The acentric nature of *trans*-stilbazole crystals and the origin of its NLO response

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L e t t e r

The X-ray crystal structure and the second order nonlinear optical response of *trans*-stilbazole are discussed. Given that diffraction intensities are completely insensitive to any small distortion from centrosymmetry, stilbazole X-ray diffraction data are better modelled in the centrosymmetric $P2_1/c$ space group and cannot be used to distinguish between alternative acentric options. However, second harmonic generation, notable in itself, sheds light on the acentric nature of the crystals and allows the most reasonable structural model to be selected. A previously unobserved low energy photoemission, probably due to through-space charge transfers, is also reported.

Nonlinear optical (NLO) properties of organic molecules and materials have been intensively studied in recent years because of their potential applications in electro-optic modulation, frequency mixing and second-harmonic generation (SHG).[1] Owing to their larger molecular polarisabilities, faster response times and higher optical damage thresholds with respect to traditional inorganic materials,[2] organic materials may offer some advantages.

During our studies on the second order NLO properties of crystalline Cu(I) halide/stilbazole adducts and Cu(I) halide/stilbazonium salts, which provide interesting responses, we incidentally observed (*via* a Kurtz–Perry powder experiment performed at a non-resonant incident wavelength of 1064 nm)[3] that pure, crystalline stilbazole itself (see Experimental) is 8 times more efficient than urea as an SH generator. In addition, we observed that the room temperature photo-luminescence (PL) spectrum of solid stilbazole (Fig. 1) consists of a strong band in the blue spectral region plus a broad and much weaker band in the 500–700 nm region. The latter is absent in the PL spectrum of stilbazole dissolved in dichloromethane, implying that its origin is related to intermolecular interactions present in the solid state. Such emissive behaviour is reminiscent of stilbene aggregates[4] and has been recently observed for paracyclophanes, which have been used as models for interchromophore delocalisation in stilbene-like compounds.[5] Both SHG activity and photoluminescence emission prompted us to attribute a primary role to stilbazole crystal packing but, to our surprise, its crystal structure was not present in the Cambridge Structural Database; therefore, we carried out an X-ray structural analysis. While non-centric packing is required for SHG to be observed in solid crystalline materials, it is noteworthy that the stilbazole X-ray diffraction

pattern can be 'perfectly' reproduced by a stilbazole molecule disordered about a crystallographic centre of symmetry, in the centrosymmetric space group $P2_1/c$. In the absence of other experimental observations (here SHG), $P2_1/c$ would be the accepted choice. Attempts to refine an ordered structure in the non-centrosymmetric space groups Pc and $P2_1$ result in better conventional R factors but also in unreasonable bond lengths.[6] Indeed, in the present case the differences between centric and acentric structural arrangements are very small, as they eventually reduce to the ordering or disordering of the terminal N/C−H moieties, all other atoms being substantially related by a centre of symmetry. Since, as a general rule, diffraction intensities are completely insensitive to any small distortion from centrosymmetry,[7] we cannot say, by means of diffraction methods alone, whether the stilbazole structure is disordered or not; thus we must rely on the structural parameters obtained from the more stable centrosymmetric refinement.

The derived $P2_1/c$ parameters do, however, contain enough information on the packing (as shown in Fig. 2, stilbazole chains grow along the [1 0 −1] direction and pack in the plane normal to such a direction with a herringbone motif) to allow a deeper understanding of the crystal structure when SHG results, prompting for an *acentric* structure, are jointly considered.
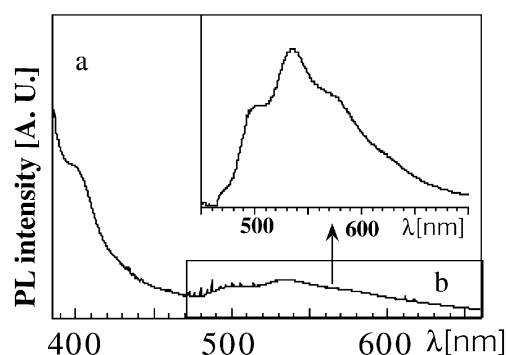

