Data collection

Nonius Kappa CCD diffractometer
ω rotation scans
Absorption correction: none
2296 measured reflections
1355 independent reflections (plus 941 Friedel-related reflections)
1912 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 26.38°$
$h = -7 \rightarrow 7$
$k = -16 \rightarrow 16$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.082$
$S = 1.13$
2296 reflections
202 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.028P)^2 + 0.0709P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.14$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.034 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.08 (9)

Table 1. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.89 (2)	2.05 (2)	2.900 (3)	159 (2)
O1—H11···O4^{ii}	0.80 (4)	2.01 (4)	2.789 (3)	166 (4)
O1—H12···O3^{iii}	0.71 (6)	2.09 (6)	2.799 (3)	173 (5)

Symmetry codes: (i) $x - \frac{1}{2}, \frac{3}{2} - y, 2 - z$; (ii) $\frac{7}{2} - x, 1 - y, z - \frac{1}{2}$; (iii) $\frac{5}{2} - x, 1 - y, z - \frac{1}{2}$.

All H atoms were found from a difference map; during the refinement H atoms were treated isotropically. No restraints were applied to H atoms during refinement; only one bond (O1—H12) has a value outside the expected range. Nonetheless, the hydrogen-bond geometry involving this atom is almost ideal.

Data collection: Nonius Kappa CCD server software. Cell refinement: *DENZO-SMN Software* (Otwinowski & Minor, 1997). Data reduction: *DENZO-SMN Software*. Program(s) used to solve structure: *SHELX*97 (Sheldrick, 1997). Program(s) used to refine structure: *SHELX*97. Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1436). Services for accessing these data are described at the back of the journal.

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Tri-*p*-tolyl-1,3,5-triazine

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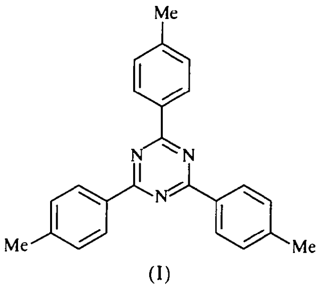
Abstract

The crystal structure of the title compound, $C_{24}H_{21}N_3$, is stabilized by C—H···N and C—H···π interactions. Its crystallization in a lower symmetry space group highlights an important problem in crystal engineering, that is the failure of symmetry carry-over from the molecule to the crystal.

Comment

The crystal structure of the title compound, (I), was determined while screening trigonal molecules for octupolar non-linear optical (NLO) behaviour. The design of an octupolar NLO crystal consists of identifying a chromophore with threefold symmetry and then being able to extend the high symmetry of the molecule into the crystal (Zyss, 1991; Zyss & Ledoux, 1994). However, the carry-over of molecular symmetry into the crystal is not trivial and the inversion centre is the only symmetry element which is routinely extended into the crystal (Kitaigorodskii, 1973; Brock & Dunitz, 1994). We have recently shown that tribenzyl isocyanurate (Thalladi *et al.*, 1997) and triaryloxytriazines (Thalladi *et al.*, 1998) have non-centrosymmetric network structures that lead to octupolar NLO behaviour including, in some cases, second harmonic generation (SHG) in the solid state. However, these molecules have low molecular hyperpolarizabilities (β) due to the lack of effective conjugation between the aromatic rings and the central heterocycle. Compound (I) was thus chosen because the three tolyl rings and the central triazine ring are conjugated and this should increase the β value. However, triazine (I) crystallizes in the centrosymmetric space group *Pnma*.



(I)

The molecule is bisected by a mirror plane; an *ORTEP*II (Johnson, 1976) diagram is shown in Fig. 1. The dihedral angles between the mean planes of the central triazine and the peripheral tolyl rings are 4.12 (8) and 7.55 (8)°. The H atoms of the methyl groups are disordered over two positions with equal occupancies. The packing diagram (Fig. 2) shows that the methyl groups are involved in C—H···N and C—H···π interactions. Molecules related by the n-glide along [100] and the 2_1-screw axis along [010] are linked through C—H···N interactions [C···N 3.413 (3) and 3.951 (2) Å]. Inversion-related molecules are connected by C—H···π interactions (C···π 3.535 and 3.832 Å). The triazine ring of one molecule is stacked over the phenyl ring bisected by the mirror plane of a molecule translated along [001] at a centroid–centroid distance of 3.712 Å. Herring-bone interactions between the phenyl groups complete the structure, with a packing coefficient of 0.68. It may be noted that the methyl-H atoms are involved in C—H···N and C—H···π hydrogen bonding. These bonds are possibly enhanced because of co-operativity effects (Madhavi *et al.*, 1997), involving the aromatic rings as π-acceptors.

