Engineering of an octupolar non-linear optical crystal: tribenzyl isocyanurate

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The title compound has a C–H⋯O hydrogen bond-mediated trigonal network structure that leads to octupolar NLO behaviour in the solid state.

Crystal engineering,[1] or solid state supramolecular synthesis,[2] is increasingly turning towards the design of functionalised materials.[3] Non-linear optical (NLO) properties, with such applications as second harmonic generation (SHG) or electrooptic (EO) modulation have attracted interest.[4] Traditional crystal engineering strategies towards SHG-active materials have been based on preventing the crystallisation of molecules with large dipole moments in an antiparallel and therefore centrosymmetric arrangement. These dipolar molecules suffer from other disadvantages.[1,5] Recently, a new class of SHG-active substances, octupolar molecules, have been proposed and been shown to display significant NLO behaviour at the molecular level.[6] The engineering problem at the crystalline or supramolecular level amounts to steering the structure of an appropriately substituted trigonal molecule **1** towards the trigonal, non-centrosymmetric network structure **2** characterised by specific interactions between unlike groups in the molecular skeleton, rather than towards the hexagonal, centrosymmetric network **3** characterised by close approaches between like groups.[7] Of course, the majority of trigonal molecules **1** adopt neither structure **2** nor **3** and instead adopt a trivial close-packed structure, and this renders the engineering problem more challenging.
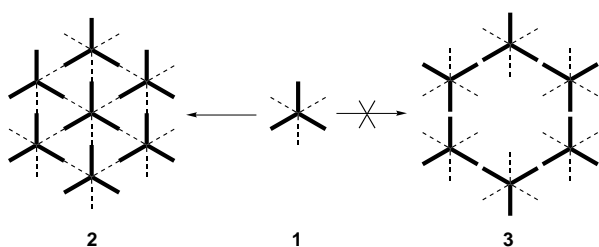
Some of us have reported the crystal structure of the 1:1 complex of trimethyl isocyanurate **4** and 1,3,5-trinitrobenzene wherein the respective components are in distinct layers, each possessing the trigonal symmetry of **2**.[8] Specifically, the molecules of **4** are linked *via* C–H⋯O mediated supramolecular synthon **5** that may be readily identified in network **2**.[2b] In general, single component crystals are preferred to molecular complexes for NLO applications because of issues connected with material purification, crystal growth and optical characterisation in both solution and the solid state. Therefore we turned our attention to the symmetrical isocyanurates, all of which have alternating C–H⋯O donors and acceptors in the molecular structure. Such an alternation is a prerequisite for the formation of network **2**. In pure **4**, the structure consists of a complicated three-dimensional networking of C–H⋯O hydrogen bonds.[9,10] In triethyl isocyanurate **6**, however, the trigonal network **2** is not
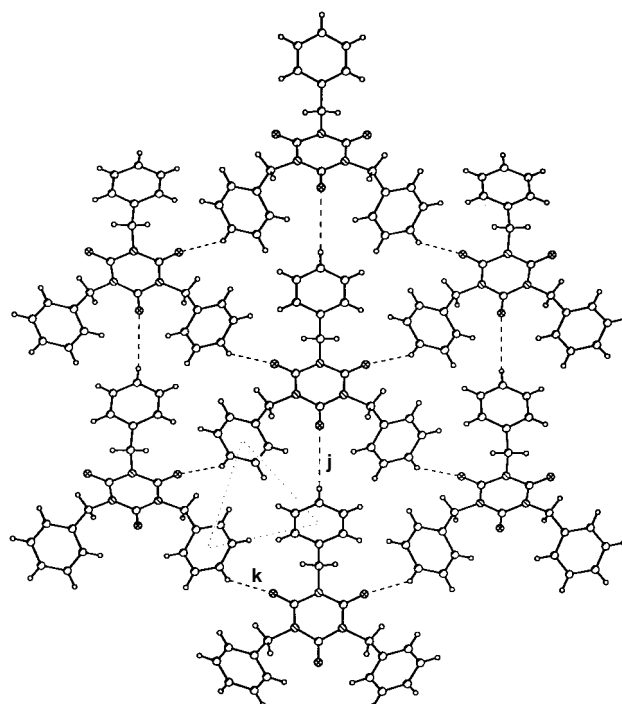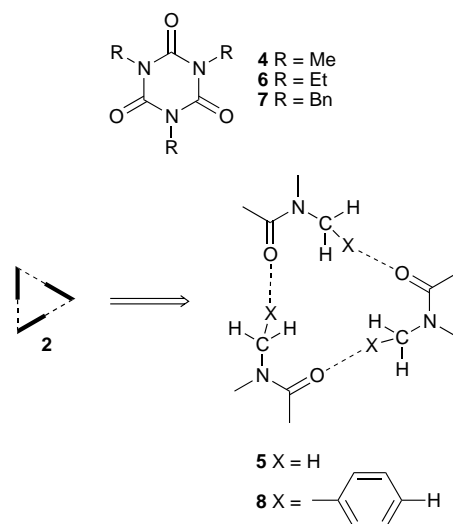

