	5	7	7	8	4	2	8	13	11	2	4	9	7	7
-6	0	6	17	16	-4	8	6	11	11	-1	5	7	11	11	-5	3	8	11	12	-3	5	9	13	13
-4	0	6	29	29	-2	8	6	9	10	3	5	7	7	7	-3	3	8	14	17	-1	5	9	16	15
-2	0	6	29	28	0	8	6	13	13	-4	6	7	15	16	-1	3	8	9	9	1	5	9	19	19
0	0	6	35	36	2	8	6	7	8	2	6	7	9	9	1	3	8	25	25	3	5	9	6	5
2	0	6	18	19	4	8	6	12	11	0	6	7	11	10	3	3	8	8	8	-2	6	9	8	8
4	0	6	38	37	-3	9	6	17	16	2	6	7	7	7	-4	4	8	3	1	0	6	9	4	3
-5	1	6	19	20	-1	9	6	13	15	4	6	7	15	14	-2	4	8	23	23	2	6	9	11	10
-3	1	6	24	24	3	9	6	19	19	-5	7	7	6	5	0	4	8	40	41	-3	7	9	12	14
-1	1	6	31	31	-2	10	6	17	17	-3	7	7	23	23	2	4	8	22	22	-1	7	9	5	5
1	1	6	37	37	0	10	6	25	25	-1	7	7	26	26	4	4	8	2	2	1	7	9	9	9
3	1	6	28	26	2	10	6	6	5	1	7	7	7	6	-3	5	8	18	18	-2	8	9	6	6
5	1	6	3	3	4	10	6	1	2	3	7	7	4	3	-1	5	8	10	9	0	8	9	12	13
-6	2	6	11	12	-3	11	6	18	18	-4	8	7	15	16	1	5	8	9	8	2	8	9	3	3
-4	2	6	25	25	-1	11	6	33	32	-2	8	7	9	9	-4	6	8	14	16	-1	9	9	8	8
-2	2	6	25	25	1	11	6	8	7	0	8	7	26	27	-2	6	8	30	32	1	9	9	9	8
0	2	6	18	20	3	11	6	7	6	2	8	7	5	6	0	6	8	6	6	0	0	10	20	20
2	2	6	31	30	-2	12	6	5	6	4	8	7	7	7	2	6	8	5	4	2	0	10	15	15
4	2	6	7	7	0	12	6	5	5	-3	9	7	5	6	-3	7	8	16	18	-3	1	10	9	10
-5	3	6	13	13	2	12	6	3	5	-1	9	7	23	23	-1	7	8	15	16	-1	1	10	9	10
-3	3	6	21	21	-3	13	6	11	9	1	9	7	4	4	1	7	8	6	5	-2	2	10	10	11
-1	3	6	34	34	-1	13	6	8	9	3	9	7	6	7	3	7	8	10	10	0	2	10	6	6
1	3	6	33	32	1	13	6	16	16	-2	10	7	9	9	-2	8	8	6	6	2	2	10	11	10
3	3	6	6	7	0	14	6	8	9	0	10	7	9	9	0	8	8	16	16	-1	3	10	16	17
5	3	6	10	9	-5	1	7	20	21	2	10	7	28	26	2	8	8	14	13	1	3	10	2	2
-6	4	6	12	13	-3	1	7	23	24	-3	11	7	13	13	-3	9	8	4	4	-2	4	10	7	7
-4	4	6	20	22	-1	1	7	41	42	-1	11	7	6	6	1	9	8	8	9	0	4	10	19	20
-2	4	6	26	26	1	1	7	28	28	1	11	7	3	2	-2	10	8	11	11	2	4	10	2	2
0	4	6	15	16	3	1	7	9	8	-2	12	7	12	12	0	10	8	3	3	-1	5	10	7	7
2	4	6	25	25	5	1	7	8	7	0	12	7	14	13	2	10	8	6	7	1	5	10	5	4
4	4	6	14	12	-4	2	7	10	10	2	12	7	8	8	-1	11	8	8	8	0	6	10	9	8
-5	5	6	9	10	-2	2	7	3	3	-1	13	7	6	6	1	11	8	10	10					

APPENDIX 2

TABLE 1. Anisotropic thermal vibration parameters ($U_{ij} \times 10^3/\text{\AA}^2$) of non-hydrogen atoms for 3-exo-chloro-6-exo-nitro-bicyclo[2.2.1]heptan-2-exo-ol, (60).

	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
C1	48(1)	53(1)	98(1)	8(1)	-3(1)	-20(1)
O(1)	50(1)	30(1)	52(1)	4(1)	-11(1)	4(1)
O(2)	70(2)	34(1)	52(2)	-5(1)	15(1)	-2(1)
O(3)	91(2)	48(2)	57(2)	21(1)	11(1)	-13(1)
N	38(1)	35(2)	46(2)	4(1)	7(1)	3(1)
C(1)	29(2)	31(2)	31(2)	-2(1)	2(1)	2(1)
C(2)	29(2)	32(2)	40(2)	-3(1)	9(1)	1(1)
C(3)	40(2)	41(2)	42(2)	-6(2)	4(1)	-10(2)
C(4)	26(2)	51(2)	50(2)	5(2)	1(1)	-1(2)
C(5)	49(2)	52(2)	37(2)	8(2)	-4(2)	-2(2)
C(6)	37(2)	32(2)	36(2)	-2(1)	12(1)	2(1)
C(7)	39(2)	40(2)	42(2)	3(2)	17(1)	7(2)

TABLE 2. Isotropic thermal vibration parameters ($U_{iso} \times 10^3/\text{\AA}^2$) of the hydrogen atoms for 3-exo-chloro-6-exo-nitro-bicyclo[2.2.1]heptan-2-exo-ol, (60).

	$U(iso)$
H(1)	22(7)
H(2)	35(8)
H(3)	38(8)
H(4)	44(8)
H(5x)	61(11)
H(5n)	52(9)
H(6)	29(7)
H(7s)	45(9)
H(7a)	41(8)
H(hydroxyl)	71(14)

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 3-EXO-CHLORO-6-EXO-NITROBICYCLO[2.2.1]HEPTAN-2-EXO-OL.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	0	0	87	-89	8	4	0	14	-14	9	1	1	3	3	-8	4	1	6	6	-6	7	1	9	-9
3	0	0	37	37	9	4	0	12	-12	10	1	1	1	1	-7	4	1	2	-1	-5	7	1	8	-8
4	0	0	137	-137	10	4	0	10	-10	11	1	1	12	12	-4	4	1	2	0	-4	7	1	3	-2
5	0	0	12	12	2	5	0	31	-31	-11	2	1	6	-6	-3	4	1	7	6	-3	7	1	11	-11
6	0	0	36	35	3	5	0	6	-6	-10	2	1	13	-14	-2	4	1	33	31	-2	7	1	6	-6
7	0	0	40	-40	4	5	0	2	-2	-9	2	1	8	-8	-1	4	1	13	-14	-1	7	1	10	10
8	0	0	16	17	5	5	0	7	-8	-8	2	1	9	8	0	4	1	11	-11	0	7	1	2	2
9	0	0	28	29	6	5	0	15	13	-7	2	1	9	9	1	4	1	22	21	2	7	1	16	17
10	0	0	2	3	7	5	0	6	6	-6	2	1	33	34	2	4	1	1	-1	3	7	1	9	-10
11	0	0	3	3	8	5	0	6	6	-5	2	1	21	21	3	4	1	10	-8	4	7	1	4	-3
1	1	0	14	14	9	5	0	12	13	-4	2	1	11	-11	4	4	1	11	-10	6	7	1	15	-15
2	1	0	66	68	0	6	0	16	16	-3	2	1	12	11	3	4	1	16	-16	-3	8	1	2	-3
3	1	0	9	7	1	6	0	5	5	-2	2	1	61	-60	6	4	1	3	3	-2	8	1	11	-11
4	1	0	21	21	2	6	0	3	-3	-1	2	1	47	-47	7	4	1	17	17	-1	8	1	3	3
5	1	0	1	1	3	6	0	5	5	0	2	1	8	-8	8	4	1	1	1	0	8	1	3	-3
6	1	0	30	-30	4	6	0	9	-9	1	2	1	31	-31	9	4	1	4	-4	2	8	1	7	7
7	1	0	6	-6	5	6	0	10	-10	2	2	1	68	71	10	4	1	3	2	3	8	1	5	-5
8	1	0	16	-16	6	6	0	5	6	3	2	1	36	37	-9	5	1	5	-5	-11	0	2	2	-1
9	1	0	5	-6	7	6	0	4	-5	4	2	1	5	5	-6	5	1	10	-9	-10	0	2	17	-17
10	1	0	13	13	8	6	0	3	-3	5	2	1	24	23	-4	5	1	5	5	-9	0	2	6	6
11	1	0	3	4	2	7	0	3	-3	6	2	1	24	-24	-3	5	1	24	24	-8	0	2	23	23
0	2	0	8	-7	3	7	0	4	-4	7	2	1	12	-12	-2	5	1	14	13	-7	0	2	3	3
1	2	0	26	27	4	7	0	2	-2	8	2	1	11	-10	0	5	1	20	-21	-6	0	2	33	33
3	2	0	35	-35	5	7	0	6	6	9	2	1	19	-19	1	5	1	22	-23	-5	0	2	13	12
4	2	0	8	8	6	7	0	3	4	10	2	1	4	3	2	5	1	1	-1	-4	0	2	66	-63
6	2	0	2	2	0	8	0	12	12	11	2	1	6	7	3	5	1	4	3	-3	0	2	12	-11
7	2	0	23	23	1	8	0	5	5	-10	3	1	5	-5	4	5	1	10	11	-2	0	2	29	-28
8	2	0	5	-5	2	8	0	1	0	-8	3	1	9	-10	5	5	1	12	12	-1	0	2	127	-132
9	2	0	7	-7	3	8	0	3	-1	-7	3	1	11	-10	6	5	1	4	4	0	0	2	66	67
10	2	0	1	1	4	8	0	10	-10	-6	3	1	16	-13	7	5	1	3	-3	1	0	2	104	104
11	2	0	9	-9	-10	1	1	10	10	-5	3	1	6	6	8	5	1	3	-9	2	0	2	7	6
1	3	0	50	-49	-9	1	1	2	1	-4	3	1	54	54	9	5	1	8	-7	3	0	2	95	93
2	3	0	67	67	-8	1	1	21	21	-3	3	1	24	23	-7	6	1	17	-17	4	0	2	36	-35
3	3	0	12	12	-7	1	1	19	19	-2	3	1	19	19	-6	6	1	10	-10	5	0	2	67	-64
4	3	0	8	8	-6	1	1	24	-23	-1	3	1	0	-7	-5	6	1	3	-3	6	0	2	17	17
5	3	0	8	9	-5	1	1	12	-11	0	3	1	71	-72	-4	6	1	10	-10	7	0	2	24	-24
6	3	0	39	-41	-4	1	1	30	-30	1	3	1	7	-6	-3	6	1	6	6	8	0	2	14	-15
7	3	0	15	-16	-3	1	1	27	-26	2	3	1	18	-18	-2	6	1	14	14	9	0	2	13	14
8	3	0	9	10	-1	1	1	21	21	3	3	1	33	-33	-1	6	1	8	9	10	0	2	8	8
9	3	0	6	6	0	1	1	15	-15	4	3	1	37	37	0	6	1	26	27	11	0	2	14	13
10	3	0	5	4	1	1	1	20	-20	5	3	1	16	16	1	6	1	2	2	-11	1	2	4	5
0	4	0	35	-36	2	1	1	22	23	6	3	1	13	14	2	6	1	28	-29	-10	1	2	19	-19
1	4	0	4	-5	3	1	1	41	42	7	3	1	20	21	3	6	1	12	-12	-9	1	2	13	-12
2	4	0	9	-9	4	1	1	15	-16	8	3	1	17	-17	4	6	1	13	-13	-8	1	2	12	12
4	4	0	27	27	5	1	1	11	-11	9	3	1	9	-10	5	6	1	3	-3	-7	1	2	7	-8
5	4	0	11	10	6	1	1	33	-32	10	3	1	3	-3	6	6	1	16	16	-6	1	2	21	21
6	4	0	17	17	7	1	1	23	-22	-10	4	1	1	0	7	6	1	5	6	-5	1	2	34	34
7	4	0	4	4	8	1	1	26	25	-9	4	1	5	-4	8	6	1	8	7	-4	1	2	20	-20

