Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Crystal Structure of Triphendioxazine as Solved by a New Ab Initio Method Utilising High Resolution Powder Diffraction and Computational Chemistry Techniques

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Version of record first published: 24 Sep 2006.

To cite this article: P G Fagan , K J Roberts , R Docherty , A P Chorlton , G D Potts & W Jones (1994): The Crystal Structure of Triphendioxazine as Solved by a New Ab Initio Method Utilising High Resolution Powder Diffraction and Computational Chemistry Techniques, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 248:1, 277-289

To link to this article: http://dx.doi.org/10.1080/10587259408027183

Mol. Cryst. Liq. Cryst. 1994, Vol. 248, pp. 277–289
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Printed in the United States of America

THE CRYSTAL STRUCTURE OF TRIPHENDIOXAZINE AS SOLVED BY A NEW *AB INITIO* METHOD UTILISING HIGH RESOLUTION POWDER DIFFRACTION AND COMPUTATIONAL CHEMISTRY TECHNIQUES.

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Abstract The crystal structure of Triphendioxazine has been solved by using a combination of high resolution powder diffraction and a number of computational chemistry techniques. The unit cell is bimolecular, space group $P2_1/c$ with a=6.875Å, b=5.197Å, c=17.735Å and β=93.617°. Validation of the approach is mediated through an independent single crystal analysis.

INTRODUCTION

In spite of the well documented importance of solid state chemistry with reference to the performance, production and design of speciality chemicals such as pharmaceuticals, agrochemicals and dyestuffs less than 1% have solved crystal structures. This has been due in part

to difficulties inherent in the preparation of samples of sufficient size and perfection[1] for conventional single crystal assessment. As a result, the generation of structural data *ab-initio* from x-ray powder data, has become an increasingly important technique in solid state analysis as is reflected in the number of structures solved by this method in recent years.[2]

This increase can, in no small part be attributed to an increased application of synchrotron radiation powder diffraction techniques for the structure solution of mainly inorganic[3,4] and latterly organic molecular systems.[5,6] The use of synchrotron radiation provides a high resolution in diffraction peaks. Increased photon flux ensures confidence in counting statistics and the availability of optimal precision hardware such as that found at Daresbury Laboratory[7] combine to facilitate the collection of data suitable for structural refinement.

Determination of crystal structure using X-ray powder data normally utilises the Rietveld technique[8] for which an accurate starting structure is essential. This structure has mainly been obtained by the application of single crystal techniques to the powder situation either through Direct Methods[9] or Patterson[10] techniques. However these demand the adequate separation and integration of diffraction peaks which becomes more taxing in systems of low symmetry as is often expressed in organic systems. Furthermore in materials where the molecule is composed of similarly scattering atom types it becomes more difficult to distinguish individual atomic sites especially in the case of lighter atoms.

A second and more controversial route to structure solution of molecular crystals would be a truly *ab-initio* solution using computational techniques alone. The limited successes in this field can be related directly to the increased understanding of the packing problem

coupled with associated improvements in intermolecular force fields, software and indeed more efficient hardware. However the development of a *reliable* methodology which allows the prediction of the actual crystal structure of an organic material based only on the molecular structure remains elusive. Progress has been hindered by problems in both global minimisation and force field accuracy where the description of the electrostatic interactions have received much consideration[11]. In recent months a number of publications have illustrated the advances to date and problems remaining in the field.[12,13]

Here we report a new approach for determining the crystal structure of a molecular system in which the initial structure for Rietveld refinement is generated using computational techniques after the unit cell and crystal symmetry have been derived from high resolution diffraction data.

Basic Approach

The overall methodology of our approach to the structure solution can be summarised :

1. Build and Optimise Molecular Structure

↓

2. Identify the Unit Cell Geometry

Collect Synchrotron Powder Diffraction Data
Index Pattern and Obtain Unit Cell
Assign number of Molecules/Unit Cell

↓

3. Generate Initial Starting Structures

Visually Refine Packing of Optimised Molecules into Lattice
Minimise Lattice Energy versus Packing Schemes
Assess Models by Confronting Pattern Simulation with Experimental Data

↓

4. Rietveld Refine Trial Structure

From either first principles or by using a similar molecule or fragment from the database[14] the molecular conformation of the compound under test is optimised, initially by molecular mechanics, MM2,[15] and then by third generation semi-empirical molecular orbital calculations using MOPAC.[16] An analysis of this structure is then performed in order to ascertain it's accuracy through direct comparison with similar molecular crystals in the database or by comparison with standard bond lengths and angles.[17]

X-ray powder diffraction is performed at the synchrotron source. From this data unit cell dimensions are obtained by utilising the indexing programs of Werner, Visser and Louër,[18-20] and refined using REFCEL.[21] The space group being determined by consideration of systematic extinction conditions.

