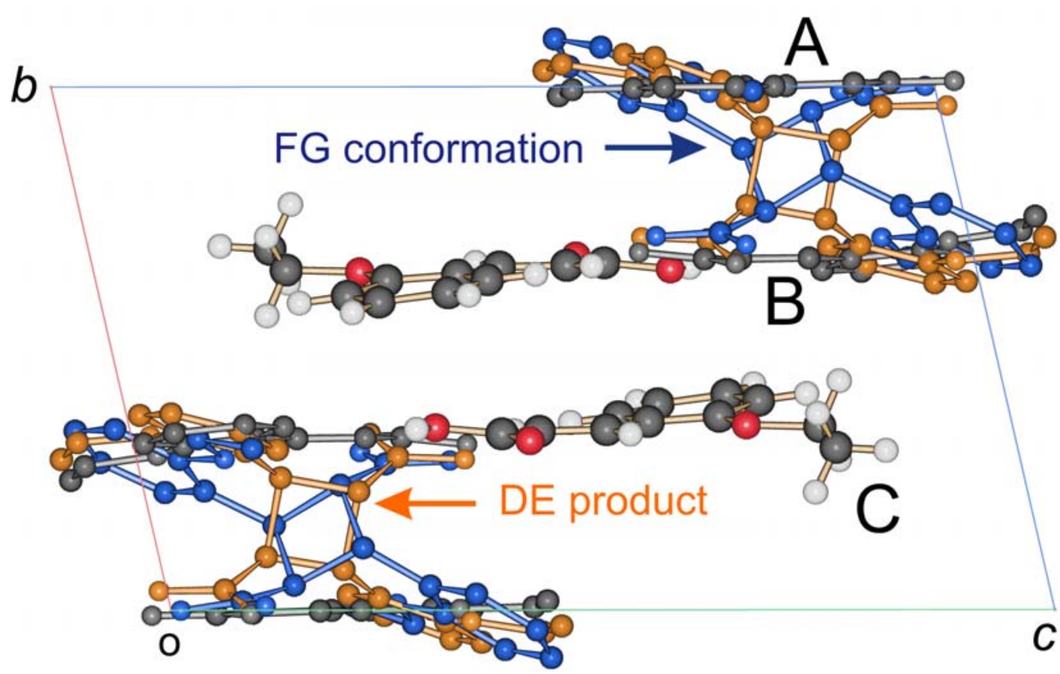
Solid-State Organic Chemistry of *ortho*-Ethoxy-*trans*-cinnamic acid



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Declaration

I declare that this thesis is my own unaided work. It is being submitted for the Degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

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Abstract

ortho-Ethoxy-*trans*-cinnamic acid (OETCA) has been known to form three polymorphs - the *α*-, *β*- and *γ*-polymorphs which crystallize in $P\bar{1}$ (Z=2), $R\bar{3}$ (Z=18) and *C*2/*c* (Z=8), respectively. These polymorphs have long been of interest from polymorphism and solid-state photoreactivity perspectives but have, until now, never been fully characterized.

In this thesis the complete structures of these polymorphs and their photodimerization products are presented. In addition, a new polymorph, the *α′*-polymorph [$P\bar{1}$ (Z=6)], which is only obtainable from the *α*-polymorph *via* a reversible solid-state phase transformation at 60 °C, has been discovered and characterised.

In all the polymorphs of OETCA, the smallest building component is the hydrogen-bonded carboxylic acid $R_2^2(8)$ dimers. These dimers further aggregate *via* CH...O interactions to form a ribbon motif in the *α*-, *α′*- and *γ*-polymorph structures. Structural and solid-state reactivity differences in these three polymorphs are therefore due to differences in the arrangement of these ribbons.

With few exceptions, solid-state [2+2] photodimerization reactions have been found to obey the topochemical principle. Such reactions occur with minimal structural movement in which the contact distance between reacting double bonds is between 3.5 and 4.2 Å. In this respect the solid-state reactivity of both the *α*- and *α′*-polymorphs is especially interesting and unusual, and indicate that significant movement - both molecular and structural - is possible and necessary for reactions to occur in these polymorphs. Both polymorphs yield the centrosymmetric dimer product - 2,2'-diethoxy-*α*-truxillic acid. Photodimerization in the layered structure of the *α*-polymorph, where the double bond contact distance is at 4.54 Å beyond reasonable photodimerization distance, is probably initially enabled by crystal defects. While the *α′*-polymorph is structurally very similar to the *α*-polymorph it is instead composed of two reaction sites with double bond contact distances of 3.72 and 4.99 Å, respectively. This

polymorph's solid-state reactivity has as a consequence been found to be temperature dependent, with only 66.7% conversion being achieved at 293 K and 100% conversion occurring at 343 K; reaction at 343 K involves both a significant conformation change in a reaction product as well as a heat and reaction driven phase change. In the *γ*-polymorph the closest distance between the double bonds is 5.26 Å, which together with the structural rigidity imposed by its herring-bone structure ensures that no photodimerization occurs.

The *β*-polymorph is really a solvate containing either benzene or thiophene within channels in the structure. The interactions between the solvent and OETCA molecules play an important role in maintaining the symmetry and integrity of the structure. The thiophene and benzene forms of the *β*-polymorph are isomorphous and yield a mirror product (2,2'-diethoxy-β-truxinic acid) upon photodimerization - the molecules involved being related by a 4.0 Å translation along the unit cell *c* axis.

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Table of Contents

List of Abbreviations and Generally used Crystal Codes

α-dimer *α*-photodimer *α*-photoproduct	The photodimerization product from the *α*- and *α′*-polymorphs - 2,2'-diethoxy-*α*-truxillic acid
β-dimer *β*-photodimer *β*-photoproduct	The photodimerization product from the *β*-polymorph - 2,2'-diethoxy-*β*-truxinic acid
BRX	The crystal structure of the *β*-photodimer
CCDC	Cambridge Crystallographic Data Centre
CSD	Cambridge Structural Database
DMF	*N*,*N*-Dimethylformamide
DMSO	Dimethyl sulfoxide
DSC	Differential Scanning Calorimetry
GK	The crystal structure of the *α*-photodimer published by Gopalan & Kulkarni (2001)
OETCA	*ortho*-ethoxy-*trans*-cinnamic acid
PXRD	Powder X-ray Diffraction
RTD	Crystal structure of the final product crystal from the photodimerization of the *α′*-polymorph at 293 K

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RX	The crystal structure of the *α*-photodimer
RXS	The crystal structure of the *α*-photodimer and DMSO-d6 solvate
SCSC	Single-crystal-to-single-crystal

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