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 3-EXO-CHLORO-6-EXO-NITROBICYCLO[2.2.1]HEPTAN-2-EXO-OL.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-3	1	2	32	32	3	3	2	12	13	-2	6	2	3	-2	8	1	3	1	-1	-5	4	3	1	-2
-2	1	2	6	7	4	3	2	6	6	-1	6	2	18	-19	10	1	3	5	-5	-4	4	3	14	14
-1	1	2	89	-89	5	3	2	28	30	0	6	2	19	19	-11	2	3	4	-4	-3	4	3	27	-27
0	1	2	12	-12	6	3	2	1	-1	1	6	2	8	8	-10	2	3	6	-6	-2	4	3	10	10
1	1	2	26	-27	7	3	2	17	-18	2	6	2	5	-5	-9	2	3	2	-3	-1	4	3	19	18
2	1	2	10	-9	8	3	2	12	-12	3	6	2	12	11	-8	2	3	20	-20	0	4	3	20	-20
3	1	2	63	63	9	3	2	8	-8	4	6	2	1	1	-7	2	3	12	-12	1	4	3	24	24
4	1	2	11	11	10	3	2	5	5	5	6	2	7	-7	-6	2	3	15	15	2	4	3	7	6
5	1	2	9	10	-10	4	2	5	4	6	6	2	2	2	-5	2	3	21	20	3	4	3	15	-15
6	1	2	11	11	-9	4	2	2	0	7	6	2	4	-3	-4	2	3	44	42	4	4	3	13	14
7	1	2	12	-12	-8	4	2	27	-26	-6	7	2	1	1	-3	2	3	21	21	5	4	3	9	-8
8	1	2	9	-10	-7	4	2	17	-17	-5	7	2	8	-7	-2	2	3	34	-33	6	4	3	16	-17
9	1	2	11	-11	-6	4	2	4	5	-4	7	2	9	-9	-1	2	3	32	-31	7	4	3	5	5
10	1	2	6	-7	-5	4	2	2	-1	-3	7	2	2	-2	0	2	3	12	-13	8	4	3	2	3
-11	2	2	3	2	-4	4	2	22	21	-2	7	2	3	4	1	2	3	28	-28	9	4	3	2	-1
-10	2	2	2	1	-3	4	2	31	30	-1	7	2	17	17	2	2	3	13	-13	-9	5	3	2	-1
-9	2	2	8	-8	-2	4	2	14	-12	0	7	2	5	-5	3	2	3	15	15	-8	5	3	2	-2
-8	2	2	21	-21	-1	4	2	11	11	1	7	2	10	-10	4	2	3	8	8	-7	5	3	7	7
-7	2	2	4	4	0	4	2	12	10	2	7	2	4	4	5	2	3	30	30	-6	5	3	18	-18
-6	2	2	17	16	1	4	2	40	-39	3	7	2	4	-4	6	2	3	23	22	-5	5	3	5	-4
-5	2	2	12	11	2	4	2	13	-14	4	7	2	3	3	7	2	3	11	-11	-3	5	3	13	-13
-4	2	2	16	16	3	4	2	13	-14	5	7	2	3	2	8	2	3	6	-6	-2	5	3	20	19
-3	2	2	34	-34	4	4	2	7	-7	6	7	2	8	-8	9	2	3	11	-10	-1	5	3	22	22
-2	2	2	18	-18	5	4	2	23	24	-3	8	2	2	-3	10	2	3	12	-12	0	5	3	2	1
-1	2	2	21	21	6	4	2	16	16	-2	8	2	11	-10	-10	3	3	2	-2	1	5	3	9	-8
0	2	2	10	-10	7	4	2	5	5	-1	8	2	2	-2	-9	3	3	4	-5	2	5	3	11	-11
1	2	2	15	16	8	4	2	3	3	0	8	2	6	6	-8	3	3	5	5	3	5	3	10	-11
2	2	2	8	-8	-7	5	2	2	1	1	8	2	2	2	-7	3	3	1	0	4	5	3	3	-3
3	2	2	17	-17	-6	5	2	16	-16	2	8	2	11	11	-6	3	3	24	-25	5	5	3	10	11
4	2	2	21	21	-5	5	2	8	-9	3	8	2	7	7	-5	3	3	17	-17	6	5	3	2	2
5	2	2	6	-6	-4	5	2	12	-12	-11	1	3	13	-13	-4	3	3	6	6	7	5	3	1	2
6	2	2	7	-8	-3	5	2	6	-5	-10	1	3	7	8	-3	3	3	4	4	8	5	3	11	10
7	2	2	9	8	-2	5	2	26	26	-9	1	3	4	4	-2	3	3	58	55	-7	6	3	5	-5
8	2	2	3	-2	-1	5	2	12	12	-8	1	3	14	14	-1	3	3	37	36	-6	6	3	11	-12
9	2	2	6	6	0	6	2	16	16	-7	1	3	16	16	0	3	3	36	-36	-5	6	3	6	6
10	2	2	8	9	1	5	2	6	6	-6	1	3	9	9	1	3	3	2	1	-4	6	3	22	-21
-10	3	2	3	-3	2	5	2	19	-19	-5	1	3	11	-11	2	3	3	10	-11	-3	6	3	4	-3
-8	3	2	15	-15	4	5	2	11	-11	-4	1	3	6	6	3	3	3	35	-34	-2	6	3	10	10
-7	3	2	5	5	5	5	2	16	-16	-3	1	3	6	-6	5	3	3	7	-7	-1	6	3	23	-24
-6	3	2	4	5	6	5	2	3	3	-2	1	3	44	-43	6	3	3	2	-1	0	6	3	23	23
-5	3	2	7	6	7	5	2	5	-4	0	1	3	2	-2	7	3	3	31	31	1	6	3	33	32
-4	3	2	32	32	8	5	2	6	6	1	1	3	11	11	8	3	3	14	15	2	6	3	6	-5
-3	3	2	8	7	9	5	2	15	15	2	1	3	49	48	9	3	3	5	-5	3	6	3	2	4
-2	3	2	23	-22	-8	6	2	7	7	3	1	3	9	9	10	3	3	4	-4	4	6	3	18	-19
-1	3	2	24	-23	-7	6	2	6	-6	4	1	3	10	-9	9	4	3	1	-1	5	6	3	24	-25
0	3	2	9	-10	-5	6	2	9	9	5	1	3	5	4	-8	4	3	7	-7	6	6	3	8	8
1	3	2	18	-18	-4	6	2	17	-17	6	1	3	5	-6	-7	4	3	5	5	7	6	3	5	4
2	3	2	7	8	-3	6	2	1	1	7	1	3	16	-16	-6	4	3	11	-12	-6	7	3	3	3