Taking the unit cell as determined experimentally this molecular structure is fitted into the lattice according to symmetry and the lattice energy minimised using the atom-atom technique described by Kitaigorodsky[22] using the PCK83 software of Williams.[23] A series of proposed systems are generated. A powder diffraction profile of each proposed system was simulated using LAZY-PULVERIX.[24] Direct confrontation with experimental data was used as a benchmark for structure selection for Rietveld refinement, thus negating the possibility of erroneously selecting one of the many surface minima which may be found in a crystal system.

In Rietveld refinement using the program DBWS[25] we allow for preferred orientation of the powders. In this a simulation of the particle morphology using the Bravais Friedel-Donnay Harker (BFDH).[26] model is obtained using the molecular modelling program CERIUS.[27] From this we derive an aspect ratio with respect to the principle

crystallographic axes which we use as an indicator of preferred orientation.

MATERIALS AND METHODS.

Triphendioxazine, (figure 1, $C_{18}H_{10}N_2O_2$, hereinafter referred to as TPD), is the basic chromophore unit of a number of commercially important dyestuffs. It was prepared as a highly crystalline powder following recrystallisation and ground to a particle size of c.a. 45μm. High resolution powder diffraction data using a Debye-Scherrer scattering geometry was taken on beamline 2.3[7] at the SERC's Synchrotron Radiation Source (SRS) at Daresbury Laboratory: storage ring operating at an energy of 1.978GeV with a current of 183mÅ; Ge (111) monochromator providing photons at a wavelength of 1.46701 Å; angular scanning range of 2θ range from 10° to 50° at a step size of 1 mdeg using counting time of 1 second/step. Unit cell dimensions obtained as described are consistent with a bimolecular unit cell.

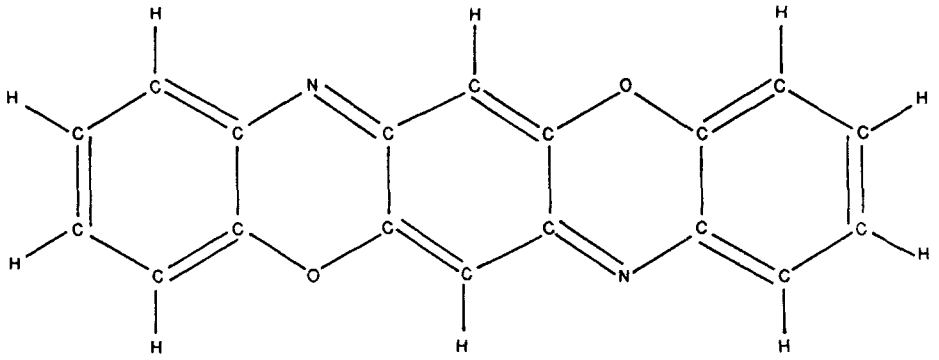

FIGURE 1 Triphendioxazine

Using the recently solved structure of 6,13 dichlorotriphendioxazine[28] as a starting conformation for the molecular model it was possible by atom substitution

and molecular orbital calculations[15] to generate an accurate molecular structure for TPD - the flat five membered aromatic system being consistent with structures published in the CSSR[14] database. By fitting this into a crystal lattice system consistent with x-ray diffraction data it was possible to optimise a series of possible lattices using the described method. Refinement of the most probable lattice gave the crystal structure to R-factor 8.7% and the appropriate Rietveld plot is illustrated in figure 2.

