

Steering non-centrosymmetry into the third dimension: crystal engineering of an octupolar nonlinear optical crystal

Venkat R. Thalladi,^a Roland Boese,^{*a} Sophie Brasselet,^b Isabelle Ledoux,^b Joseph Zyss,^{*b} Ram K. R. Jetti^c and Gautam R. Desiraju^{*c}

^a Institut für Anorganische Chemie, FB 8, Universität-GH Essen, Universitätsstrasse 5-7, D-45177 Essen, Germany. E-mail: boese@structchem.uni-essen.de

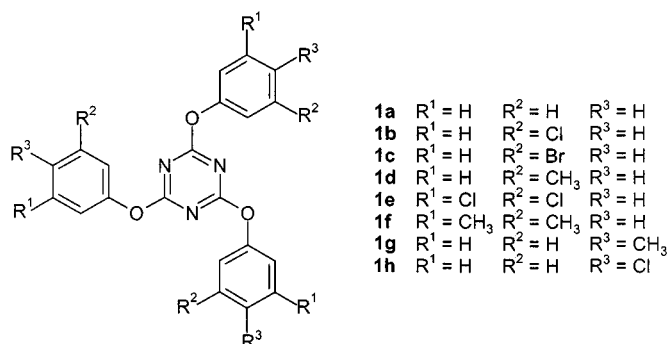
^b Département de Physique, École Normale Supérieure de Cachan, 61, Avenue du Président Wilson, 94235 Cachan Cedex, France. E-mail: zyss@lpqm.ens-cachan.fr

^c School of Chemistry, University of Hyderabad, Hyderabad 500 046, India. E-mail: grdch@uohyd.ernet.in

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The ability of CH₃ groups to form helical chains of C–H... π interactions with phenyl rings leads to polar stacking of trigonal octupolar networks in a substituted triazine, and therefore to three-dimensional non-centrosymmetry.

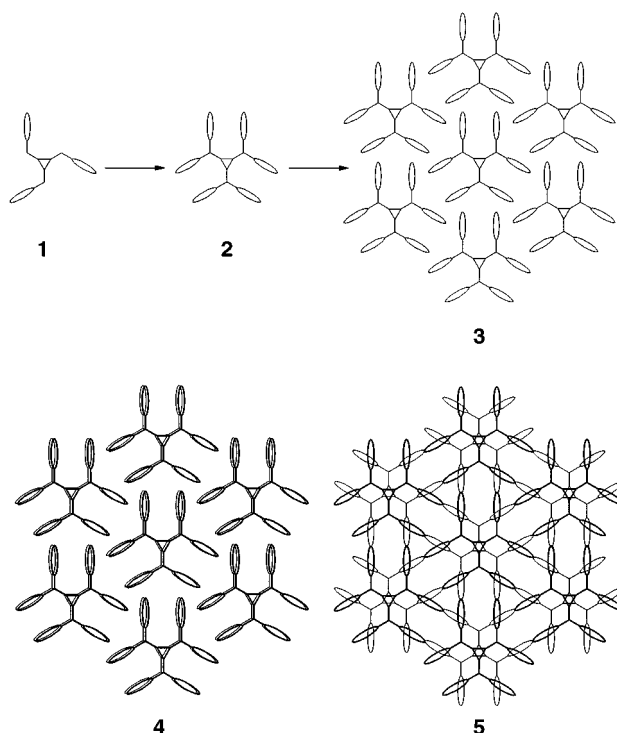
Structural control in the third dimension continues to be one of the most sought-after goals in crystal engineering.^{1,2} We have recently reported that a family of *sym*-triaryloxytriazines **1** lend themselves well, *via* dimeric Piedfort units (PU) **2**, to the adoption of trigonal two-dimensional networks **3** (Scheme 1).³ This disymmetric network stacks in a parallel or anti-parallel fashion to give, respectively, **4** and **5**. Arrangement **4** meets the requirements of crystalline octupolar nonlinear optical (NLO) behaviour⁴ and is seen in compound **1a**. A number of other derivatives **1b–f** crystallise in arrangement **5**, that is, they do not



display Second Harmonic Generation (SHG). The undesirable anti-parallel stacking in these cases may be attributed to the steric bulk of Cl, Br and CH₃ substituent groups located in the *meta* position of the phenoxy rings.

