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1,3-Dibromo-2,4,6-trinitrobenzene (DBTNB). Crystal engineering and perfect polar alignment of two-dimensional hyperpolarizable chromophores

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1,3-Dibromo-2,4,6-trinitrobenzene (DBTNB), a two-dimensional charge transfer hyperpolarisable chromophore, crystallises in the non-centrosymmetric space group *C*2 in perfect polar order leading to an intense powder SHG signal at 1.06 μm.

In the materials science context, crystal engineering implies the design of solid materials wherein a specific supramolecular arrangement is associated with predefined physical properties.[1] Of particular interest is the design of non-linear optical (NLO) materials with such applications as second harmonic generation (SHG) or electro-optic (EO) modulation. In this case, the design of non-centrosymmetric polar crystals with optimized orientation of the chromophores is needed to avoid cancellation of the non-linear susceptibility $\chi^{(2)}$. Traditional crystal engineering strategies towards SHG active materials have been conducted with highly polar one-dimensional (1D) NLO chromophores, and attempt to avoid an antiparallel, hence centrosymmetric, arrangement.[2] Since 1D NLO chromophores exploit only one tensorial component of the hyperpolarisability β, a novel way of enlarging this field of investigation is to use chromophores with a higher dimensionality in their charge transfer interactions. The off-diagonal contributions may be of consequence and by reducing their orientational requirements, one attempts to get specific $\chi^{(2)}$ processes.[3]

Although investigations of octupolar 2D and 3D systems have been made with such an aim, the resulting crystalline materials still have only modest SHG activity.[4] 2D chromophores with several in plane charge transfer interactions appear to be interesting in this context. We have investigated such 2D chromophores in order to check their interest in quadratic non-linear optics. Here we report the X-ray crystal structure of 1,3-dibromo-2,4,6-trinitrobenzene (DBTNB, Fig. 1), its NLO properties as a two-dimensional charge transfer hyperpolarisable chromophore and the high SHG response of the corresponding polar crystals of DBTNB.

The chromophore has been prepared according to the literature procedure.[5] Single crystals (yellow coloured thin needles) of DBTNB suitable for X-ray diffraction were grown from acetic acid. The X-ray data were collected at room temperature and the crystals were found to belong to the non-centrosymmetric space group *C*2.† The crystal structural analysis revealed the formation of layers parallel to the (302) plane, within which the chromophores adopt a hexagonal packing with a perfect polar order along the [010] direction, as shown in Fig. 2. Indeed, within each layer all the chromophores are arranged in a head-to-tail fashion oriented along the C(1)–C(4) molecular axis that is also the molecular dipole axis. The supramolecular hexagons are assembled with bifurcated C–H···O (2.60 Å, 155.2°) hydrogen bonded and Br···O_2N (2.93 Å, 169°) supramolecular synthons. This latter Br···O distance is the shortest ever observed for a contact between Br and nitro groups and is surely of significance (CSD Version 5.21, April 2001).[6] The layers are interconnected by very weak additional Br···O_2N interactions (3.48 Å), as shown in Fig. 3, and stacked in a parallel fashion so that within the crystal all the chromophores are oriented in the same direction. This crystal packing leads to a complete additivity of the molecular β tensor components for the macroscopic $\chi^{(2)}$ susceptibility.

The DBTNB molecule is not planar (ORTEP drawing in Fig. 1); due to steric hindrance between the two *ortho* Br atoms the nitro group on C(1) is twisted nearly perpendicularly to the phenyl ring (dihedral angle 85.2°). This orientation prevents intramolecular charge transfer with either of the two adjacent Br donor atoms. Such a situation is favourable for the 2D hyperpolarisability because the dihedral angles between the two other nitro groups and the phenyl ring are only 30° allowing the

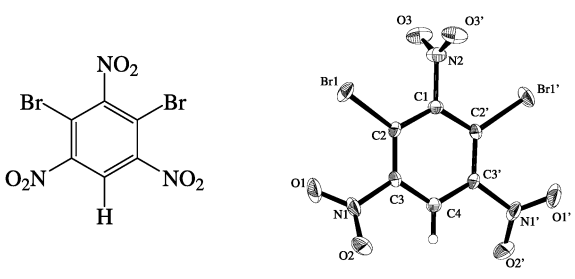

Fig. 1 Molecular structure and ORTEP drawing of DBTNB

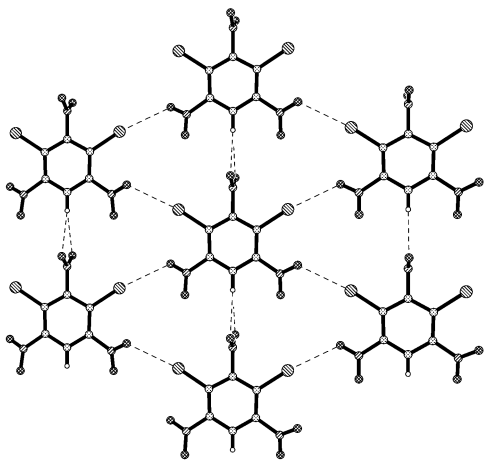

Fig. 2 The hexagonal network structure of DBTNB. Note the C–H···O hydrogen bonds along the polar axis.

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concomitant 2D bromo–nitro intramolecular charge transfer. The twisted nitro group at C(1) is, however, very useful for the non-centrosymmetric crystal packing as it is involved in the bifurcated C–H···O synthon that holds the chromophores along the polar axis.

