

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

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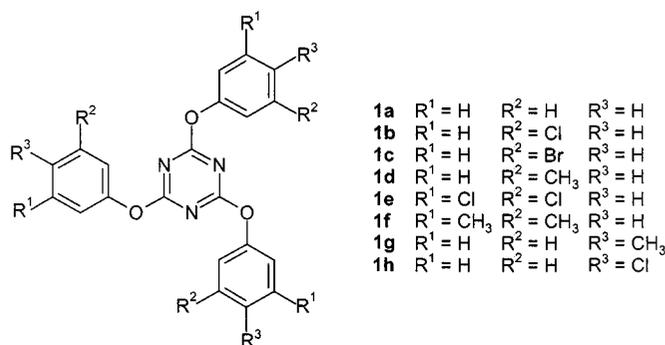
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The ability of CH<sub>3</sub> groups to form helical chains of C–H... $\pi$  interactions with phenyl rings leads to polar stacking of trigonal octupolar networks in a substituted triazine, and therefore to three-dimensional non-centrosymmetry.

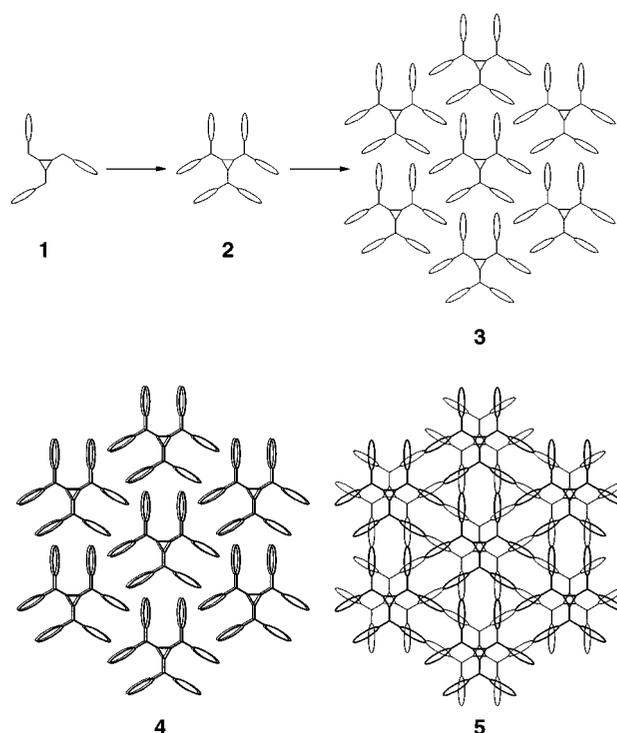
Structural control in the third dimension continues to be one of the most sought-after goals in crystal engineering.<sup>1,2</sup> We have recently reported that a family of *sym*-triaryloxytriazines **1** lend themselves well, *via* dimeric Piedfort units (PU) **2**, to the adoption of trigonal two-dimensional networks **3** (Scheme 1).<sup>3</sup> 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) behaviour<sup>4</sup> 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 CH<sub>3</sub> 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... $\pi$  interactions that are implicated in the formation of trigonal network **3**.<sup>3</sup> Here, we show that 2,4,6-tris(4-methylphenoxy)-1,3,5-triazine **1g** adopts a non-centrosymmetric packing because the *para* CH<sub>3</sub> substituent can form C–H... $\pi$  interactions with an orientation that sustains three-dimensional chirality.

