An Ab Initio Approach to Crystal Structure Determination Using High-Resolution Powder Diffraction and Computational Chemistry Techniques: Application to 6,13-Dichlorotriphendioxazine

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An alternative route for the crystal structure solution of molecular crystals is proposed and described. Using molecular and crystal modeling techniques in combination with high-resolution powder diffraction, the crystal structure of 6,13-dichlorotriphendioxazine, a commercially important dye molecule, has been solved. An independent single-crystal validation is performed by way of structure verification. The approach has particular application where, for example, sample size considerations preclude analysis by single-crystal techniques and provides an accessible alternative to existing strategies, especially where established powder methods fail.

Introduction

Despite the importance of molecular engineering concepts in the development of novel speciality effect chemicals, our knowledge of the solid-state structure of such materials is surprisingly limited with less than 1% having a solved crystal structure. This has been due, in part, to difficulties inherent in the preparation of crystals of sufficient size and quality for single crystal structure determination. As the result of this the generation of structural data ab initio has become, in recent years, both a significant scientific goal[1] and the subject of some controversy.[2] The works of Gavezzotti[3] and Karfunkel[1] represent considerable advances in this area. The increased sophistication of intermolecular force fields has meant that the interpretation of structural models, via the well established atom–atom potential method,[4] has in some cases, become routine.[2] However, the development of a reliable methodology which allows the prediction of the crystal structure of an organic material based solely on the molecular structure, remains despite some notable successes, elusive. Progress has been hindered by problems in both global minimisation and force field accuracy where the description of the electrostatic interactions has received much consideration.[5] Concurrently we have witnessed the application of predominantly synchrotron X-radiation powder diffraction techniques for the structure solution of mainly inorganic crystals,[6] and latterly organic molecular systems[7] although conventional laboratory X-ray powder diffraction has been used for the solution of small-molecule systems.[8] Crystal structures solved from powder X-ray data normally use the Rietveld refinement technique[9] for which an accurate starting structure is needed.

Starting models for structure solution from powder data have, to date, been obtained by Patterson[10] or direct methods[11] techniques which involve the separa-

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tion and integration of individual diffraction peaks. These approaches struggle to cope with systems of low symmetry where peak overlap is significant. Molecular mechanics and quantum chemical molecular modeling techniques, which can be utilized to provide sensible starting structures ab initio, will thus be of benefit where the above techniques fail. Molecular modeling techniques have in the past decade advanced to such a high level that the accurate prediction of molecular structures has become to an extent, albeit nontrivial, routine. Clearly molecules with a high degree of conformational flexibility present the greatest challenge, but with modern computational facilities the torsional degrees of freedom, in the context of the crystal lattice, can be systematically searched on a reasonable time scale. The advantage is that the intramolecular coordinates of all atoms in the molecule can be predicted in contrast to X-ray techniques where only the higher electron density sites can be resolved before Rietveld refinement.[12] Such effects can be significant when the scattering matrix is composed of similarly, poorly scattering atoms predominant in organic molecules. This contrasts with the analysis of inorganic materials where high scattering atom types dominate. For example McCusker,[13] in her study of a clathrasil phase, was able to derive the Si and some O atomic sites but was not able to resolve the C atom intramolecular coordinates using direct methods.

In this paper we report the application of a combination of high-resolution powder diffraction and computational chemistry techniques as a new ab initio approach to crystal structure determination. We demonstrate the method through an application to the commercially important organic pigment 6,13-dichlorotriphendioxazine. The work is validated through an independent single-crystal analysis. The specific aim of this study was to assess the reliability of the technique in cases where good single crystals cannot easily be obtained and to examine alternatives to other, equally viable, techniques.

Crystal Structure Determination Using a Combination of Powder Diffraction and Molecular Modeling Techniques

Basic Approach. Our overall approach to crystal structure determination using the new route involves essentially four main stages, each well established but never before utilized together in such a way to provide structure solution.