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 3-EXO-CHLORO-6-EXO-NITROBICYCLO[2.2.1]HEPTAN-2-EXO-OL.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-5	7	3	4	4	1	1	4	33	-34	-9	4	4	14	14	-4	7	4	3	-2	-7	3	5	4	4
-4	7	3	10	-10	2	1	4	37	-37	-8	4	4	8	-9	-3	7	4	12	-12	-6	3	5	15	-15
-3	7	3	5	-5	3	1	4	1	-1	-7	4	4	10	-11	-2	7	4	3	-1	-5	3	5	5	-6
-2	7	3	5	-5	4	1	4	28	27	-6	4	4	5	-4	-1	7	4	5	5	-4	3	5	4	-4
-1	7	3	11	-11	5	1	4	11	11	-5	4	4	24	-24	0	7	4	7	7	-3	3	5	20	-19
0	7	3	3	4	6	1	4	12	12	-3	4	4	15	15	2	7	4	2	-3	-2	3	5	11	11
1	7	3	2	1	7	1	4	2	2	-2	4	4	15	15	3	7	4	2	-2	-1	3	5	22	22
2	7	3	10	10	8	1	4	1	-1	-1	4	4	16	16	4	7	4	4	-3	1	3	5	18	17
3	7	3	13	13	10	1	4	9	-10	0	4	4	8	8	-10	1	5	7	-8	2	3	5	5	4
4	7	3	2	-3	-10	2	4	5	5	2	4	4	18	-18	-9	1	5	13	-13	3	3	5	14	-15
5	7	3	2	2	-9	2	4	2	2	3	4	4	11	-11	-8	1	5	1	1	4	3	5	7	-7
-2	8	3	9	-9	-8	2	4	4	-4	4	4	4	14	-14	-7	1	5	7	7	5	3	5	14	-14
-1	8	3	1	-2	-7	2	4	20	-20	5	4	4	11	-10	-6	1	5	5	4	6	3	5	12	-11
0	8	3	3	-4	-5	2	4	15	15	6	4	4	13	13	-5	1	5	13	14	7	3	5	3	2
1	8	3	3	-4	-4	2	4	2	0	7	4	4	9	9	-4	1	5	3	3	8	3	5	13	14
2	8	3	10	10	-3	2	4	17	16	8	4	4	4	3	-3	1	5	11	11	9	3	5	11	11
-11	0	4	2	1	-2	2	4	5	-4	9	4	4	5	5	-2	1	5	7	-7	-9	4	5	4	4
-10	0	4	5	-5	-1	2	4	16	-15	-8	5	4	6	6	-1	1	5	32	-31	-8	4	5	3	3
-9	0	4	7	-7	0	2	4	18	18	-7	5	4	5	6	0	1	5	14	-14	-7	4	5	5	-5
-8	0	4	6	-6	1	2	4	1	-2	-6	5	4	6	6	1	1	5	22	-22	-6	4	5	6	-6
-7	0	4	5	-4	2	2	4	20	-19	-5	5	4	14	-14	2	1	5	24	24	-5	4	5	1	0
-6	0	4	38	38	3	2	4	6	-6	-4	5	4	19	-19	3	1	5	32	32	-4	4	5	8	8
-5	0	4	28	28	4	2	4	7	6	-3	5	4	7	-7	4	1	5	6	-6	-2	4	5	16	-16
-4	0	4	13	-13	5	2	4	4	4	-2	5	4	3	3	5	1	5	6	6	-1	4	5	6	6
-3	0	4	9	9	6	2	4	5	6	-1	5	4	3	4	6	1	5	6	-6	0	4	5	4	-4
-2	0	4	46	-47	7	2	4	4	-4	0	5	4	21	23	7	1	5	5	-6	2	4	5	20	20
-1	0	4	16	-16	8	2	4	13	-13	1	5	4	9	9	8	1	5	7	7	3	4	5	12	-12
0	0	4	2	2	9	2	4	2	3	2	5	4	5	-4	9	1	5	5	-4	5	4	5	12	12
1	0	4	47	-46	10	2	4	9	8	3	5	4	13	13	10	1	5	7	-7	6	4	5	10	-11
2	0	4	13	14	-10	3	4	3	-3	4	5	4	7	-7	-10	2	5	6	-6	7	4	5	2	-1
3	0	4	24	23	-9	3	4	2	-2	5	5	4	12	-12	-9	2	5	4	4	8	4	5	1	0
4	0	4	40	39	-8	3	4	10	-10	7	5	4	12	-12	-8	2	5	4	-4	-8	5	5	3	-3
5	0	4	27	27	-6	3	4	6	6	8	5	4	3	-3	-7	2	5	23	-24	-7	5	5	10	10
6	0	4	20	-19	-5	3	4	19	-19	-7	6	4	4	4	-6	2	5	1	1	-6	5	5	3	2
7	0	4	17	-17	-4	3	4	18	17	-6	6	4	2	0	-5	2	5	10	-9	-5	5	5	24	-23
8	0	4	20	-20	-3	3	4	8	9	-5	6	4	5	5	-4	2	5	3	2	-4	5	5	17	18
9	0	4	10	-10	-2	3	4	5	4	-4	6	4	5	-5	-3	2	5	56	55	-3	5	5	5	-4
10	0	4	7	7	-1	3	4	41	40	-3	6	4	8	-7	-2	2	5	8	8	-2	5	5	22	-22
-10	1	4	2	-1	0	3	4	38	-39	-2	6	4	12	12	-1	2	5	10	-9	-1	5	5	21	20
-9	1	4	15	-16	1	3	4	22	-22	-1	6	4	14	-14	0	2	5	2	-3	0	5	5	2	-3
-8	1	4	4	-4	2	3	4	4	3	0	6	4	8	-8	1	2	5	28	-28	1	5	5	6	6
-7	1	4	12	-12	3	3	4	20	-20	1	6	4	13	12	2	2	5	7	-7	2	5	5	21	21
-6	1	4	5	5	4	3	4	14	14	2	6	4	12	-11	3	2	5	4	-4	3	5	5	18	-17
-5	1	4	19	18	5	3	4	10	10	3	6	4	8	9	4	2	5	11	-11	4	5	5	15	-14
-3	1	4	11	12	6	3	4	2	-2	4	6	4	13	13	6	2	5	20	19	5	5	5	3	3
-2	1	4	24	24	7	3	4	13	13	5	6	4	9	-9	7	2	5	18	17	6	5	5	2	-1
-1	1	4	13	12	8	3	4	3	-3	6	6	4	6	5	-9	3	5	4	-4	7	5	5	3	2
0	1	4	20	-20	9	3	4	9	-9	-5	7	4	2	0	-8	3	5	6	6	-6	6	5	3	-3

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 3-EXO-CHLORO-6-EXO NITRONICYCLO[2.2.1]HEPTAN-2-EXO-OL.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-5	6	5	9	9	4	1	6	19	-20	1	4	6	10	10	8	1	7	3	4	-2	5	7	7	-7
-3	6	5	15	-15	5	1	6	16	16	2	4	6	2	2	-7	2	7	10	-9	-1	5	7	2	1
-2	6	5	2	2	6	1	6	7	7	3	4	6	16	-16	-6	2	7	5	-6	0	5	7	2	0
-1	6	5	14	-13	7	1	6	3	2	4	4	6	3	2	-5	2	7	2	-1	1	5	7	13	-14
0	6	5	6	-6	8	1	6	6	7	5	4	6	7	-6	-4	2	7	10	-10	2	5	7	17	16
1	6	5	18	18	-9	2	6	1	1	6	4	6	11	-11	-3	2	7	5	-6	3	5	7	12	12
2	6	5	5	4	-8	2	6	6	5	7	4	6	5	5	-2	2	7	16	16	4	5	7	8	-8
3	6	5	11	11	-7	2	6	3	-3	-7	5	6	3	3	-1	2	7	16	16	-4	6	7	5	5
4	6	5	5	6	-6	2	6	7	-6	-6	5	6	14	14	0	2	7	11	11	-3	6	7	2	2
5	6	5	13	-13	-5	2	6	6	5	-5	5	6	7	7	1	2	7	3	3	-2	6	7	6	-6
6	6	5	6	-7	-4	2	6	15	-15	-4	5	6	20	-20	2	2	7	16	-16	-1	6	7	7	-6
-3	7	5	4	-3	-3	2	6	1	-1	-3	5	6	2	-2	3	2	7	13	-13	0	6	7	4	-4
-1	7	5	10	-10	-2	2	6	24	23	-2	5	6	4	-3	5	2	7	5	-5	1	6	7	2	-2
0	7	5	6	-6	-1	2	6	17	-16	-1	5	6	15	-15	6	2	7	4	-4	2	6	7	5	4
2	7	5	3	-3	0	2	6	14	15	0	5	6	10	11	7	2	7	9	8	3	6	7	4	4
3	7	5	9	9	1	2	6	18	13	1	5	6	3	1	8	2	7	5	5	-7	0	8	16	-17
-10	0	6	6	-6	2	2	6	27	-27	2	5	6	3	-3	-8	3	7	3	5	-6	0	8	6	6
-9	0	6	2	2	3	2	6	5	6	3	5	6	19	20	-7	3	7	10	10	-5	0	8	9	9
-8	0	6	12	-12	5	2	6	12	-13	4	5	6	3	3	-6	3	7	14	-14	-4	0	8	5	-6
-7	0	6	11	-11	7	2	6	4	5	5	5	6	7	-6	-5	3	7	1	-1	-3	0	8	7	7
-6	0	6	14	14	8	2	6	10	-10	-5	6	6	6	7	-4	3	7	5	5	-2	0	8	5	-5
-5	0	6	7	8	9	2	6	2	0	-4	6	6	5	-6	-3	3	7	15	-15	-1	0	8	7	8
-4	0	6	8	9	-9	3	6	1	-2	-3	6	6	2	0	-2	3	7	5	5	0	0	8	11	11
-3	0	6	17	17	-8	3	6	1	-2	-2	6	6	2	-3	0	3	7	9	-9	1	0	8	6	-6
-2	0	6	7	-7	-6	3	6	4	-5	-1	6	6	2	1	1	3	7	14	14	2	0	8	7	-7
-1	0	6	7	-6	-5	3	6	5	-5	0	6	6	2	2	2	3	7	8	8	3	0	8	17	-17
1	0	6	25	-26	-4	3	6	5	-5	1	6	6	2	-1	3	3	7	4	4	4	0	8	2	-3
2	0	6	16	-15	-3	3	6	4	3	2	6	6	5	-5	4	3	7	4	3	5	0	8	8	8
3	0	6	3	-3	-2	3	6	3	4	3	6	6	7	-7	5	3	7	9	-9	6	0	8	3	2
4	0	6	1	1	-1	3	6	16	15	5	6	6	4	4	6	3	7	7	-8	7	0	8	9	9
5	0	6	32	32	0	3	6	11	11	-2	7	6	4	-3	7	3	7	6	-7	-8	1	8	5	-5
6	0	6	14	14	1	3	6	13	-13	-1	7	6	4	4	-7	4	7	2	3	-7	1	8	1	2
7	0	6	2	1	2	3	6	2	-1	0	7	6	7	-7	-6	4	7	11	-11	-6	1	8	12	12
8	0	6	4	-5	3	3	6	13	-13	1	7	6	3	3	-5	4	7	4	5	-5	1	8	27	-28
9	0	6	18	-18	4	3	6	7	-7	-8	1	7	5	-6	-4	4	7	2	2	-4	1	8	2	-4
-10	1	6	7	7	5	3	6	11	10	-7	1	7	3	-3	-3	4	7	1	-2	-3	1	8	16	16
-9	1	6	5	5	6	3	6	3	-2	-6	1	7	8	-8	-2	4	7	4	3	-2	1	8	10	-10
-8	1	6	9	-9	7	3	6	6	5	-5	1	7	5	-5	-1	4	7	11	-12	-1	1	8	14	14
-7	1	6	4	-5	8	3	6	6	6	-4	1	7	20	21	0	4	7	1	1	0	1	8	6	6
-6	1	6	10	-10	-8	4	6	3	3	-3	1	7	14	14	1	4	7	4	4	1	1	8	14	-14
-4	1	6	14	14	-7	4	6	2	1	-2	1	7	2	1	3	4	7	3	4	2	1	8	14	14
-3	1	6	12	13	-6	4	6	3	4	-1	1	7	2	2	4	4	7	7	-6	3	1	8	5	5
-2	1	6	10	-10	-5	4	6	8	-8	0	1	7	17	-17	5	4	7	4	3	4	1	8	17	-17
-1	1	6	18	17	-4	4	6	12	-13	1	1	7	18	18	6	4	7	5	5	5	1	8	2	-4
0	1	6	18	17	-3	4	6	14	-14	3	1	7	3	3	-6	5	7	8	8	6	1	8	3	-2
1	1	6	15	-15	-2	4	6	6	-5	5	1	7	11	11	-5	5	7	9	-9	-8	2	8	2	-2
2	1	6	1	0	-1	4	6	23	23	6	1	7	3	3	-4	5	7	6	-5	-7	2	8	3	-3
3	1	6	21	-21	0	4	6	14	14	7	1	7	5	-5	-3	5	7	8	9	-6	2	8	10	10