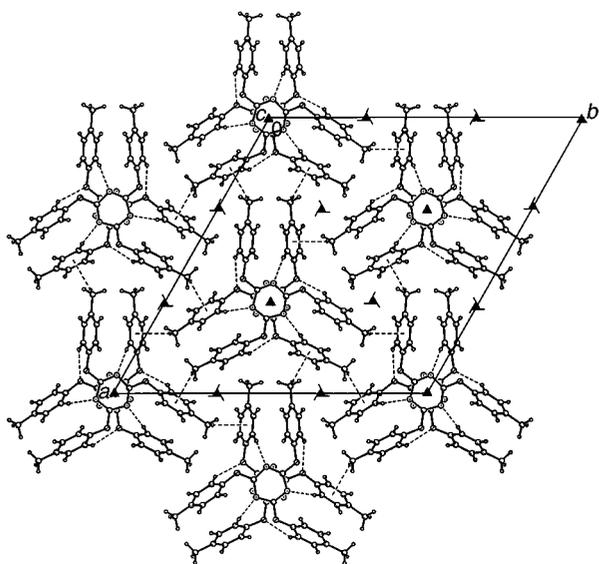
Single crystals of **1g** suitable for X-ray diffraction (non-centrosymmetric space group *R3c*) were grown from slow evaporation of an *o*-xylene solution.<sup>†</sup> The molecules are positioned on three-fold axes and retain their molecular symmetry in the crystal. Successive *c*-glide related molecules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



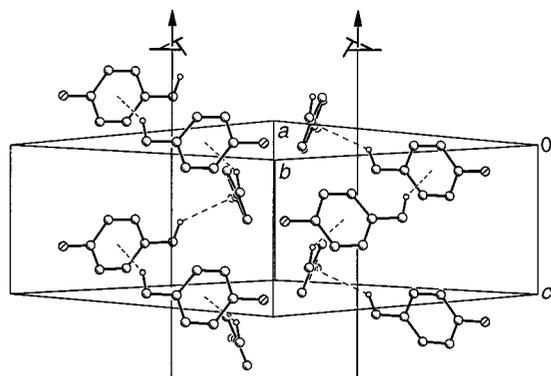
Scheme 1

The *para* CH<sub>3</sub> groups participate in C–H... $\pi$  interactions<sup>5</sup> (*D*, 3.60 Å, *d*, 2.77 Å;  $\theta$ , 133°) that link interlayer *D*<sub>3</sub>-PUs. This ability of the CH<sub>3</sub> groups to form C–H... $\pi$  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.<sup>6</sup> Fig. 2 shows that the C–H... $\pi$  interactions are arranged around 3<sub>1</sub> and 3<sub>2</sub>-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... $\pi$  interactions always run along [001]. Thus all C–H... $\pi$  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°).<sup>§</sup> 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 CH<sub>3</sub> 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... $\pi$  interactions extend to the third dimension in a helical manner around  $3_1$ - and  $3_2$ -axes.



**Fig. 2** Helical arrangement of C–H... $\pi$  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  $\mu\text{m}$  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.<sup>7</sup> One can further infer<sup>8</sup> a rough estimate of the crystalline  $d$  susceptibility, assuming the oriented gas model<sup>9</sup> with optimal  $\cos(3\theta)$  projection factors corresponding to a fully eclipsed stacking,<sup>8</sup> 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  $120 \times 10^{-9}$  esu comparable to that of *N*-4-nitrophenyl-L-prolinol, a prototype crystal often used as a standard.<sup>10</sup> The comparatively modest powder SHG signal of **1g** may be related to absence of phase-matching at the 1.06  $\mu\text{m}$  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<sub>3</sub> groups can be interchanged with no structural change when these groups contribute merely to the close packing.<sup>11</sup> However, in this case the corresponding chloro triazine **1h** forms an entirely different structure that is stabilised by trimeric Cl<sub>3</sub> supramolecular synthons.<sup>3</sup> This emphasizes the fact that the CH<sub>3</sub> 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... $\pi$  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 tribenzylisocyanurate<sup>12</sup> 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... $\pi$  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.<sup>8</sup>

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## Notes and references

† Crystal data for **1g**: C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub>,  $M = 399.44$ , rhombohedral, space group  $R3c$ ,  $a = 23.576(3)$ ,  $c = 6.5913(8)$  Å,  $V = 3172.9(7)$  Å<sup>3</sup>,  $Z = 6$ ,  $\lambda = 0.71073$  Å,  $T = 223(2)$  K,  $\mu = 0.084$  mm<sup>-1</sup>, 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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