We had explored variations in the *meta* substituent, arguing that tampering with the *ortho* H-atoms of the phenoxy rings would disturb the formation of the PU itself, while the *para* H-atom was needed for the C–H... π interactions that are implicated in the formation of trigonal network **3**.³ Here, we show that 2,4,6-tris(4-methylphenoxy)-1,3,5-triazine **1g** adopts a non-centrosymmetric packing because the *para* CH₃ substituent can form C–H... π interactions with an orientation that sustains three-dimensional chirality.

Single crystals of **1g** suitable for X-ray diffraction (non-centrosymmetric space group *R3c*) were grown from slow evaporation of an *o*-xylene solution.[†] The molecules are positioned on three-fold axes and retain their molecular symmetry in the crystal. Successive *c*-glide related molecules are stacked and are interconnected by C–H...O (*D*, 3.57 Å, *d*, 2.64 Å; θ , 143°)[‡] and C–H...N (3.46 Å, 2.43 Å, 160°) hydrogen bonds to form the *D*₃-symmetric PUs. The trigonal assembly of *D*₃-PUs generates an octupolar network structure parallel to (001) as shown in Fig. 1.



Scheme 1

The *para* CH₃ groups participate in C–H... π interactions⁵ (*D*, 3.60 Å, *d*, 2.77 Å; θ , 133°) that link interlayer *D*₃-PUs. This ability of the CH₃ groups to form C–H... π interactions coupled with fact that the C–H vectors are bent with respect to the plane of the trigonal network allows these groups to link with molecules in the third dimension.⁶ Fig. 2 shows that the C–H... π interactions are arranged around 3₁ and 3₂-axes and that they extend to the third dimension in a helical manner. Any two adjacent helices have opposite handedness, but the chains of C–H... π interactions always run along [001]. Thus all C–H... π helices have the *same* polarity. Consequently, successive layers are compelled to stack in an eclipsed manner leading to bulk non-centrosymmetry.

It is of interest to note that, in triazines **1b–f**, the peripheral aryloxy rings are inclined perpendicular to the central heterocyclic ring (with an inclination angle of 89–92°) whereas they are inclined at a much shallower angle in **1g** (67°).[§] The C–H...O and C–H...N bonds become shorter and linear with such flattening and as such are more effective. Additionally, the central rings in **1g** are stacked at a separation of 3.30 Å. This is much shorter when compared to the stacking found in triazines **1a–f** (3.6–4.0 Å). In summary, the CH₃ groups not only maintain the eclipsed stacking of the layers but also reinforce

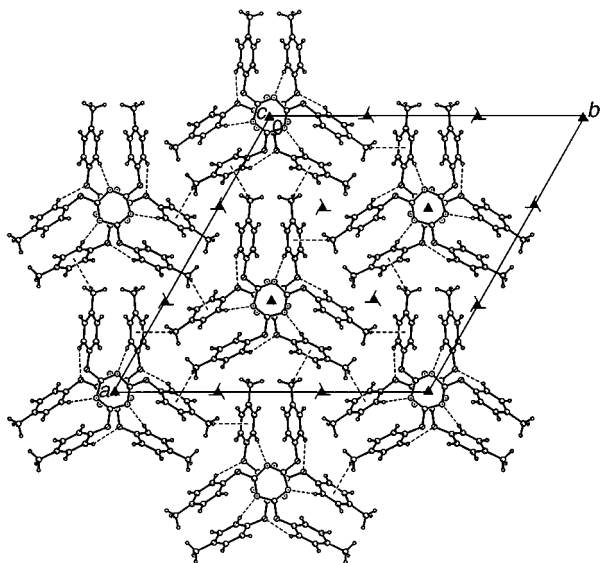


Fig. 1 Octupolar trigonal network structure in **1g**. The 3-fold, 3_1 - and 3_2 -axes are indicated. Notice the C–H...O and C–H...N hydrogen bonds within a D_3 -PU. Notice that the C–H... π interactions extend to the third dimension in a helical manner around 3_1 - and 3_2 -axes.