Stage 1. Using standard modeling approaches with the aid of routinely available software packages,[14,15] molecular arrangements are obtained for the molecule under consideration. In turn the structure is optimized and refined using molecular mechanics and semiempirical quantum chemistry techniques to obtain precision in bond lengths and angles. These calculations allow determination of the molecular geometry with respect to these two parameters with a high degree of accuracy. By way of structure validation a comparison with a table of standard bond lengths and angles[16] is performed. However, in cases where the molecule possesses internal conformational flexibility the modeling of torsion bonds confers a nontrivial component. The use of an existing database of structures may provide an alternative route to the initial structure but cannot be considered as a routine approach to more complex systems and is thus not pursued in this paper.

Stage 2. High-resolution (synchrotron) powder diffraction data are collected on the sample material. Following normalization, to account for beam decay, using the PODSUM[17] program, individual peaks are identified visually before being modeled mathematically using PKFIT[17] according to a prescribed peak-shape function. The peak positions so obtained are passed to a series of indexing programs which should in turn proffer the unit-cell dimensions for the system under test. From systematic absences the symmetry is obtained, and from density the number of molecules in the unit cell calculated. Synchrotron radiation is crucial in providing the peak resolution required (generally taken as 0.03°) for indexing in systems of low symmetry characteristic of organic materials.

Stage 3. Using the information obtained from the above stages, it is possible to construct a series of starting crystal models for the system under test. Initially, with appropriate graphical display this can be achieved visually to obtain a sensible structure for energy minimization. After manual, but stepwise and systematic, variation of molecular orientation within the unit cell, by applying rotations and then translations to the rigid molecular framework, and adjusting torsion angles in flexible molecules, atom–atom potential minimization methods, using such programs as PCK83[18] are used to calculate a series of possible low-energy crystal structures for further consideration. As a preliminary illustration of the method we treat here a centrosymmetric molecule; hence the inversion center is constrained to lie at the unit-cell origin, and only rotations need be applied to the molecule. This, although serving as a useful example, does not imply that the methodology is limited to such cases as will be addressed in future work. Additionally, a computer algorithm to automate the search for starting structures by the systematic application of rotations, translations and molecular torsions is almost complete. The number of structures generated in the manual approach, it can be argued, is proportional to the time spent searching for them. Consequently, to ascertain the feasibility of one structure with respect to another, the powder diffraction profile for each is simulated and compared directly with the experimental data with respect to peak intensities—positions by virtue of indexing techniques must concur. This is done quantitatively by refining the scale factor and observing the difference spectrum. On comparing the theoretical structures in such a way, we obtain a rapid and reliable way of filtering out improbable structures. Given that all the trial packing configurations have a low potential energy, a structure is

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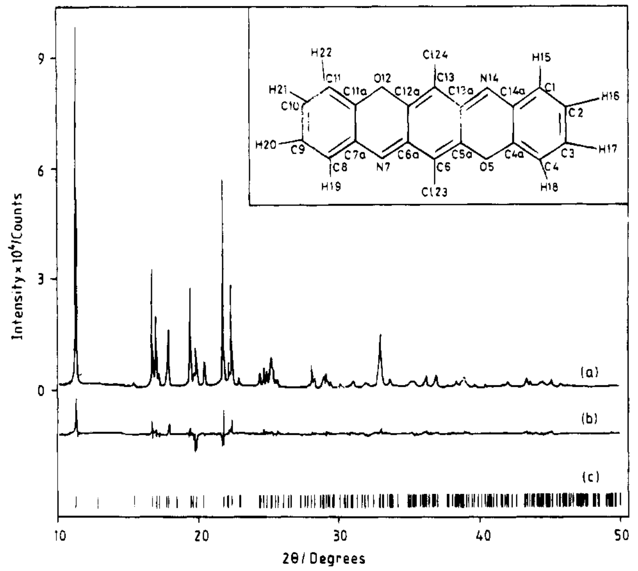

Figure 1. Results of the Rietveld refinement of DCTPD: (a) experimental high-resolution powder diffraction pattern; (b) residual plot showing the difference between experimental and theoretically modelled diffraction patterns; (c) marker points showing the location of diffraction points. The inset shows the molecular structure of DCTPD.

only considered for final refinement if the powder diffraction simulation presents a good match with experimental data.