Fig. 1 A view of the crystal structure of tribenzyl isocyanurate **7** down [010] to show the trigonal network structure. C–H⋯O hydrogen bonds are indicated as **j** and **k**, while herringbone interactions are indicated as dotted lines. Notice the occurrence of supramolecular synthon **8** and the overall non-centrosymmetry of the network.

found;[10] the very low acidity of the C–H groups probably leads to non-adoption of the desired structure, based as it is on C–H⋯O hydrogen bonds.

Keeping such carbon acidity considerations in mind,[11] tribenzyl isocyanurate **7** was examined. The crystal structure (Fig. 1) shows that the desired non-centrosymmetric trigonal network has been obtained.‡ The structure is characterised by synthon **8**, which is the tris-phenylogous extension of synthon **5**. Fig. 2 shows that **7** is far from planar. With respect to the central heterocyclic ring, two benzyl groups point in one direction whilst the third points in the other, leading to an overall 'chair'-shape. The layer structure in **7** is corrugated as shown in Fig. 3, with two distinct intralayer C–H⋯O hydrogen bonds. Molecules translated along [001] are connected by the interaction designated **j** in Fig. 1 (D, 3.91 Å; d, 2.97 Å; θ, 145°) to form chains. Adjacent chains are *n*-glide related and connected by interaction **k** (D, 3.43 Å; d, 2.51 Å; θ, 142°). The chains are additionally interconnected by herringbone interactions (dotted lines in Fig. 1). The corrugated layers are stacked along [010] and weak C–H⋯π interactions (D, 3.51, 3.63 Å; d, 2.73, 3.32 Å; θ, 139, 150°) complete the structure.

The non-centrosymmetric nature of crystalline **7** was confirmed by a visible SHG powder signal at 1.064 μm of the order of 0.1 × urea. The nonlinear characterisation of **7** at the molecular level was performed by harmonic light scattering (HLS) measurements in solution.[5,12,13] The nonlinear $\beta = \sqrt{\langle\beta^2\rangle}$ HLS coefficient measured at 1.064 μm in CHCl₃ is $(10 \pm 2) \times 10^{-30}$ esu, which is comparable to that of the classical dipolar PNA molecule under the same measurement conditions. We note that **7** is completely transparent in the
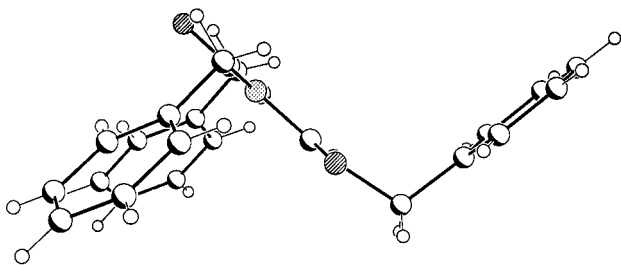

Fig. 2 View of an individual molecule of **7** to show its non-planar character. Nitrogen and oxygen atoms are shown as dotted and hatched circles.
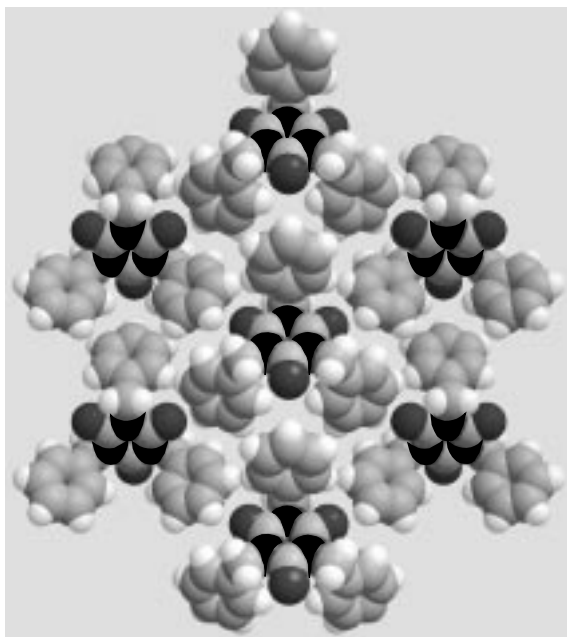

