Design of an SHG-active crystal, 4-iodo-4′-nitrobiphenyl: the role of supramolecular synthons

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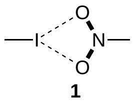
The crystal structure of 4-iodo-4′-nitrobiphenyl has been determined with packing calculations and the presence of polar and parallel iodo···nitro supramolecular synthons leads to non-centrosymmetry and measurable SHG activity

We have, in previous publications, described the identification of the I···O mediated, iodo···nitro supramolecular synthon **1** and its use in retrosynthetically guided supramolecular synthesis.[1–3] We conclude from this earlier work that: (*i*) synthon **1** is a polarisation-based structural unit; (*ii*) **1** is reasonably robust and as such it can be employed reliably in the design of new crystal structures. Here, we show that these ideas can be further extended to the design of an organic crystal with the property of second harmonic generation (SHG).

Synthon **1** can be used as a linear extender and so the ribbon structures of 4-iodonitrobenzene **2** and the 1 : 1 complex **3** of 1,4-diiodobenzene and 1,4-dinitrobenzene are not hard to anticipate.[1,2] However, these structures are centrosymmetric and therefore not viable for SHG applications. In **3**, the constituent molecules are themselves centrosymmetric, while in **2** the polar ribbon pattern is stacked in an antiparallel fashion leading to centrosymmetry. This is a general problem and our inability to control tertiary structural features, such as parallel *vs.* antiparallel stacking of polar structural units, is a major challenge in the practice of crystal engineering.

In order to design a non-centrosymmetric crystal, we decided to introduce the iodo and nitro substituents on a biphenyl framework and 4-iodo-4′-nitrobiphenyl **4** was prepared according to literature procedures.[4] While we were reasonably sure that **4** would yield a ribbon structure like **2** and **3**, a twisted and therefore chiral molecular conformation was further anticipated in view of the known structural chemistry of the biphenyls.[5] Finally, it was hoped that the (microscopic) molecular chirality of the twisted biphenyls units would lead to (macroscopic) crystal chirality.[6,7] There is some precedent for this, for in many classes of molecules, chiral sub-structural units (say helices) of the same handedness pack better than those of opposite handedness.[8] In any case, our optimism was furthered when we noted that crystals of **4** were obtained in the *F*-centred orthorhombic system, because the most common space group here, *Fdd*2 is non-centrosymmetric. Crystals of **4** seemingly suitable for X-ray diffraction analysis were obtained by recrystallisation. In fact crystals of two different morphologies were obtained; long needles from benzene and prisms from nitromethane. However, both forms have the same cell parameters and space groups and single-crystal data were collected.†

At this stage, a problem arose. The structure failed to solve despite all reasonable attempts and it was decided to attempt structure solution with packing energy calculations. The Cerius^2 program from molecular simulations was used.[9] The starting points were the experimental unit cell (a = 8.06, b = 18.812, c = 14.364 Å) and the measured crystal density of 1.98 g cm^{-3} which together indicate that Z = 8. Accordingly, the more likely space group is *Fdd*2 with the molecules bisected by [001], the twofold direction. Molecular optimisation with MOPAC[10] (AM1 Hamiltonian) gave a non-planar conformation which was used in the crystal optimisation with the crystal packer module of the Cerius^2 program. The structure rapidly moved into an energy minimum. The molecule was free to rotate about [001] during the minimisation and no effort was made to refine the unit cell. The final structure of **4** is shown in Fig. 1 and the final simulated X-ray powder pattern agrees very well with the experimentally recorded pattern (Fig. 2). In retrospect, it appears that all the crystals chosen for single-crystal data collection were flawed. Even when the coordinates obtained by



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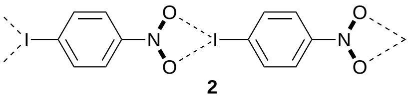

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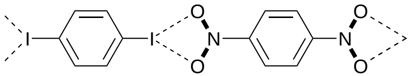

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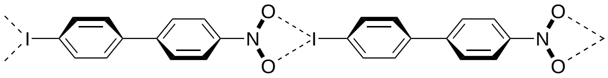