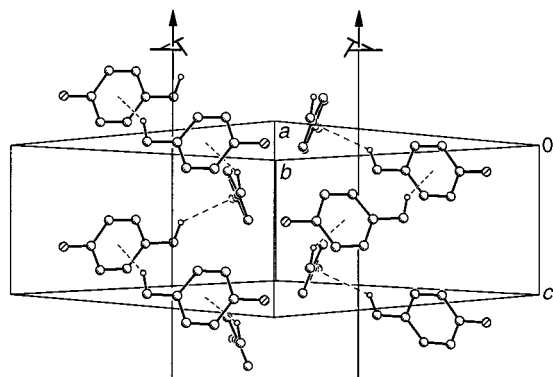


Fig. 2 Helical arrangement of C–H... π hydrogen bonds in triazine **1g** (several atoms deleted). Note that the two helices have opposite handedness but that they run in the same direction, [001].

other interactions which are important for effective three-dimensional packing.

The non-centrosymmetric nature of **1g** was confirmed by a powder SHG signal at 1.064 μm which is $\sim 1 \times \text{KDP}$. Due to the weak donor property of the methyl group, the quadratic hyperpolarisability of **1g** may be assumed to be very close to that of **1a**. Indeed there is evidence for the equivalence of the unsubstituted and *para*-methyl substituted aromatic rings towards quadratic effects in NLO.⁷ One can further infer⁸ a rough estimate of the crystalline d susceptibility, assuming the oriented gas model⁹ with optimal $\cos(3\theta)$ projection factors corresponding to a fully eclipsed stacking,⁸ and assuming a cubic order Lorentz–Lorentz local field correction factor of 3.5 corresponding to a realistic value of 1.6 for the index of refraction. This simplified model is known to be reliable and leads in the present case to a magnitude of 120×10^{-9} esu comparable to that of *N*-4-nitrophenyl-L-prolinol, a prototype crystal often used as a standard.¹⁰ The comparatively modest powder SHG signal of **1g** may be related to absence of phase-matching at the 1.06 μm fundamental wavelength used by us. Alternatively, a noticeably small average grain size may prevent any benefit from a cumulative phase-matching in a non-resonant configuration considering that the coherence length must be significantly larger than the grain size.

The structure of **1g** is also important from a different perspective. Usually, Cl and CH_3 groups can be interchanged with no structural change when these groups contribute merely to the close packing.¹¹ However, in this case the corresponding chloro triazine **1h** forms an entirely different structure that is stabilised by trimeric Cl_3 supramolecular synthons.³ This emphasizes the fact that the CH_3 and Cl groups in **1g** and **1h** respectively play structurally distinct roles and that they are involved in interactions specific to the functional groups.

This work demonstrates that the weak C–H... π interactions may be employed to achieve third dimensional control of a crystal structure, which leads in the present case to an interesting physical property, namely crystalline octupolar NLO with a remarkably large estimated d coefficient. In tribenzylisocyanurate¹² and in **1a**, bulk non-centrosymmetry was not designed and is not easily extendable to other examples. This is not so in the present case, where the preferred C–H... π interactions clearly discriminate in favour of a polar packing. Our continued interest in this family of compounds stems from their transparency in the blue region and from their possible utilization in unphase-matched thin film configurations for short pulse NLO.⁸

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Notes and references

[†] Crystal data for **1g**: $\text{C}_{24}\text{H}_{21}\text{N}_3\text{O}_3$, $M = 399.44$, rhombohedral, space group $R3c$, $a = 23.576(3)$, $c = 6.5913(8)$ Å, $V = 3172.9(7)$ Å³, $Z = 6$, $\lambda = 0.71073$ Å, $T = 223(2)$ K, $\mu = 0.084$ mm⁻¹, 750 independent reflections ($R_{\text{int}} = 0.142$), $R = 0.058$, $wR_2 = 0.127$. CCDC 182/1337. See <http://www.rsc.org/suppdata/cc/1999/1639/> for crystallographic data in .cif format.

[‡] The C–H bond lengths are always neutron-normalised to 1.083 Å.

[§] A similar shallow inclination is also observed in **1a** which is also non-centrosymmetric, see ref. 3.

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