Stage 4. In this, the final stage, the Rietveld method[9] is used to refine the theoretically produced structure. In this well-documented technique, a calculated diffraction profile according to the proposed structure is fitted to the experimental data in a series of least-squares minimizations. Both structural (atomic positions, lattice and thermal) parameters and parameterized profile functions are treated in the refinement.

Application to 6,13-Dichlorotriphendioxazine. 6,13-Dichlorotriphendioxazine ($C_{18}H_8N_2O_2Cl_2$, see inset to Figure 1, hereafter referred to as DCTPD) is the basic chromophore unit of a number of commercially important dyestuffs. It was prepared as a highly crystalline powder following recrystallization from nitrobenzene and ground to a particle size of ca. 45 μm.

High-resolution powder diffraction data using a Debye–Scherrer scattering geometry were taken on beamline 2.3[19] at the Synchrotron Radiation Source (SRS) at CCRL Daresbury Laboratory in the UK. The storage ring operated at an energy of ca. 2 GeV with a stored beam current of ca. 175 mA. The incident beam wavelength was selected using a Ge(111) monochromator to provide photons at a wavelength of 1.202 29 Å. Data were collected using an angular scanning range of 2θ angle from 2° to 50° at a step size of 1 mdeg using a counting time of 1 s/point. Unit-cell dimensions were obtained from the first 30 reflections using the indexing programs of Werner et al.[20] and refined using REFCEL.[17] The space group was determined by consideration of systematic extinction conditions. The lattice parameters as determined were consistent with a bimolecular unit cell forcing the molecule to lie on a center of symmetry and thus halving the number of atoms involved in structure refinement.

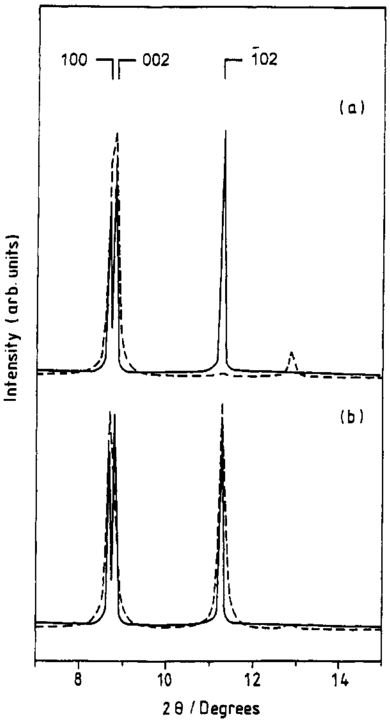

Figure 2. Experimental (—) and theoretical (– – –) powder diffraction patterns illustrating how comparison between two packing motifs (a and b) reveals a suitable starting structure (b) for subsequent Rietveld refinement. (NB: zero-point correction not applied).

An approximate molecular model of DCTPD was gen erated via building modules within standard software, optimized using the molecular mechanics package MM2,[21] and refined using semiempirical molecular orbital methods.[22] The optimized molecular conformation was placed in a proposed lattice from the unit-cell dimensions and by using molecular packing minimization methods together with the atom–atom technique a series of optimized lattice systems postulated. For these calculations we used the universal force field[23] together with charges calculated by the equilibrium method.[24] Because of symmetry considerations, there were no translational elements involved in the minimization.