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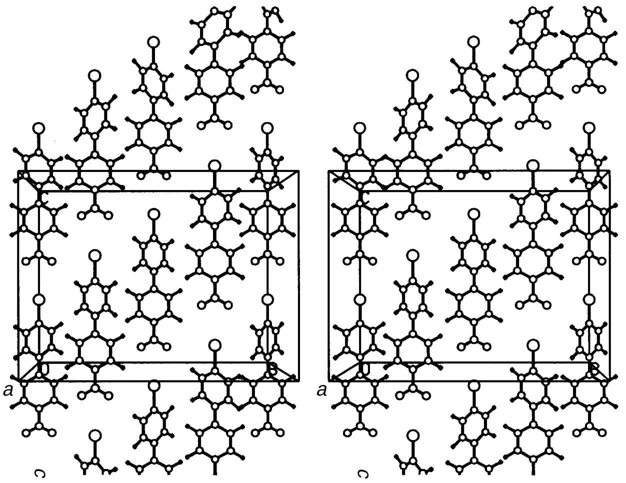

Fig. 1 Stereoview of a molecular layer of 4-iodo-4′-nitrobiphenyl **4** as obtained by its crystal structure simulation. Notice the parallel arrangement of polar iodo···nitro synthons.

simulation were used in least-squares refinement, such refinements were unsatisfactory. The R values routinely fell to below 0.05, but the atomic displacement parameters were generally unacceptable. Alternative disordered or twinned structures in both $Fdd2$ and the alternative $Fddd$ were considered but showed no improvement in the fit of the model to the data.

The appearance of the simulated diffraction pattern was found to depend on the assumed particle size along the three crystallographic directions and the value chosen were 300, 600 and 50 Å. These numbers were not picked at random but were obtained from an inspection of Fig. 1. The more numerous herringbone interactions along [100] and [010] were expected to lead to larger values of the particle size in these directions. Yet, the efficacy of the interactions (in effect, the growth rates) appear to be the same along either [100] or [010]. Therefore, noting the relative values of the a and b parameters, the particle size along [100] was taken, somewhat subjectively, to be half that along [010]. These considerations are important because it was found that the appearance of the spectrum is quite sensitive to the particle size chosen, though naturally the peak positions themselves do not change during these operations.

It may be noted from Fig. 1 that all the iodo···nitro synthons **1** in the structure of **4** are parallel, leading to macroscopic crystal polarity. Preliminary SHG measurements (Nd^{3+}/YAG laser, 1064 nm) indicate that crystalline **4** is SHG active. A higher initial activity falls rapidly because of material decomposition in the laser beam and the final activity is in the region of six times that of urea. More interestingly, the calculated molecular hyperpolarisability β is only 4.3×10^{-36} esu. This observation hints that the crystal SHG has contributions also from the polarisation-based synthons, **1**. It is important to note that supramolecular synthons as defined previously,[3] not only have structural connotations but also are relevant to crystal properties. Many useful crystal properties are a consequence of molecular and supramolecular structure. It is therefore not surprising that supramolecular hyperpolarisability as manifested in synthons such as **1** is important and should be considered in studies of SHG materials.

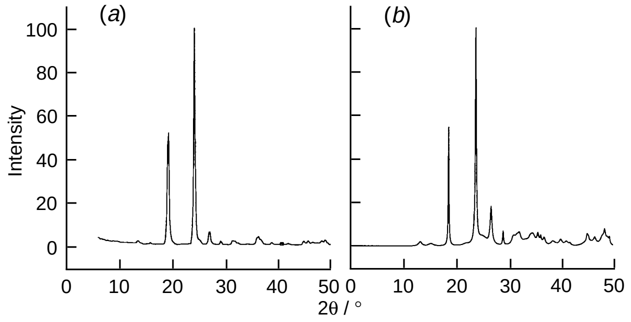

Fig. 2 Experimental (*a*) and simulated (*b*) X-ray powder spectra of biphenyl **4**. These plots were obtained with the Cerius² program.

This study shows that: (*i*) the principles of supramolecular retrosynthesis may be combined with molecular engineering techniques to obtain non-centrosymmetric crystal structures; (*ii*) supramolecular synthons such as **1** are structural units that are also of relevance in determining the magnitude of SHG activity because they can contribute to supramolecular hyperpolarisability; (*iii*) the use of simulation software is a valuable alternative method of crystal structure determination when single-crystal X-ray diffraction methods prove problematic, and if partial crystallographic information, such as cell parameters and space group, is available.

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Footnote

† Atomic coordinates have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/309.

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