Vacuum sublimation at temperatures c.a. 400°C produced dark red platy crystals. A suitable crystal of dimensions 0.35 x 0.19 0.05 mm was selected for further analysis on an Enraf Nonius CAD4 diffractometer using MoK α (λ = 0.71069 Å). Data collection was carried out at ambient conditions with a 2θ scan range of 3-50°. Of 1136 reflections measured 613 reflections were flagged as observed based on the criteria $|F| > 3\ |F|$. The (−3 0 6) and (0 −2 8) reflections were used as standard and measured after every 100 reflections. The structure was solved using direct methods using SHELXTL/PC (version 4.1) a derivative of SHELX86[29] and refined using full matrix least squares. Hydrogen atoms not located from the Fourier difference maps were geometrically fixed. The final R-factor for this structure was 9.3%.

To allow for the effects of preferred orientation the BFDH predicted morphology (figure 3) was generated. The derived aspect ratio of 2.24 with respect to crystallographic directions, was subsequently used as an indicator of the orientation of the crystal within the sample and was consistent with exaggerated peaks in the diffraction profile.

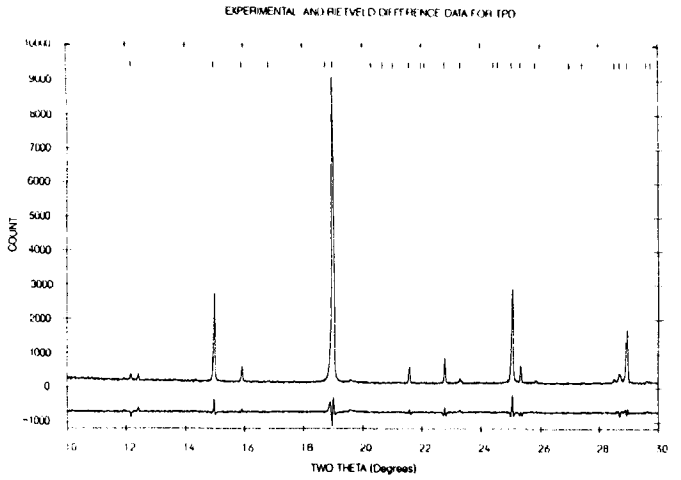

FIGURE 2 Plot Showing Experimental and Rietveld Difference Profiles.

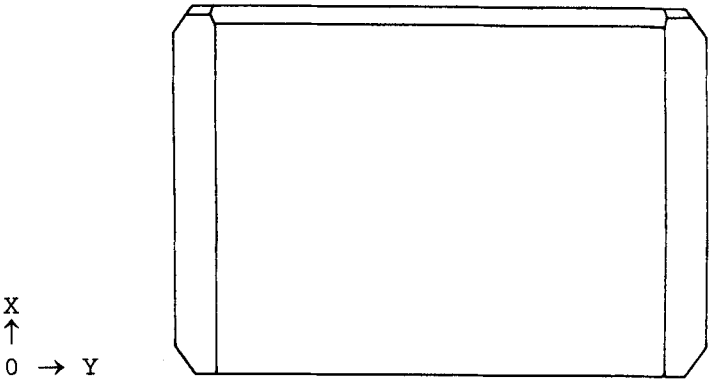

FIGURE 3 BFDH Model of TPD Morphology

As was shown for 6,13 dichlorotriphendioxazine there exists a close correlation between the structure obtained by both techniques. Superposition of the crystal lattices determined figure 4 reveals the high consistency achieved in both techniques.

Full crystallographic data is presented in table 1 and atomic coordinates are presented in table 2.

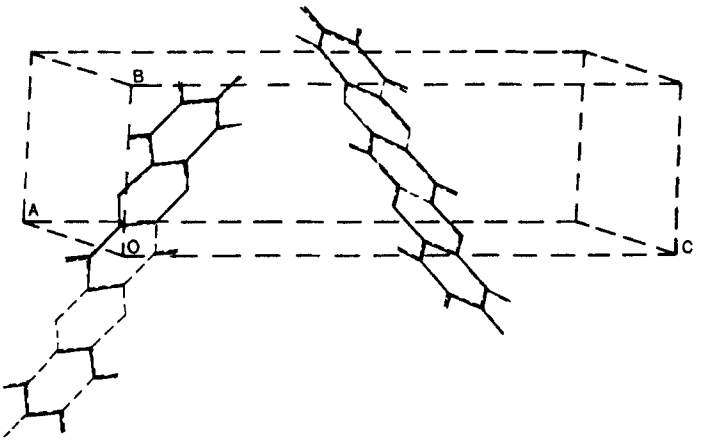

FIGURE 4 Overlay of Structures. Powder (Broken Lines), Single Crystal (Solid)