The hypothetical crystal structures derived from the molecular packing calculations were then used to simulate the powder diffraction patterns[25] which were, in turn, compared with the experimental data. In this way, through the on-line manipulation of the trial structures, a model structure having the best fit to the experimental data was obtained. For example, a structure of feasible lattice energy of −46.9 kcal/mol was obtained in the first set of minimizations. Comparing the diffraction simulation data with the real profile (Figure 2a) revealed reasonable agreement across the 2θ range with only a few significant peaks missing. The

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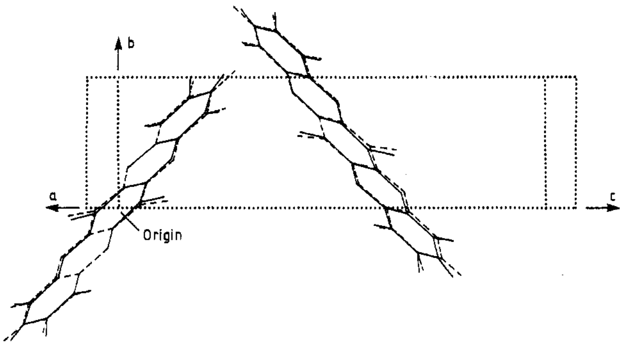

Figure 3. Overlay of the molecular structures which result from single-crystal (– – –) and combined modeling/powder diffraction (—) approaches.

Table 1. Crystallographic Data for 6,13-Dichlorotriphendioxazine[a]

empirical formula	$C_{18}H_8N_2O_2Cl_2$
formula weight	355.2
density/mg cm^{-3}	1.646

	single crystal	powder
morphology	prism	
size/μm	370 × 150 × 70	ca. 45
space group	$P2_1/c$	$P2_1/c$
a/Å	8.700(2)	8.717(1)
b/Å	4.870(1)	4.887(1)
c/Å	17.064(3)	17.147(2)
β/deg	97.50(3)	97.865(3)
vol/Å^3	716.8	723.59
Z	2	2
abs coeff/mm^{-1}	0.467	
temp/K	298	298
wavelength/Å	0.710 69	1.202 29
2θ range/deg	3–50	2–50
standard reflections	($\bar{3}$06) and (10 10)	
R factor	0.073	0.136

[a] The R factor is defined as $R = \sum|Y_{obs} - Y_{cal}|/\sum|Y_{obs}|$, where Y is diffracted intensity for the powder data and $|F|$ for the single-crystal data.

most significant of these ($\bar{1}$ 0 2) should have occurred at approximately 11°, 2θ. The exaggerated presence of the (1 0 2) peak led the authors to rotate the minimized structure at 90° relative to the b axis. Subsequent minimization of the new arrangement led to a new structure of −47.2 kcal/mol which on pattern simulation presented a very close match (Figure 2b) and was thus selected, on both criteria, for Rietveld refinement. The program DBWS[26] was used and yielded a structure solution with a final R factor of 0.1369 (for definition see Table 1). The mean isotropic temperature factor, based on all the atoms in the molecule, was refined to be 4.14(2) Å^2. The resulting Rietveld fit to the data is shown in Figure 1. In this the first two diffraction peaks had to be omitted from the refinement because they occurred close to an area of residual low-angle scattering produced by the flat-plate sample holder. This produced a nonlinear background in the pattern which proved difficult to model.

Verification of the Proposed Structure Using Single-Crystal Methods. Suitable crystals proved difficult to obtain using standard solution growth techniques. However, using vacuum sublimation at temperature ca. 400 °C, we were able to produce dark red prism-shaped crystals of 6,13-dichlorotriphendioxazine. A suitable crystal of dimensions 0.37 × 0.15 × 0.07 mm was selected for further analysis on an Enraf Nonius CAD4 diffractometer using Mo Kα (0.710 69 Å) radiation. Data collection was carried out at ambient conditions with a 2θ scan range of 3–50°. Of 1314 reflections measured 800 reflections were flagged as observed based on the criteria $|F| > 3\sigma|F_o|$. The ($\bar{3}$06) and (10 10) reflections were used as standard and measured after every 100 reflections. The structure was solved by

Table 2. Anisotropic Temperature Factors (Å^2 × 10^3) As Refined from Single-Crystal Data[a]