Fig. 1 Room temperature PL spectrum of solid stilbazole excited by the 365 nm line of an Ar ion laser: the strong band in the blue spectral region is labelled a; the broad and weaker band in the 500–700 nm region is labelled b. The spectrum in region b, obtained by exciting with the 488 nm Ar$^+$ line, is shown in the inset.
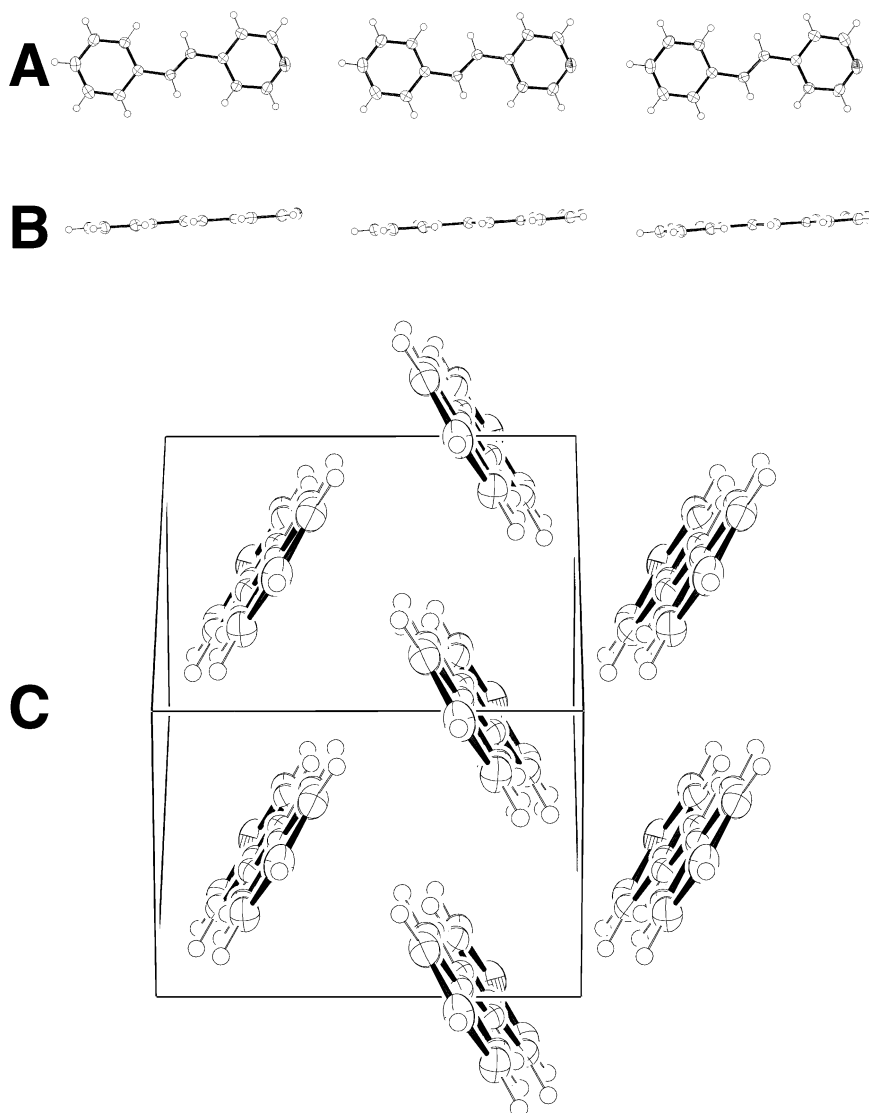
Fig. 2 Crystal packing of an ordered stilbazole molecule (N location arbitrarily assigned), assuming the *Pc* space group. (A) The chain motif, parallel to the [1 0 −1] direction; (B) as before, side view (the angle between the largest inertial molecular axis and the [1 0 −1] direction is *ca.* 4°); (C) the herringbone motif viewed down the [1 0 −1] direction.

Actually, the presence of a significant SHG response allows us to give an answer to: (i) the order/disorder dichotomy along the chains in favour of an ordered polar arrangement of equi-oriented stilbazole molecules interconnected by loose C−H···N interactions,[8] thus allowing the build up of a macroscopic chain polarity, and (ii) the parallel/antiparallel dichotomy among neighbouring chains in favour of a parallel arrangement; otherwise, the SHG contribution of a polar chain would be counterbalanced by that of nearby ones with inverted polarity. This suggests that, among the two non-centrosymmetric subgroups of *P*2₁/*c*, namely *Pc* and *P*2₁, the former is the proper one.[9]

There is however, another more subtle way to explain the significant SHG response, prompted by the recent proposal of a general mechanism of polarity formation in crystals.[10] Indeed, judging from the averaged crystal structure in *P*2₁/*c*, sequence errors are in principle allowed[11] and stilbazole crystals could be systematically twinned with a disordered central part that gradually transforms into two ordered (*Pc*) domains, of opposite polarity, on the two sides of the needles.[12]

Packing energy computations[13] show that van der Waals interactions do not discriminate between *Pc* and *P*2₁, while Coulombic interactions slightly favour the *P*2₁ packing motif.

If polarity (*i.e.*, *Pc* domains) develops, it seems more reasonable to believe, according to Hulliger *et al.*,[10] that " the primary confinement for the alignment of dipolar molecules is given by the surface–nutrient interface and not by the bulk state, as usually assumed for the prediction of crystal structures by computational methods". As a consequence, stilbazole crystals, like those of other dipolar but achiral molecules,[14] could consist of at least two symmetry related (180° racemic twin) *Pc* domains.