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 3-EXO-CHLORO-6-EXO-NITROBICYCLO[2.2.1]HEPTAN-2-EXO-OL.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-5	6	5	9	9	4	1	6	19	-20	1	4	6	10	10	8	1	7	3	4	-2	5	7	7	-7
-3	6	5	15	-15	5	1	6	16	16	2	4	6	2	2	-7	2	7	10	-9	-1	5	7	2	1
-2	6	5	2	2	6	1	6	7	7	3	4	6	16	-16	-6	2	7	5	-6	0	5	7	2	0
-1	6	5	14	-13	7	1	6	3	2	4	4	6	3	2	-5	2	7	2	-1	1	5	7	13	-14
0	6	5	6	-6	8	1	6	6	7	5	4	6	7	-6	-4	2	7	10	-10	2	5	7	17	16
1	6	5	18	18	-9	2	6	1	1	6	4	6	11	-11	-3	2	7	5	-6	3	5	7	12	12
2	6	5	5	4	-8	2	6	6	5	7	4	6	5	5	-2	2	7	16	16	4	5	7	8	-8
3	6	5	11	11	-7	2	6	3	-3	-7	5	6	3	3	-1	2	7	16	16	-4	6	7	5	5
4	6	5	5	6	-6	2	6	7	-6	-6	5	6	14	14	0	2	7	11	11	-3	6	7	2	2
5	6	5	13	-13	-5	2	6	6	5	-5	5	6	7	7	1	2	7	3	3	-2	6	7	6	-6
6	6	5	6	-7	-4	2	6	15	-15	-4	5	6	20	-20	2	2	7	16	-16	-1	6	7	7	-6
7	6	5	4	-3	-3	2	6	1	-1	-3	5	6	2	-2	3	2	7	13	-13	0	6	7	4	-4
8	6	5	10	-10	-2	2	6	24	23	-2	5	6	4	-3	5	2	7	5	-5	1	6	7	2	-2
9	6	5	6	-6	-1	2	6	17	-16	-1	5	6	15	-15	6	2	7	4	-4	2	6	7	5	4
10	6	5	3	-3	0	2	6	14	15	0	5	6	10	11	7	2	7	9	8	3	6	7	4	4
11	6	5	9	9	1	2	6	18	18	1	5	6	3	1	8	2	7	5	5	-7	0	8	16	-17
12	6	5	6	-6	2	2	6	27	-27	2	5	6	3	-3	-8	3	7	3	5	-6	0	8	6	6
13	6	5	2	2	3	2	6	5	6	3	5	6	19	20	-7	3	7	10	10	-5	0	8	9	9
14	6	5	12	-12	5	2	6	12	-13	4	5	6	3	3	-6	3	7	14	-14	-4	0	8	5	-6
15	6	5	11	-11	7	2	6	4	3	5	5	6	7	-6	-5	3	7	1	-1	-3	0	8	7	7
16	6	5	14	14	8	2	6	10	-10	-5	6	6	6	7	-4	3	7	5	5	-2	0	8	5	-5
17	6	5	7	8	9	2	6	2	0	-4	6	6	5	-6	-3	3	7	15	-15	-1	0	8	7	8
18	6	5	8	9	-9	3	6	1	-2	-3	6	6	2	0	-2	3	7	5	5	0	0	8	11	11
19	6	5	17	17	-8	3	6	1	-2	-2	6	6	2	-3	0	3	7	9	-9	1	0	8	6	-6
20	6	5	7	-7	-6	3	6	4	-5	-1	6	6	2	1	1	3	7	14	14	2	0	8	7	-7
21	6	5	7	-6	-5	3	6	5	-5	0	6	6	2	2	2	3	7	8	8	3	0	8	17	-17
22	6	5	25	-26	-4	3	6	5	-5	1	6	6	2	-1	3	3	7	4	4	4	0	8	2	-3
23	6	5	16	-15	-3	3	6	4	3	2	6	6	5	-5	4	3	7	4	3	5	0	8	8	8
24	6	5	3	-3	-2	3	6	3	4	-2	6	6	7	-7	5	3	7	9	-9	6	0	8	3	2
25	6	5	1	1	-1	3	6	16	15	5	6	6	4	4	6	3	7	7	-8	7	0	8	9	9
26	6	5	32	32	0	3	6	11	11	-2	7	6	4	-3	7	3	7	6	-7	-8	1	8	5	-5
27	6	5	14	14	1	3	6	13	-13	-1	7	6	4	4	-7	4	7	2	3	-7	1	8	1	2
28	6	5	2	1	2	3	6	2	-1	0	7	6	7	-7	-6	4	7	11	-11	-6	1	8	12	12
29	6	5	4	-5	3	3	6	13	-13	1	7	6	3	3	-5	4	7	4	5	-5	1	8	27	-28
30	6	5	18	-18	4	3	6	7	-7	-8	1	7	5	-6	-4	4	7	2	2	-4	1	8	2	-4
31	6	5	7	7	5	3	6	11	10	-7	1	7	3	-3	-3	4	7	1	-2	-3	1	8	16	16
32	6	5	5	5	6	3	6	3	-2	-6	1	7	8	-8	-2	4	7	4	3	-2	1	8	10	-10
33	6	5	9	-9	7	3	6	6	5	-5	1	7	5	-5	-1	4	7	11	-12	-1	1	8	14	14
34	6	5	4	-5	8	3	6	6	6	-4	1	7	20	21	0	4	7	1	1	0	1	8	6	6
35	6	5	10	-10	-0	4	6	3	3	-3	1	7	14	14	1	4	7	4	4	1	1	8	14	-14
36	6	5	14	14	-7	4	6	2	1	-2	1	7	2	1	3	4	7	3	4	2	1	8	14	14
37	6	5	12	13	-6	4	6	3	4	-1	1	7	2	2	4	4	7	7	-6	3	1	8	5	5
38	6	5	10	-10	-5	4	6	8	-8	0	1	7	17	-17	5	4	7	4	3	4	1	8	17	-17
39	6	5	18	17	-4	4	6	12	-13	1	1	7	18	-18	6	5	7	5	5	5	1	8	2	-4
40	6	5	18	17	-3	4	6	14	-14	3	1	7	3	3	-6	5	7	8	8	6	1	8	3	-2
41	6	5	15	-15	-2	4	6	6	-5	5	1	7	11	11	-5	5	7	9	-9	-8	2	8	2	-2
42	6	5	1	0	-1	4	6	23	23	6	1	7	3	3	-4	5	7	6	-5	-7	2	8	3	-3
43	6	5	21	-21	0	4	6	14	14	7	1	7	5	-5	-3	5	7	8	9	-6	2	8	10	10