TABLE 1 Crystallographic Data for Triphendioxazine

	Single Crystal	Powder
Morphology	Plate	
Size/μm	350 x 190 x 50	c.a. 45
Spacegroup	$P2_1/c$	$P2_1/c$
a/Å	6.867	6.875
b/Å	5.191	5.197
c/Å	17.675	17.735
β/°	93.620	93.617
Volume/Å^3	628.79	632.40
Temperature/K	298	298
Wavelength/Å	0.71069	1.20229
2θ range/°	3-50	10-50
Standard Reflections	($\bar{3}$ 0 6)(0 -2 8)	
R-factor	0.093	0.087
Empirical Formula	$C_{18}H_{10}N_2O_2$	
Formula Weight	286	
Density/mg cm^{-3}	1.501	

TABLE 2 Atomic Coordinates of Non-Hydrogen Positions Obtained From Powder Structure Solution. A full list of thermal parameters for the structure is available

C1	0.0934	-0.7317	-0.1801
C2	0.2560	-0.8729	-0.2037
C3	0.4365	-0.8202	-0.1760
C4	0.4570	-0.6247	-0.1240
O5	-0.3227	-0.2892	-0.0479
C6	0.1888	0.0446	0.0245
N7	-0.0578	0.3871	0.1027
C8	0.0934	0.7317	0.1801
C9	0.2560	0.8729	0.2037
C10	0.4365	0.8202	0.1760
C11	0.4570	0.6247	0.1240
O12	0.3227	0.2892	0.0479
C13	0.1888	-0.0446	-0.0245
N14	0.0578	-0.3871	-0.1027
C15	-0.1086	-0.5313	-0.1272
C16	-0.2931	-0.4820	-0.1001
C17	0.0284	-0.2050	-0.0537
C18	-0.1609	-0.1461	-0.0240
C19	0.1609	0.1461	0.0240
C20	-0.0284	0.2050	0.0537
C21	0.2931	0.4820	0.1001
C22	0.1086	0.5313	0.1272

DISCUSSION

Although still a relatively new approach it is evident that this technique represents a potentially strong tool in the field of structure solution by the powder route.

Molecular modelling techniques, shown in the past to be of value in predicting molecular structures[30,31], have, in the past decade, advanced to a level such that the accurate prediction of molecular structures has become routine.[32] This coupled with the propensity of solid state data available for comparison in the databases permits a high degree of confidence in the predicted molecular conformation. Conformational

polymorphism although problematic, may often be identified quickly through unsuccessful attempts on lattice energy minimisation and subsequently addressed. Furthermore the use of systematic conformational searches may also prove fruitful in the identification of potential conformers.

The existence of well developed force field parameters with complementary software allows full and accurate utilisation of the atom-atom method in a range of molecular crystals as demonstrated by previous studies.[33] The parameters evolved for the more frequently investigated atom types of the organic systems are particularly well refined[34,35] although in the case of 6,13 dichlorotriphendioxazine we showed that the use of a universal force field[36] adequately overcame the problems of less common interactions.

A greater proportion of molecular crystals adopt a low symmetry monoclinic lattice. Consequently there will be consistently a high degree of overlap within the profile which makes separation and integration of peaks more problematic. As this method does not rely on data extraction in this way it is possible in theory to facilitate the extraction of maximum structural information in systems of even the lowest symmetry. Furthermore *Direct Methods* and *Patterson* techniques in practice yield only a proportion of the atomic positions as shown by McCusker[37] and Rudolf.[38] This approach gives reasonable starting positions for all atoms before structural refinement irrespective of scattering power and can distinguish between similarly scattering atoms predominant in organic systems.

CONCLUSION

Whereas true *ab initio* structure determination is an

admirable long term goal, this work demonstrates the utility of molecular modelling and diffraction techniques together as a route to the crystal structure of low symmetry organic systems. Although in this case the structure is validated by single crystal analysis there are many speciality chemicals where single crystals of sufficient size and perfection cannot be obtained and thus this technique presents a new tool in attempts to examine their solid state characteristics.

ACKNOWLEDGEMENTS

This work is supported by a SERC CASE award in collaboration with Zeneca Specialties. Financial support of both bodies is acknowledged as is the provision of synchrotron radiation beamtime at the SERC Laboratory, Daresbury, UK.

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