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	48(5)	43(5)	35(4)	0(4)	8(4)	−2(5)
C2	54(5)	42(5)	28(4)	4(4)	−5(4)	10(5)
C3	48(5)	52(6)	34(4)	0(4)	−3(4)	4(5)
C4	38(4)	49(6)	37(4)	1(4)	2(3)	−1(4)
O5	41(3)	52(4)	38(3)	7(3)	7(2)	5(3)
C13	39(4)	39(5)	27(4)	−4(4)	11(3)	−2(4)
N14	33(3)	31(4)	26(3)	7(3)	7(2)	10(3)
C14a	43(4)	34(5)	21(4)	0(3)	3(3)	2(4)
C4a	46(4)	33(5)	23(4)	−2(3)	5(3)	3(3)
C13a	37(4)	37(5)	23(3)	−6(3)	2(3)	0(4)
C5a	31(4)	32(5)	32(4)	−2(3)	5(3)	3(3)
Cl24	44(1)	74(2)	52(1)	18(1)	24(1)	11(1)

[a] The temperature factor exponent takes the form $-2\pi^2(U_131h^2a^{*2} + ... + 2U_{12}hka^*b^*)$.

Table 3. Comparison of Non-Hydrogen Atom Positions for Two Methods (Coordinates Derived from Powder Technique Given First)

atom	x	y	z
C1	0.1422(15)	0.7244(21)	0.2040(7)
C1	0.1394(10)	0.7260(19)	0.1987(5)
C2	0.2782(13)	0.8774(21)	0.2226(9)
C2	0.2711(10)	0.8756(20)	0.2195(5)
C3	0.4053(13)	0.8428(22)	0.1818(7)
C3	0.3988(10)	0.8387(20)	0.1809(5)
C4	0.3994(11)	0.6534(22)	0.1220(7)
C4	0.3972(9)	0.6472(19)	0.1213(5)
O5	0.2665(8)	0.3128(17)	0.0414(3)
O5	0.2634(6)	0.3083(12)	0.0400(3)
C13	0.1351(11)	−0.0244(20)	−0.0391(5)
C13	0.1322(8)	−0.0407(17)	−0.0380(4)
N14	0.0000(9)	0.3727(18)	0.1219(4)
N14	0.0007(6)	0.3807(14)	0.1184(3)
C14a	0.1338(11)	0.5300(22)	0.1426(6)
C14a	0.1331(8)	0.5323(16)	0.1388(4)
C4a	0.2643(12)	0.4986(21)	0.1024(6)
C4a	0.2644(9)	0.4973(16)	0.1009(4)
C13a	0.0006(10)	0.1967(20)	0.0644(7)
C13a	−0.0013(8)	0.1980(17)	0.0615(4)
C5a	0.1336(11)	0.1567(22)	0.0208(5)
C5a	0.1360(8)	0.1549(16)	0.0211(4)
Cl24	0.2897(4)	−0.0562(9)	−0.0881(2)
Cl24	0.2942(2)	−0.0881(6)	−0.0837(1)

Table 4. Comparison of Bond Lengths (Å) Obtained from the Powder and Single-Crystal Data

	powder data	single-crystal data
Cl24–C13	1.69	1.71
C13–C12a	1.36	1.39
C12a–C6a	1.48	1.47
C6a–C6	1.47	1.39
C6a–N7	1.31	1.32
N7–C7a	1.40	1.37
C7a–C8	1.41	1.39
C8–C9	1.40	1.36
C9–C10	1.40	1.39
C10–C11	1.38	1.38
C11–C11a	1.40	1.37
C11a–O12	1.39	1.39
O12–C12a	1.39	1.34

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(26) Sakthivel, A.; Young, R. A. DBWS, School of Physics, Georgia Institute of Technology, Atlanta, GA 30332.

(27) The SHELX86 program is available from G. M. Sheldrick at the University of Gottingen, Germany.