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 3-EXO-CHLORO-6-EXO-NITROBICYCLO[2.2.1]HEPTAN-2-EXO-OL.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-5	2	8	7	7	6	3	8	2	-1	-1	1	9	7	6	-1	3	9	6	6	-5	1	10	1	-2
-4	2	8	11	-11	-6	4	8	4	4	0	1	9	6	6	0	3	9	13	-14	-4	1	10	10	-10
-3	2	8	9	-10	-5	4	8	1	-1	1	1	9	18	-18	1	3	9	2	2	-3	1	10	5	5
-2	2	8	2	2	-4	4	8	4	5	2	1	9	2	1	2	3	9	9	9	-2	1	10	10	-10
-1	2	8	1	-2	-3	4	8	12	-13	3	1	9	4	4	3	3	9	2	-2	-1	1	10	4	4
0	2	8	5	5	-2	4	8	12	-11	4	1	9	11	-10	4	3	9	5	5	0	1	10	13	13
1	2	8	12	13	-1	4	8	4	-3	5	1	9	3	3	5	3	9	3	2	2	1	10	2	2
2	2	8	11	-11	0	4	8	2	-1	6	1	9	3	4	-4	4	9	1	3	3	1	10	5	4
4	2	8	9	9	1	4	8	15	15	-6	2	9	2	-1	-3	4	9	3	-3	4	1	10	3	-2
5	2	8	11	-12	2	4	8	10	10	-5	2	9	9	-9	-2	4	9	4	2	-4	2	10	4	-2
6	2	8	2	2	3	4	8	2	-3	-4	2	9	5	5	-1	4	9	2	-2	-2	2	10	3	-3
7	2	8	4	5	5	4	8	3	-2	-3	2	9	2	-1	0	4	9	6	-6	-1	2	10	8	-8
-7	3	8	4	4	-3	5	8	5	-5	-2	2	9	16	-16	1	4	9	6	5	0	2	10	5	5
-6	3	8	2	3	-2	5	8	5	5	-1	2	9	9	9	2	4	9	2	0	1	2	10	5	6
-5	3	8	6	-6	-1	5	8	8	-9	0	2	9	3	7	-1	5	9	2	2	2	2	10	4	-4
-4	3	8	5	-4	0	5	8	5	-5	1	2	9	9	9	-5	0	10	6	6	-3	3	10	2	-1
-3	3	8	7	-7	1	5	8	2	0	2	2	9	18	18	-3	0	10	3	-2	-2	3	10	2	-1
-2	3	8	7	6	2	5	8	7	-7	3	2	9	16	-16	-2	0	10	7	7	0	3	10	4	3
-1	3	8	6	6	3	5	8	7	7	4	2	9	9	9	-1	0	10	5	-5	1	3	10	4	-4
1	3	8	5	5	-6	1	9	2	-3	-6	3	9	6	-6	0	0	10	2	1	2	3	10	2	-2
2	3	8	5	-5	-5	1	9	12	-12	-5	7	9	9	-9	1	0	10	6	6	-2	1	11	1	1
3	3	8	3	3	-4	1	9	8	-7	-4	3	9	10	11	2	0	10	2	2	-1	1	11	2	-2
4	3	8	2	2	-3	1	9	16	17	-3	3	9	6	-6	3	0	10	5	-4	0	1	11	6	7
5	3	8	10	-10	-2	1	9	3	5	-2	9	9	2	-2	4	0	10	7	-7					

APPENDIX 3

TABLE 1. Anisotropic thermal vibration parameters ($U_{ij} \times 10^3/\text{\AA}^2$) of non-hydrogen atoms for 3-exo-chloro-6-exo-nitro-bicyclo[2.2.1]heptan-2-endo-ol, (59).

	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Cl	52(1)	62(1)	61(1)	2(1)	19(1)	-15(1)
O(1)	69(2)	66(2)	56(2)	-26(1)	26(1)	-34(1)
O(2)	35(1)	85(2)	62(2)	-1(1)	9(1)	1(1)
O(3)	79(2)	68(2)	52(2)	-21(1)	18(1)	-16(1)
N	50(2)	40(2)	40(2)	4(1)	8(1)	1(1)
C(1)	30(2)	55(2)	41(2)	73(2)	-3(1)	3(2)
C(2)	42(2)	53(2)	35(2)	-2(2)	3(1)	-11(2)
C(3)	36(2)	38(2)	49(2)	3(2)	7(1)	-2(1)
C(4)	31(2)	40(2)	47(2)	-3(2)	-4(1)	-3(1)
C(5)	38(2)	45(2)	42(2)	3(2)	-3(1)	1(2)
C(6)	35(2)	39(2)	36(2)	-4(1)	7(1)	-3(1)
C(7)	47(2)	38(2)	51(2)	4(2)	7(2)	3(2)

TABLE 2. Isotropic thermal parameters ($U_{iso} \times 10^3/\text{\AA}^2$) of the hydrogen atoms of 3-exo-chloro-6-exo-nitro-bicyclo[2.2.1]heptan-2-endo-ol, (59).

	U(iso)
H(1)	42(9)
H(2)	54(9)
H(3)	37(8)
H(4)	34(8)
H(5x)	52(9)
H(5n)	54(10)
H(6)	41(8)
H(7s)	48(9)
H(7a)	52(9)
H(hydroxyl)	85(14)

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 3-EXO-CHLORO-6-EXO-NITROBICYCLO[2.2.1]HEPTAN-2-ENDO-OL.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	0	0	34	-34	4	7	0	5	5	5	2	1	12	-13	2	6	1	4	2	6	0	2	7	8
4	0	0	2	2	5	7	0	11	-11	6	2	1	2	0	3	6	1	15	-15	-6	1	2	19	-19
6	0	0	9	9	1	8	0	1	-1	7	2	1	6	6	4	6	1	3	2	-5	1	2	12	13
1	1	0	30	-30	2	8	0	7	7	-6	3	1	21	22	5	6	1	18	17	-4	1	2	13	13
2	1	0	20	19	3	8	0	8	6	-4	3	1	7	7	6	6	1	13	-12	-3	1	2	7	-8
3	1	0	14	-13	4	8	0	2	3	-3	3	1	27	-28	-5	7	1	2	4	-2	1	2	2	-2
4	1	0	10	-11	5	8	0	3	3	-2	3	1	26	26	-4	7	1	11	11	-1	1	2	4	-4
5	1	0	9	8	1	9	0	9	-9	-1	3	1	59	59	-3	7	1	7	-7	0	1	2	1	1
6	1	0	5	-4	2	9	0	6	-6	0	3	1	54	-55	-2	7	1	14	-14	1	1	2	103	101
7	1	0	13	-13	3	9	0	3	3	1	3	1	47	-46	-1	7	1	7	-7	2	1	2	7	6
0	2	0	20	-21	4	9	0	9	8	3	3	1	25	24	0	7	1	13	14	3	1	2	31	-31
1	2	0	13	13	0	10	0	7	7	4	3	1	7	-7	1	7	1	5	-4	4	1	2	15	-16
2	2	0	36	-34	1	10	0	14	-13	5	3	1	5	5	2	7	1	5	-4	5	1	2	14	14
3	2	0	10	10	2	10	0	8	8	7	3	1	9	-10	3	7	1	5	5	6	1	2	5	-5
4	2	0	18	17	3	10	0	2	-3	-7	4	1	4	-4	4	7	1	2	0	7	1	2	10	9
5	2	0	17	-16	-7	0	1	5	6	-6	4	1	4	5	5	7	1	3	3	-6	2	2	1	2
6	2	0	-13	13	-5	0	1	34	-34	-5	4	1	7	8	-5	8	1	9	9	-5	2	2	12	12
7	2	0	8	8	-3	0	1	13	14	-4	4	1	28	-28	-4	8	1	7	8	-4	2	2	30	30
1	3	0	8	-8	-1	0	1	15	16	-3	4	1	11	-11	-3	8	1	7	-7	-3	2	2	11	11
2	3	0	24	24	1	0	1	18	17	-2	4	1	8	-8	-2	8	1	7	-7	-2	2	2	27	-28
3	3	0	31	-29	3	0	1	85	83	-1	4	1	1	0	-1	8	1	8	-8	-1	2	2	3	-3
4	3	0	22	-21	7	0	1	3	-3	0	4	1	12	-11	0	8	1	7	-7	0	2	2	10	10
5	3	0	3	3	-7	1	1	2	-3	1	4	1	5	-5	1	8	1	7	7	1	2	2	21	-21
6	3	0	15	15	-6	1	1	11	-11	2	4	1	37	-36	3	8	1	15	-14	2	2	2	39	-38
7	3	0	3	4	-5	1	1	8	7	3	4	1	1	-1	4	8	1	3	3	4	2	2	35	-36
0	4	0	48	-48	-4	1	1	3	-4	4	4	1	21	21	5	8	1	2	2	5	2	2	6	-5
1	4	0	32	32	-3	1	1	10	-10	6	4	1	6	7	-4	9	1	2	3	6	2	2	4	-4
2	4	0	32	30	-2	1	1	14	15	7	4	1	6	5	-3	9	1	3	2	-7	3	2	2	-3
3	4	0	7	-7	-1	1	1	4	-5	-5	5	1	3	-4	-2	9	1	4	3	-6	3	2	14	-14
4	4	0	8	7	1	1	1	104	-104	-4	5	1	9	-8	-1	9	1	5	-4	-5	3	2	7	7
5	4	0	2	-1	2	1	1	12	12	-3	5	1	5	-5	0	9	1	3	2	-4	3	2	27	28
6	4	0	2	-4	3	1	1	54	53	-2	5	1	7	-7	1	9	1	13	12	-3	3	2	23	22
7	4	0	12	11	4	1	1	10	10	-1	5	1	32	33	2	9	1	15	-15	-2	3	2	16	-16
1	5	0	11	-10	5	1	1	9	8	0	5	1	24	23	3	9	1	4	-4	-1	3	2	28	29
2	5	0	12	12	6	1	1	17	-16	1	5	1	2	2	4	9	1	2	-1	0	3	2	40	-40
3	5	0	4	-4	7	1	1	10	-11	2	5	1	13	13	-3	10	1	2	2	1	3	2	27	-26
4	5	0	21	-20	-7	2	1	9	8	3	5	1	9	-9	2	10	1	2	-2	2	3	2	39	38
5	5	0	9	-8	-6	2	1	21	21	4	5	1	14	-13	-1	10	1	4	-4	3	3	2	14	12
6	5	0	12	11	-5	2	1	17	-17	5	5	1	2	2	0	10	1	8	-8	4	3	2	12	-13
0	6	0	10	9	-4	2	1	14	-14	6	5	1	2	1	1	10	1	2	1	5	3	2	3	3
1	6	0	16	16	-3	2	1	19	19	-6	6	1	6	6	2	10	1	9	9	6	3	2	2	4
2	6	0	37	35	-2	2	1	6	-7	-5	6	1	11	11	3	10	1	6	6	7	3	2	2	0
3	6	0	15	-14	-1	2	1	4	-4	-4	6	1	4	3	-6	0	2	30	-30	-7	4	2	1	0
5	6	0	3	-3	0	2	1	104	103	-3	6	1	22	-23	-4	0	2	7	7	-6	4	2	3	2
6	6	0	12	-11	1	2	1	61	-60	-2	6	1	11	11	-2	0	2	109	-112	-5	4	2	28	-29
1	7	0	5	-5	2	2	1	55	-54	-1	6	1	4	5	0	0	2	14	-15	-4	4	2	14	-14
2	7	0	6	-7	3	2	1	5	6	0	6	1	10	9	2	0	2	33	31	-3	4	2	18	18
3	7	0	8	8	4	2	1	3	-2	1	6	1	39	39	4	0	2	33	32	-2	4	2	15	15