Fig. 3 Space-filling view of the network structure shown in Fig. 1. Notice the corrugation in the layer structure.

visible region. The weak second harmonic signal of **7** can be ascribed to poor charge transfer, the methylene groups preventing conjugation between the peripheral and central rings. The octupolar structure of **7** was confirmed by a HLS depolarisation measurement and the depolarisation ratio[14] $D = 0.65$ is close to the theoretical value of 2/3 for purely octupolar molecular structures.[14] In the context of planar octupolar structures, the orientational isotropic averaging relation[5] $\langle\beta\rangle = 8/21\beta_{\gamma\gamma}^2$ leads to a predominant molecular nonlinear coefficient $\beta_{\gamma\gamma} = 16.2 \times 10^{-30}$ esu. The theoretical crystalline nonlinear coefficient was inferred from the molecular hyperpolarisability using the oriented gas model. From the geometry of the unit cell, the overall norm of the macroscopic coefficient is 96×10^{-9} esu.

This work describes a successful application of the supramolecular retrosynthetic strategy for the design of an octupolar nonlinear crystal and shows that network structures can be developed with the supposedly weak C–H⋯O interactions. Further molecular engineering that seeks to optimise the electronic charge transfer is necessary, but such manipulations must keep the favourable crystal packing intact and this is not a trivial exercise, involving as it does a carry-over of molecular symmetry into crystal symmetry or pseudosymmetry.

Footnotes and References

‡ *Crystal structure determination* of tribenzyl isocyanurate **7**: C₂₄H₂₁N₃O₃, $M = 399.44$, orthorhombic, $Pmn2_1$, $a = 18.986(3)$, $b = 4.574(1)$, $c = 11.421(2)$ Å, $V = 991.8(3)$ Å³, $Z = 2$, $F(000) = 420$, $D_c = 1.338$ Mg m⁻³, μ(MoKα) = 0.90 cm⁻¹, $T = 293$ K, 1442 non-zero (4 σ) reflections out of 1889 collected with $4.16 < 2\theta < 50.84$, number of parameters 156, solution SHELXS-86, refinement SHELXL-93 on F^2, R_1(observed) = 0.053, R_1 (all data) = 0.064, wR_2 (observed) = 0.133, wR_2 (all data) = 0.156; C, N, O anisotropic, H isotropic. Space group *Pmnm* which is also compatible with the crystal symmetry and systematic absences was evaluated and discarded. This was validated by the subsequent SHG measurements. Full-matrix least-squares refinement in $Pmn2_1$ proceeded satisfactorily with no correlations due to any pseudosymmetry. CCDC 182/575.

1 G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, 1989.
2 (*a*) D. Philp and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.,* 1996, **35**, 1154; (*b*) G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.,* 1995, **34**, 2311; (*c*) J. A. Zerkowski, C. T. Seto and G. M. Whitesides, *J. Am. Chem. Soc.,* 1992, **114**, 5473.
3 A. Gavezzotti, *Curr. Opin. Solid State Mater. Sci.,* 1996, **1**(4), 501; G. R. Desiraju, *Curr. Opin. Solid State Mater. Sci.,* 1997, **2**(4), 451.
4 I. Ledoux and J. Zyss, in *Novel Optical Materials and Applications,* ed. I. C. Khao, F. Simoni and C. Umeton, Wiley, Chichester, 1997, pp. 1–48.
5 J. Zyss and I. Ledoux, *Chem. Rev.,* 1994, **94**, 77.
6 C. Dhenaut, I. Ledoux, I. D. W. Samuel, J. Zyss, M. Bourgault and H. L. Bozec, *Nature,* 1995, **374**, 339.
7 I. Ledoux, J. Zyss, J. Siegel, J. Brienne and J.-M. Lehn, *Chem. Phys. Lett.,* 1990, **172**, 440.
8 V. R. Thalladi, K. Panneerselvam, C. J. Carrell, H. L. Carrell and G. R. Desiraju, *J. Chem. Soc., Chem. Commun.,* 1995, 341.
9 F. Belaj and E. Nachbaur, *Montasch. Chem.,* 1987, **118**, 1077.
10 V. R. Thalladi, A. K. Katz, H. L. Carrell, A. Nangia and G. R. Desiraju, unpublished work.
11 V. R. Pedireddi and G. R. Desiraju, *J. Chem. Soc., Chem. Commun.,* 1992, 988.
12 D. Maker, *Phys. Rev. A,* 1970, **1**, 923.
13 J. Zyss, *J. Chem. Phys.,* 1993, **98**, 6583.
14 S. Brasselet and J. Zyss, *J. Nonlinear Phys. Mater.,* 1996, **5**, 4.