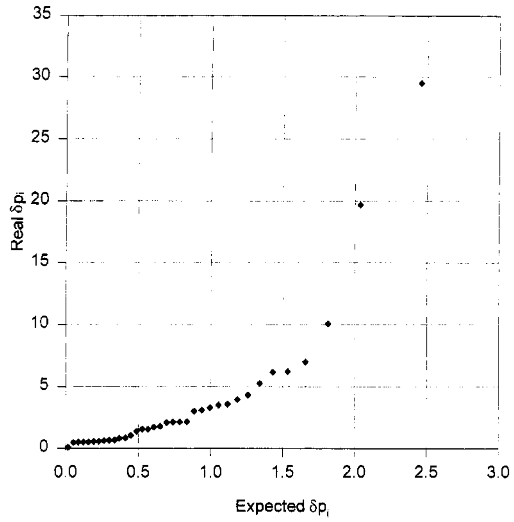

Figure 4. Half-normal probability plot of differences in the fractional coordinates of the main-group atoms (with associated standard deviations) for the two independently determined structures.

direct methods using SHELXTL/PC (version 4.1), a derivative of SHELX86,[24] and refined 113 parameters 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 0.073 (Table 1). The anisotropic temperature factors refined from the single-crystal study are given in Table 2.

Comparison between the results of the refinement from the powder and single crystal data is given in Tables 1, 3, and 4. The magnitudes of the differences between the cell parameters obtained from powder and single-crystal methods, although seemingly high in terms of the quoted standard deviations, are not unexpected or unprecedented. It is generally accepted that cell parameters obtained from high-resolution powder diffractograms are more accurate than those obtained from single-crystal techniques, given, in the case of powder diffraction, a statistical averaging over a very large number of crystallites. A half-normal probability plot[28] (Figure 4) was constructed for the two independently determined sets of 36 fractional coordinates of the main-group atoms. The ratio, δp_i, of the ranked absolute differences in the fractional coordinates to the root of the average variance, is plotted against the expected value of δp_i given a normal probability distribution. This plot indicates that there are significant differences in three fractional coordinates. These correspond to the chlorine atom of the asymmetric unit. We believe that this is a subtle manifestation of a disorder effect operating in the single crystal, grown by sublimation, but not manifest in the powdered sample, grown from solution. The disorder arises from an interchange in position of the nitrogen and oxygen atoms. The averaging of the molecular orientation effectively removes the single-bond, double-bond character in the central ring of the molecule in the single crystal structure (note in Table 4 the equal carbon–carbon bond lengths C6a–C6 and C13–C12a). This has greatest effect on the positioning of the chlorine atoms attached to the central carbon atoms. Taking into account this disorder effect it can be seen that the atomic positions (Table 3) and intramolecular bond lengths (Table 4) derived from both approaches are in satisfactory agreement. The similarity in derived structures can be easily illustrated through the overlay of the two molecular conformations shown in Figure 3 which reflects the small value of 0.051 for the RMS[15] fit between the two structures expressed in Cartesian coordinates.

Conclusions

Although the molecular and crystallographic structures of DCTPD are constrained via the ring systems and space-group symmetry, there is much we can conclude from this work with a view to the application of the technique for more complex systems.

Despite the fact that ab initio prediction of crystal structures from calculations based purely on molecular modeling calculations remains a long-term goal, the use of high-resolution X-ray diffraction provides, perhaps, one of the key experimental benchmarks needed to test molecular modeling calculations and mitigate concerns over global minimization and force-field accuracy. This work demonstrates the utility of combining molecular modeling and diffraction techniques to solve molecular structure ab initio, particularly in the case of low-symmetry organic structures. Although, in the case presented here, validation is provided by single-crystal analysis, there are many examples within specialty fine chemicals, such as pharmaceutical materials, where single crystals of sufficient quality and size cannot be obtained. It is in the examination of such materials that our approach offers the most promise. Work is currently in hand to extend the methodology developed toward an approach for the routine consideration of molecules with conformationally flexibility. Results from this will be reported in future papers.

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