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 3-EXO-CHLORO-6-EXO-NITROBICYCLO[2.2.1]HEPTAN-2-ENDO-OL.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-1	4	2	20	-21	2	8	2	8	-8	4	2	3	24	23	0	6	3	17	18	1	1	4	21	21
0	4	2	19	-19	3	8	2	14	-14	5	2	3	7	-8	2	6	3	5	-4	2	1	4	5	5
1	4	2	5	-5	4	8	2	9	-8	6	2	3	1	-3	3	6	3	7	-6	3	1	4	5	-6
2	4	2	20	-19	5	8	2	8	7	7	2	3	7	-7	4	6	3	11	11	4	1	4	9	8
3	4	2	6	7	-4	9	2	4	-4	-7	3	3	2	2	5	6	3	2	3	5	1	4	12	-11
4	4	2	12	-12	-3	9	2	3	-1	-6	3	3	9	-8	6	6	3	8	7	6	1	4	2	-1
5	4	2	24	-24	-2	9	2	3	2	-5	3	3	14	14	-5	7	3	10	10	7	1	4	3	4
6	4	2	2	2	-1	9	2	14	14	-4	3	3	8	-8	-4	7	3	5	6	-6	2	4	12	-12
-6	5	2	3	-2	0	9	2	2	3	-3	3	3	-48	-49	-3	7	3	12	12	-5	2	4	23	-23
-4	5	2	1	1	1	9	2	8	-8	-2	3	3	46	46	-2	7	3	20	-21	-4	2	4	11	12
-3	5	2	7	7	2	9	2	13	-13	-1	3	3	62	63	-1	7	3	16	-17	-3	2	4	26	26
-2	5	2	5	5	3	9	2	11	11	0	3	3	11	10	0	7	3	7	7	-2	2	4	26	25
-1	5	2	4	4	4	9	2	11	11	1	3	3	21	-20	2	7	3	12	12	-1	2	4	15	14
0	5	2	10	-11	-1	10	2	2	2	-1	3	3	11	-11	3	7	3	2	-3	0	2	4	75	75
1	5	2	10	9	0	10	2	6	-6	3	3	3	27	-26	4	7	3	21	-22	1	2	4	26	-26
2	5	2	30	30	1	10	2	6	6	4	3	3	9	-9	5	7	3	4	-4	2	2	4	14	14
3	5	2	26	25	-7	0	3	16	15	5	3	3	17	18	-3	8	3	13	13	3	2	4	20	20
4	5	2	18	-17	-5	0	3	38	-38	6	3	3	11	-12	-1	8	3	3	-3	4	2	4	3	-3
5	5	2	4	-4	-3	0	3	10	-10	-6	4	3	15	15	1	8	3	5	5	5	2	4	8	-8
6	5	2	7	6	-1	0	3	19	-19	-5	4	3	14	13	2	8	3	6	-6	6	2	4	4	4
-6	6	2	4	-4	1	0	3	40	-38	-4	4	3	9	9	3	8	3	6	-7	7	2	4	2	3
5	6	2	2	-2	3	0	3	15	15	-3	4	3	15	-15	4	8	3	4	4	-7	3	4	7	-6
-3	6	2	21	21	5	0	3	2	1	-2	4	3	34	-34	-4	9	3	7	6	-6	3	4	8	-8
-2	6	2	6	6	7	0	3	2	1	-1	4	3	16	16	-3	9	3	10	9	-5	3	4	2	1
-1	6	2	6	-6	-6	1	3	10	10	0	4	3	3	4	-2	9	3	1	-1	-4	3	4	3	-3
0	6	2	22	-21	-5	1	3	21	22	1	4	3	12	11	-1	9	3	8	-9	-3	3	4	8	-7
1	6	2	5	5	-4	1	3	25	-25	2	4	3	11	-11	0	9	3	2	3	-2	3	4	17	17
2	6	2	7	7	-3	1	3	21	-21	3	4	3	8	-9	1	9	3	4	2	-1	3	4	6	-6
3	6	2	11	11	-2	1	3	4	-4	4	4	3	12	-12	2	9	3	4	3	0	3	4	22	-23
4	6	2	18	18	-1	1	3	15	15	5	4	3	8	-8	3	9	3	4	5	1	3	4	4	4
5	6	2	2	3	0	1	3	2	-3	6	4	3	2	-1	-2	10	3	5	5	2	3	4	13	13
6	6	2	3	-3	1	1	3	4	-4	-6	5	3	2	1	-1	10	3	4	4	3	3	4	12	-11
-5	7	2	7	-7	2	1	3	23	-22	-5	5	3	2	3	0	10	3	10	-10	4	3	4	5	-6
-4	7	2	4	-3	3	1	3	32	31	-4	5	3	11	11	2	10	3	6	6	5	3	4	10	-10
-3	7	2	10	11	4	1	3	37	37	-3	5	3	22	-23	-4	0	4	32	32	6	3	4	8	-8
-2	7	2	2	1	5	1	3	5	6	-2	5	3	24	-24	-2	0	4	70	-71	-6	4	4	2	2
-1	7	2	7	7	6	1	3	3	-3	-1	5	3	22	22	0	0	4	46	-46	-4	4	4	2	3
0	7	2	2	2	-7	2	3	8	7	0	5	3	20	-20	2	0	4	8	7	-3	4	4	5	6
1	7	2	11	-11	-6	2	3	5	-6	2	5	3	25	26	4	0	4	16	-15	-2	4	4	14	14
2	7	2	3	-3	-5	2	3	11	11	3	5	3	6	5	6	0	4	23	24	-1	4	4	4	-3
3	7	2	11	11	-4	2	3	14	14	4	5	3	3	3	-7	1	4	8	-8	0	4	4	2	2
5	7	2	6	6	-3	2	3	15	15	5	5	3	5	6	-6	1	4	9	-9	1	4	4	25	-25
-5	8	2	5	4	-2	2	3	18	-18	6	5	3	13	13	-5	1	4	8	-8	2	4	4	15	14
-4	8	2	3	-3	-1	2	3	39	39	-6	6	3	3	-3	-4	1	4	15	15	3	4	4	25	25
-3	8	2	11	-12	0	2	3	46	46	-4	6	3	6	-7	-3	1	4	33	33	4	4	4	12	12
-2	8	2	14	14	1	2	3	27	-26	-3	6	3	5	4	-2	1	4	7	-7	5	4	4	14	-14
-1	8	2	6	6	2	2	3	12	-13	-2	6	3	6	6	-1	1	4	87	-89	6	4	4	8	-8
0	8	2	12	-12	3	2	3	9	7	-1	6	3	30	-31	0	1	4	1	1	-6	5	4	6	-5