The consequence of this perfect alignment of chromophores is evidenced by the SHG measurement (Nd^{3+}-YAG laser at 1064 nm) on microcrystalline DBTNB that indicates a strong, possibly phase-matched, quadratic non-linear efficiency, with a green signal (530 nm) about 15 × urea, nearly equivalent to that of the benchmark crystal 3-methyl-4-nitropyridine-1-oxide (POM).[7]

The crystal structure of DBTNB illustrates a situation that is all too common in crystal engineering. The 2D crystal packing of a near planar molecule can be satisfactorily rationalised, or even predicted but the factors that lead to parallel (non-centrosymmetric) or anti-parallel (centrosymmetric) stacking of the 2D motifs are so subtle that the final outcome is difficult to predict. In DBTNB, the packing is non-centrosymmetric and additionally the bulk SHG efficiency is very good. The 2D arrangement in DBTNB is certainly a favoured one. Computations with the Polymorph Predictor program (Accelrys)[8] in space group *C*2 reveal the hexagonal network and the parallel stacking repeatedly. In these calculations the experimental structure in fact appears as one of the two lowest in energy.

In order to better understand the origin of the quadratic non-linear efficiency of the material, we have calculated the molecular static β tensor components from the geometric structure found in the crystal, using the "Time Dependent Hartree-Fock" method within the MOPAC93/AM1 program. The chromophore, of C_2 symmetry, presents only two significant components β_{xxx} and β_{xyy} (−0.86 and −2.6 in 10^{-30} esu respectively). This gives a planar anisotropy β_{xyy}/β_{xxx} = 3.02 that confirms the 2D character of the chromophores. These calculated hyperpolarisabilities could be considered as relatively modest, but it must be noticed that Br is quite electronegative, and so its mesomeric donor effect is somewhat reduced. The charge transfer can also be altered by the 30° angle twist of each NO_2 group relative to the phenyl plane. All this can have an effect on decreasing the molecular hyperpolarisability; however, Zhao *et al*. have recently outlined the important role of the bromo group in improving the NLO properties of organic materials.[9] Nevertheless the calculated β values cannot account for the observed SHG signal, which is a bulk property. This led us to investigate how the perfect crystal packing could affect the NLO properties at the molecular scale. With that aim we calculated the global hyperpolarisability of a cluster of seven chromophores, such as shown in Fig. 2. Neglecting the border effects and the interlayer interactions, the results scaled to one chromophore evidenced enhanced β values: β_{xxx} = −1.25 and β_{xyy} = −4.6 (in 10^{-30} esu). Beyond the classical local field effect, this suggests that with such a crystal packing some kind of supramolecular cooperative effect occurs, at least within a layer, and increases significantly the hyperpolarisability of each chromophore.

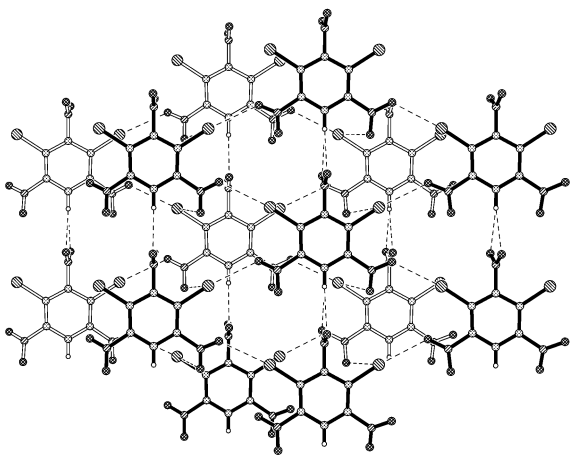

Fig. 3 The two layers of DBTNB, stabilised by additional Br···nitro interactions.

In conclusion, the chromophore DBTNB has a unique crystal structure with perfect polar order and as a consequence, the bulk SHG is very high. Other advantages of the material are the simple molecular structure and small size, the presence of just one H atom that could be easily replaced by a deuterium atom to improve the near IR transparency, the pale yellow colour of the material and the ease with which crystals may be obtained. All these features make it an NLO material with much scope for further detailed experimental and theoretical study.

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Notes and references

† *Crystal data* for DBTNB: $C_6HBr_2N_3O_6$, M = 370.90, yellow prism, 0.16 × 0.40 × 0.40 mm, monoclinic, space group $C2$, D_c = 2.342 g cm^{-3}, a = 10.4037(5), b = 8.0950(4), c = 6.3192(3) Å, β = 98.835(4)°, V = 525.88(4) Å^3, Z = 2, T = 296.2 K. 5323 reflections were collected with a Kappa-CCD Nonius diffractometer using Ag-Kα radiation, $2\theta_{max}$ = 53.8°. Absorption correction done with μ = 4.139 mm^{-1}. A total of 1219 unique reflections were preserved of which 910 ($I > 3\sigma(I)$) were used in the structure solution (direct methods). Refinements (full-matrix least-squares) converged to R = 0.028 and R_w = 0.034. Residual electron density 0.31 e Å^{-3}. Intermolecular bonds in (302) plane: C4–H1···O3,O3′ with C4···O3,O3′ = 3.493(6) Å, C4–H1 = 0.96 Å, H1···O3,O3′ = 2.60 Å, angle C4–H1···O3 = 155.2°, Br1···O1 = 2.931(5) Å. Van der Waals bonds Br···O2 = 3.481(5), Br···O3 = 3.595(4) Å between the family of (302) planes.

CCDC reference number 179246. See http://www.rsc.org/suppdata/cc/b2/b201224c/ for crystallographic data in CIF or other electronic format.

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