The geometrical relationships linking the molecular hyperpolarisability tensor (β_{ijk}) to the bulk susceptibility tensor (b_{IJK}) have been extensively studied by Zyss[1] for all Kleinman-allowed[15] crystal point groups. For point group *m*, assuming a one-dimensional molecular system, phase-matched SHG and electro-optic effects reach their optimum when the angle between the monoclinic axis and the molecular charge transfer (CT) axis are 35.3 and 90°, respectively. Indeed, the largest inertial axis of stilbazole makes an angle of 86° with *b*, thus being clearly close to maximising the electro-optic effect rather than SHG, which, however, is still significant.

In conclusion, the synergy between X-ray diffraction and SHG has allowed not only the assessment of the non-centrosymmetric nature of stilbazole crystals, but also the selection of their proper packing motif.

Experimental

Preparation and characterisation of stilbazole

4-*trans*-Stilbazole (Eastman Organic Chemicals) was recrystallised from water–acetone. The purity of the white solid was checked by ^{1}H NMR (in $CHCl_3$), elemental analysis, GC mass spectrometry and X-ray powder diffraction. The latter confirmed that the single crystal used in the X-ray analysis was representative of the bulk used in optical measurements.

X-Ray structure determination

Crystal data. $C_{13}H_{11}N$, $M = 181.24$ g mol^{-1}, monoclinic, see text for the space group, $a = 5.8169(4)$, $b = 7.5284(5)$, $c = 11.2744(8)$ Å, $\beta = 93.259(2)°$, $U = 492.9(1)$ Å^3, $Z = 2$, $D_c = 1.221$ Mg m^{-3}, $T = 163(2)$ K, μ(Mo-Kα) = 0.07 mm^{-1}, $F(000) = 192$, 11 404 reflections collected, 2074 unique [R(int) = 0.0247].

The diffraction experiment was performed by mounting a suitable crystal (of dimensions $0.60 \times 0.22 \times 0.20$ mm^3) on a Bruker SMART CCD area-detector diffractometer and measuring 2424 frames (30 s per frame; ω scan method, $\Delta\omega = 0.3°$; sample-to-detector distance fixed at 3.417 cm) that, upon data reduction, afforded almost all reflections belonging to the sphere with $2\theta < 70°$. The structure was solved by direct methods (SIR97)[16] and refined in space group $P2_1/c$ with full-matrix least-squares methods (SHELX97)[17]. Anisotropic temperature factors were assigned to all atoms except the hydrogens.

Free $P2_1/c$ refinement: data/restraints/parameters 2074/ 0/88; GoF (on F^2) = 0.959; $R = 0.0466$, $wR_2 = 0.1306$ for $I > 2\sigma$; $R = 0.0565$, $wR_2 = 0.1306$ for all data; largest difference peak and hole 0.48 and -0.17 e Å^{-3}. Restrained Pc refinement: data/restraints/parameters 4022/42/85; GoF (on F^2) = 0.869; $R = 0.0466$, $wR_2 = 0.1252$ for $I > 2\sigma$; $R = 0.0596$, $wR_2 = 0.1296$ for all data; largest difference peak and hole 0.47 and -0.16 e Å^{-3}.

CCDC reference numbers 163020 and 163021. See http://www.rsc.org/suppdata/nj/b1/b107632a/ for crystallographic data in CIF or other electronic format.

References and notes

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6   As a reference, we computed the optimised geometry at the B3LYP/6-31 + G(2d,2p) level. The $P2_1/c$ bond distances well agree with the averaged theoretical values, while in Pc and $P2_1$ the chemically equivalent bond lengths are unreasonably different. The only way to obtain reasonable parameters for the acentric structures is to restrain them (hydrogens riding on their carbon atoms, same distances on chemically equivalent bonds and equal anisotropic thermal parameters for *pseudo* centrosymmetric atoms). The results of the restrained Pc refinement are reported in the text.
7   "It simply cannot be determined, by diffraction methods alone, whether a particular structure is centrosymmetric or only *approximately* so since the diffraction intensities are completely insensitive to any small distortion from centrosymmetry." R. E. Marsh, *Acta Crystallogr., Sect. B*, 1995, **51**, 897.
8   Idealising the C–H bond distance in C1–H···N1 to 1.08 Å, we obtain an H···N contact of 2.62 Å and a C–H···N angle of 156° to be compared with 2.38 Å and 155° reported in: M. Mascal, *Chem. Commun.*, 1998, 303.
9   The stilbazole dipole moment makes an angle of *ca.* 86° with *b*; thus, even in the $P2_1$ space group there would be a residual polarity (though very small, being proportional to the cosine of 86°).
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11 A rigid inversion of one stilbazole (*i.e.*, a couple of sequence errors) produces, at worst, a couple of facing C–H bonds with a short H···H contact of 1.69 Å (for C–H bond distances idealised to 1.08 Å). However, small shifts or tilts from its average location allow it to fit into the available cavity. A single sequence error should be even less demanding.
12 Stilbazole crystallises from water–acetone solution as long needles growing approximately along the [2 0 − 1] direction, which makes an angle of 4° with the [1 0 −1] chain direction.
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