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 3-EXO-CHLORO-6-EXO-NITROBICYCLO[2.2.1]HEPTAN-2-ENDO-OL.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-5	5	4	10	-10	-2	10	4	2	-3	4	3	5	3	4	-1	8	5	5	-5	-5	3	6	2	0
-4	5	4	11	-11	-1	10	4	1	0	5	3	5	3	-2	0	8	5	6	-5	-4	3	6	10	-10
-3	5	4	22	-22	0	10	4	5	5	6	3	5	7	-7	1	8	5	15	15	-3	3	6	4	-3
-2	5	4	29	29	1	10	4	2	3	-6	4	5	6	5	2	8	5	7	6	-2	3	6	20	20
-1	5	4	28	29	-7	0	5	10	9	-4	4	5	13	14	3	8	5	2	2	-1	3	6	9	9
0	5	4	37	-37	-5	0	5	7	7	-3	4	5	1	-1	-3	9	5	5	4	0	3	6	5	-5
1	5	4	24	-23	-3			7	-7	-2	4	5	8	-9	-2	9	5	6	-5	1	3	6	31	30
2	5	4	12	12	-1	0	5	7	-6	-1	4	5	1	-1	-1	9	5	7	-7	2	3	6	10	-11
3	5	4	11	-11	1	0	5	42	-41	0	4	5	48	47	0	9	5	4	5	3	3	6	1	1
4	5	4	7	7	3	0	5	18	-18	1	4	5	4	-4	1	9	5	5	-5	4	3	6	8	7
5	5	4	14	15	5	0	5	8	8	2	4	5	17	-17	3	9	5	2	3	5	3	6	2	3
6	5	4	6	-5	-7	1	5	8	-8	3	4	5	6	7	-1	10	5	3	-2	6	3	6	4	-4
-6	6	4	11	11	-6	1	5	19	19	4	4	5	11	-12	0	10	5	4	-4	-6	4	6	2	-2
-5	6	4	10	-9	-5	1	5	3	-1	5	4	5	4	5	1	10	5	5	-5	-5	4	6	1	1
-4	6	4	2	-2	-4	1	5	10	-9	6	4	5	6	7	-6	0	6	3	-3	-4	4	6	13	-14
-3	6	4	4	-5	-3	1	5	2	-3	-6	5	5	2	-1	-4	0	6	22	22	-3	4	6	2	3
-2	6	4	6	7	-2	1	5	4	4	-5	5	5	12	12	-2	0	6	21	21	-1	4	6	30	30
-1	6	4	1	1	-1	1	5	26	25	-4	5	5	11	11	0	0	6	24	-24	0	4	6	3	3
0	6	4	31	-30	0	1	5	15	15	-3	5	5	11	-11	2	0	6	6	-6	1	4	6	37	-37
1	6	4	6	6	1	1	5	33	32	-2	5	5	6	5	4	0	6	33	-33	2	4	6	15	-15
2	6	4	3	4	2	1	5	43	-42	0	5	5	27	-27	6	0	6	10	-11	3	4		28	28
3	6	4	4	4	3	1	5	16	-16	1	5	5	2	-1	-6	1	6	2	2	3	4		3	-2
4	6	4	6	6	4	1	5	11	11	2	5	5	12	12	-5	1	6	18	-17	6	4	6	2	3
5	6	4	7	-7	5	1	5	2	2	4	5	5	10	-10	-4	1	6	12	-12	-5	5	6	16	15
-5	7	4	2	-2	6	1	5	2	-2	5	5	5	2	2	-3	1	6	39	39	-4	5	6	8	-7
-4	7	4	2	-1	-6	2	5	9	-9	6	5	5	2	1	-2	1	6	6	6	-3	5	6	5	-5
-3	7	4	16	-16	-5	2	5	4	-4	-5	6	5	5	4	-1	1	6	9	-10	-2	5	6	3	2
-1	7	4	9	9	-4	2	5	11	11	-4	6	5	4	4	0	1	6	7	-7	0	5	6	1	2
0	7	4	4	4	-3	2	5	19	-19	-3	6	5	8	7	1	1	6	7	-6	1	5	6	6	-5
1	7	4	20	-20	-2	2	5	42	-42	-2	6	5	18	-18	2	1	6	8	8	2	5	6	6	-7
2	7	4	3	-2	-1	2	5	33	34	-1	6	5	23	-23	3	1	6	12	12	3	5	6	6	5
3	7	4	3	-5	0	2	5	29	30	0	6	5	8	-9	4	1	6	9	10	5	5	6	5	5
4	7	4	2	1	1	2	5	9	9	1	6	5	6	6	5	1	6	4	-4	-5	6	6	7	-7
-4	8	4	10	-11	2	2	5	8	-8	3	6	5	6	-6	6	1	6	2	1	-4	6	6	11	-11
-3	8	4	8	8	3	2	5	11	12	4	6	5	5	5	-6	2	6	16	-15	-3	6	6	3	-3
-2	8	4	20	20	4	2	5	7	-7	5	6	5	6	-6	-5	2	6	21	-21	-2	6	6	12	12
-1	8	4	2	-3	5	2	5	7	7	-5	7	5	8	-9	-4	2	6	1	-1	-1	6	6	4	5
0	8	4	21	21	6	2	5	16	17	-4	7	5	9	9	-3	2	6	5	-5	0	6	6	6	6
1	8	4	2	2	-6	3	5	3	-1	-3	7	5	5	5	-2	2	6	23	-23	1	6	6	16	-16
3	8	4	8	-8	-5	3	5	26	25	-2	7	5	16	16	-3	2	6	10	10	2	6	6	25	-25
4	8	4	7	7	-4	3	5	2	-2	-1	7	5	13	13	0	2	6	29	-29	3	6	6	2	2
-3	9	4	5	-5	-3	3	5	8	-8	0	7	5	24	-25	1	2	6	13	-13	4	6	6	10	-11
-2	9	4	11	-11	-2	3	5	19	-18	1	7	5	10	9	2	2	6	25	26	5	6	6	2	-1
-1	9	4	3	2	-1	3	5	33	-32	2	7	5	11	12	3	2	6	8	8	-4	7	6	6	-5
0	9	4	15	15	0	3	5	42	43	3	7	5	12	-13	4	2	6	8	8	-3	7	6	7	-7
1	9	4	8	-8	1	3	5	16	16	4	7	5	7	-7	5	2	6	4	-5	-1	7	6	21	21
2	9	4	2	-3	2	3	5	3	3	-4	8	5	5	4	6	2	6	4	-4	0	7	6	2	2
3	9	4	3	3	3	3	5	2	-2	-2	8	5	8	7	-6	3	6	2	-1	1	7	6	5	4

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 3-EXO-CHLORO-6-EXO-NITROBICYCLO[2.2.1]HEPTAN-2-ENDO-OL.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	7	6	2	2	2	3	7	3	3	2	8	7	3	-3	-2	4	8	4	-4	5	1	9	10	-10
3	7	6	2	-1	3	3	7	9	-9	3	8	7	7	8	-1	4	8	29	30	-5	2	9	9	8
4	7	6	2	1	4	3	7	19	20	-1	9	7	2	2	0	4	8	2	2	-4	2	9	5	5
-4	8	6	7	-7	-5	4	7	4	4	0	9	7	2	-2	1	4	8	11	-10	-3	2	9	3	2
-3	8	6	2	-1	-4	4	7	27	26	1	9	7	3	-2	2	4	8	10	10	-2	2	9	18	18
-2	8	6	14	-15	-3	4	7	2	2	-6	0	8	9	-8	3	4	8	5	-5	-1	2	9	21	-22
-1	8	6	10	-10	-2	4	7	17	-16	-4	0	8	15	-15	4	4	8	5	-5	0	2	9	13	-12
1	8	6	22	22	-1	4	7	8	-9	-2	0	8	59	58	5	4	8	2	2	1	2	9	5	5
2	8	6	2	0	0	4	7	2	2	0	0	8	7	7	-5	5	8	6	7	2	2	9	2	2
3	8	6	6	-6	1	4	7	4	4	2	0	8	3	4	-4	5	8	3	-3	3	2	9	4	-5
-2	9	6	1	0	2	4	7	16	16	4	0	8	19	19	-3	5	8	17	-16	5	2	9	3	4
-1	9	6	8	8	3	4	7	2	-1	-6	1	8	3	2	-2	5	8	3	2	-5	3	9	4	-4
0	9	6	2	-3	4	4	7	3	3	-5	1	8	11	-11	-1	5	8	9	8	-4	3	9	8	7
2	9	6	2	1	5	4	7	2	-2	-4	1	8	12	-12	0	5	8	13	13	-3	3	9	15	15
-5	0	7	26	26	-5	5	7	11	11	-3	1	8	9	10	1	5	8	3	-3	-2	3	9	2	2
-3	0	7	3	-4	-4	5	7	2	-1	-2	1	8	2	2	2	5	8	14	-15	-1	3	9	11	-12
-1	0	7	26	27	-3	5	7	4	5	-1	1	8	12	-12	3	5	8	19	-19	0	3	9	8	-7
1	0	7	3	2	-2	5	7	19	19	0	1	8	4	-4	4	5	8	12	12	1	3	9	5	5
3	0	7	10	-10	-1	5	7	3	-3	1	1	8	6	-5	-4	6	8	3	4	2	3	9	3	-4
5	0	7	2	2	0	5	7	14	-14	2	1	8	6	-6	-3	6	8	8	-7	3	3	9	8	9
-6	1	7	4	3	1	5	7	5	5	3	1	8	9	9	-1	6	8	1	1	4	3	9	8	-8
-5	1	7	12	-12	2	5	7	2	2	4	1	8	7	-7	0	6	8	17	16	-5	4	9	5	-4
-4	1	7	2	1	3	5	7	10	-9	5	1	8	15	-16	2	6	8	12	12	-4	4	9	6	6
-3	1	7	3	1	4	5	7	10	-10	-6	2	8	5	5	3	6	8	2	1	-3	4	9	3	3
-2	1	7	12	-12	5	5	7	1	-2	-5	2	8	5	4	4	6	8	2	-1	-2	4	9	12	-12
-1	1	7	16	-16	-5	5	7	4	-4	-4	2	8	5	-4	-3	7	8	13	-13	-1	4	9	2	2
0	1	7	31	31	-3	6	7	14	14	-3	2	8	17	-18	-2	7	8	2	1	0	4	9	5	-5
2	1	7	19	-19	-2	6	7	3	-2	-2	2	8	1	1	-1	7	8	4	3	1	4	9	1	-1
3	1	7	11	11	-1	6	7	10	10	-1	2	8	14	14	0	7	8	6	-5	2	4	9	6	6
4	1	7	3	-2	0	6	7	4	3	0	2	8	12	-13	2	7	8	2	2	3	4	9	3	-2
5	1	7	7	6	1	6	7	13	-14	1	2	8	21	-21	3	7	8	3	-4	4	4	9	2	-3
-5	2	7	2	1	2	6	7	9	-9	3	2	8	8	8	-2	8	8	11	-10	-4	5	9	5	-4
-4	2	7	23	21	3	6	7	11	11	4	2	8	3	3	1	8	8	5	-6	-3	5	9	11	12
-3	2	7	15	-15	4	6	7	7	-7	5	2	8	4	5	0	8	8	3	3	-2	5	9	10	9
-2	2	7	36	-36	-4	7	7	4	-3	-5	3	8	12	-13	2	8	8	4	-4	-1	5	9	3	-2
-1	2	7	7	-6	-3	7	7	2	2	-4	3	8	7	-7	-5	0	9	2	-1	0	5	9	4	-5
0	2	7	2	-2	-2	7	7	5	6	-3	3	8	5	5	-3	0	9	4	-4	1	5	9	7	6
1	2	7	11	11	-1	7	7	12	-11	-2	3	8	1	-1	-1	0	9	3	2	2	5	9	6	6
2	2	7	21	19	0	7	7	10	-10	-1	3	8	12	-12	1	0	9	25	25	3	5	9	3	2
3	2	7	15	-14	1	7	7	8	8	0	3	8	8	8	3	0	9	5	-5	4	5	9	2	2
4	2	7	24	-24	2	7	7	18	18	1	3	8	9	-9	-5	1	9	9	9	-3	6	9	3	-4
5	2	7	6	7	3	7	7	7	8	2	3	8	7	-7	-4	1	9	11	11	-1	6	9	12	13
6	2	7	3	4	4	7	7	4	-4	3	3	8	3	3	-3	1	9	3	-3	1	6	9	8	-8
-3	3	7	5	5	-3	8	7	8	8	4	3	8	10	11	-1	1	9	27	-27	2	6	9	3	4
-2	3	7	20	-20	-2	8	7	9	9	5	3	8	6	7	0	1	9	21	21	3	6	9	9	9
-1	3	7	4	2	-1	8	7	5	-4	-5	4	8	3	-3	1	1	9	3	-2	-3	7	9	3	-2
0	3	7	4	-4	0	8	7	2	-2	-4	4	8	11	11	2	1	9	4	-4	-2	7	9	10	10
1	3	7	6	6	1	8	7	7	-7	-3	4	8	11	-11	3	1	9	3	4	-1	7	9	7	-6

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 3-EXO-CHLORO-6-EXO-NITROBICYCLO[2.2.1]HEPTAN-2-ENDO-OL.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	7	9	7	-6	3	2	10	2	1	3	5	10	1	-1	0	2	11	5	-4	-1	1	12	1	-2
1	7	9	4	-4	4	2	10	4	-3	-3	6	10	2	0	1	2	11	7	7	0	1	12	10	10
0	8	7	4	-4	-4	3	10	2	-5	-2	6	10	15	-16	2	2	11	12	12	1	1	12	2	2
-4	0	10	16	-15	-3	3	10	1	2	-1	6	10	2	1	3	2	11	4	-3	-3	2	12	4	-4
-7	0	10	24	-24	-2	3	10	10	-10	0	6	10	1	-2	-3	3	11	8	8	-2	2	12	8	8
0	0	10	1	1	-1	3	10	9	-9	1	6	10	4	5	-2	3	11	5	5	-1	2	12	5	5
2	0	10	5	5	0	3	10	18	18	2	6	10	3	4	0	3	11	6	-5	0	2	12	6	7
4	0	10	9	9	1	3	10	3	4	-1	7	10	4	-4	1	3	11	11	-11	1	2	12	2	2
-5	1	10	10	-10	2	3	10	10	-10	1	7	10	4	4	2	3	11	1	2	2	2	12	2	3
-4	1	10	5	5	3	3	10	3	2	-3	0	11	5	5	3	3	11	12	11	-2	3	12	11	-11
-3	1	10	4	4	4	3	10	2	1	-1	0	11	22	-23	-1	4	11	6	6	-1	3	12	7	7
-2	1	10	4	-5	-4	4	10	4	-3	1	0	11	11	10	0	4	11	4	-4	0	3	12	8	8
-1	1	10	22	22	-3	4	10	15	-14	3	0	11	4	-4	1	4	11	4	-4	1	3	12	9	-9
0	1	10	2	1	-2	4	10	4	4	-4	1	11	9	9	-2	5	11	2	2	2	3	12	5	-4
1	1	10	12	-12	-1	4	10	2	2	-3	1	11	11	11	-1	5	11	8	-8	-2	4	12	2	1
2	1	10	8	-8	0	4	10	7	-7	-2	1	11	11	-11	1	5	11	4	4	-1	4	12	5	-5
3	1	10	6	7	1	4	10	3	2	-1	1	11	18	18	2	5	11	2	3	0	4	12	3	1
-5	2	10	10	10	2	4	10	1	-1	0	1	11	2	1	-1	6	11	5	5	1	4	12	5	5
-4	2	10	6	-6	3	4	10	3	-3	1	1	11	17	-17	0	6	11	4	-4	-1	0	13	15	-15
-3	2	10	8	-7	-3	5	10	3	1	2	1	11	5	5	-2	0	12	3	2	1	0	13	3	3
-2	2	10	15	15	-2	5	10	8	-8	3	1	11	3	-3	0	0	12	6	6	-1	1	13	9	8
-1	2	10	15	15	-1	5	10	6	6	-4	2	11	6	5	2	0	12	21	-22	0	1	13	4	-5
0	2	10	3	-4	0	5	10	12	13	-3	2	11	10	10	-3	1	12	9	-9	1	1	13	2	3
1	2	10	10	-9	1	5	10	14	14	-2	2	11	2	-2	-2	1	12	2	-3	0	2	13	2	0
2	2	10	14	-13	2	5	10	7	-7	-1	2	11	3	-3										

APPENDIX 4

TABLE 1. Force-field potential function constants.

(a) Bond stretching force constants.

Type	$10^{-5}k_r(ij)$ dyn/cm	r^0 Å	Ref
C-C	4.40	1.54	186
C-N	3.89	1.47	206,223
C-O	5.36	1.43	225
C-H	4.60	1.09	187,223
C-Cl	6.50	1.78	225-227
O-H	4.60	0.94	224
O-N	6.50	1.24	228
CN	18.00	1.21	228

(b) Valence angle deformation force constants.

Angle	$10^{-5}k(ijk)$ dyn/cm	rad	Ref
H-C-H	0.20	1.894	186
C-C-C	0.40	1.923	186,187
C-C-N	0.69	1.911	223
C-C-O	0.56	1.911	208,223
C-C-Cl	0.95	1.911	226
C-C-CN	0.65	3.140	228
C-O-H	0.35	2.095	224
C-N-O	0.50	2.095	-
O-N-O	0.80	2.095	-
H-C-N	0.49	1.911	206
Cl-C-N	1.00	1.911	228
Cl-C-H	0.90	1.911	226,228
O-C-H	0.35	2.095	224

(c) Non-bonded potential function constants.

Atoms	$10^{11}a$ erg/ molecule	b $^{\circ-1}\text{erg}\text{\AA}^6/molecule$	$10^{11}c$	Ref.
H...H	375.0	4.685	0.6041	223
C...H	363.7	4.384	0.8771	223
C...O	1472.0	4.440	1.6950	208
O...H	195.0	4.320	0.6900	208
C...N	304.3	4.259	0.8713	223
N...O	1295.0	4.550	1.3900	208
H...N	481.1	4.544	0.9342	223
C...Cl	558.7	3.811	3.1170	223
O...Cl	739.0	3.933	3.4160	-
H...Cl	883.3	4.038	3.3850	223
N...Cl	739.0	3.933	3.4160	223
Cl...Cl	1357.0	3.548	11.6400	223
C...C	229.9	4.117	0.807	223
N...N	402.5	4.441	0.9337	223
O...O	1295.0	4.550	1.3900	-

(d) A torsional force constant of 0.000567×10^{11} erg/molecule was used for interactions of the type U-V-W-X.

Constants which are not referenced represent estimated values that gave the best agreement with geometrical constraints.

TABLE 2. Orthogonalised atomic coordinates for bicyclo[2.2.1]heptane, (66).

		x	y	z
1	C(1)	0.685443	2.286513	5.701483
2	H(1)	-0.318114	2.576712	5.367439
3	C(2)	0.802273	0.788944	6.074071
4	H(2x)	0.266335	0.159918	5.351634
5	H(2n)	0.333424	0.539838	7.032385
6	C(3)	2.330544	0.539575	6.032534
7	H(3n)	2.745995	0.146183	6.966317
8	H(3x)	2.598005	-0.220222	5.288321
9	C(4)	2.897140	1.925626	5.641361
10	H(4)	3.921745	1.884881	5.252191
11	C(5)	2.734279	2.877555	6.850697
12	H(5x)	3.148151	2.474973	7.781760
13	H(5n)	3.293680	3.808397	6.698108
14	C(6)	1.206008	3.126920	6.892244
15	H(6x)	0.964008	4.188527	6.761449
16	H(6n)	0.735579	2.868622	7.847346
17	C(7)	1.820383	2.450911	4.671655
18	H(7a)	1.979320	3.481219	4.333938
19	H(7s)	1.697707	1.850421	3.763245

TABLE 3. Bond lengths (angstrom) for bicyclo[2.2.1]heptane, (66).

C(1)-C(2)	1.5476
C(1)-C(6)	1.5476
C(1)-C(7)	1.5413
C(1)-H(1)	1.0968
C(2)-C(3)	1.5490
C(2)-H(2x)	1.0967
C(2)-H(2n)	1.0956
C(3)-C(4)	1.5476
C(3)-H(3x)	1.0967
C(3)-H(3n)	1.0956
C(4)-C(5)	1.5476
C(4)-C(7)	1.5413
C(4)-H(4)	1.0968
C(5)-C(6)	1.5490
C(5)-H(5x)	1.0967
C(5)-H(5n)	1.0956
C(6)-H(6x)	1.0967
C(6)-H(6n)	1.0956
C(7)-H(7a)	1.0958
C(7)-H(7s)	1.0953

Author Denner L

Name of thesis Intramolecular Hydrogen bonding in Norbornyl systems 1983

PUBLISHER:

University of the Witwatersrand, Johannesburg

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