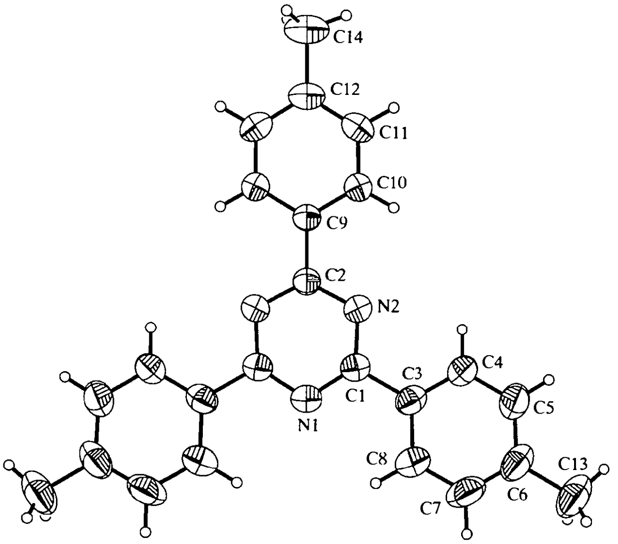


Fig. 1. An *ORTEP*II (Johnson, 1976) diagram of (I). Displacement ellipsoids are drawn at the 30% probability level. For clarity, H atoms are shown as small circles.

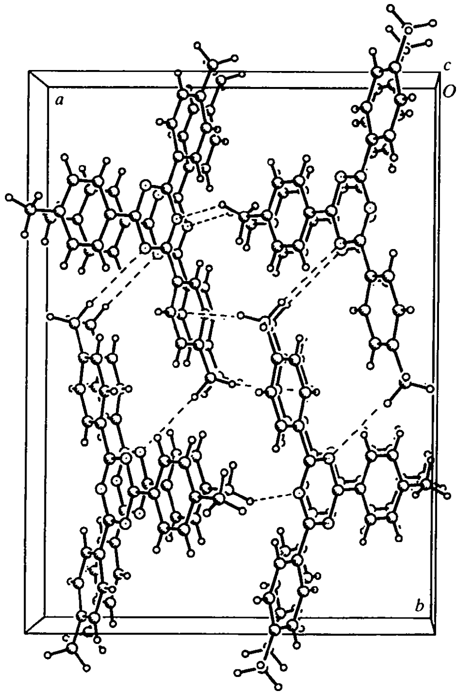


Fig. 2. The packing of (I) showing C—H···N and C—H···π interactions (dashed lines).

The analysis of the crystal structure of (I) suggests that molecular as well as crystal engineering considerations are relevant in the design of octupolar NLO materials.

Experimental

The title compound was synthesized by the trimerization of 4-methylbenzonitrile in the presence of $ClSO_3H$ (Cook & Jones, 1941). Slow evaporation of a toluene solution gave single crystals suitable for X-ray diffraction.

Crystal data

$C_{24}H_{21}N_3$
$M_r = 351.44$
Orthorhombic
Pnma
$a = 15.005\,(3)$ Å
$b = 20.397\,(4)$ Å
$c = 6.3420\,(13)$ Å
$V = 1940.9\,(7)$ Å^3
$Z = 4$
$D_x = 1.203$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6$–$12°$
$\mu = 0.072$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.38 × 0.32 × 0.24 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
2θ scans
Absorption correction: none
4113 measured reflections
2154 independent reflections
1597 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.013$
$\theta_{\max} = 27°$
$h = -22 \rightarrow 22$
$k = -31 \rightarrow 31$
$l = 0 \rightarrow 9$
2 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.140$
$S = 1.171$
2154 reflections
156 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2 + 0.2081P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.148$ e Å^{-3}
$\Delta\rho_{\min} = -0.121$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

The disorder of the methyl-H atoms was modelled by placing each H atom over two positions with equal occupancies. The coordinates of all methyl-H atoms were constrained to ride on the parent C atoms. The U_{eq} values of the methyl-H atoms were varied, but constrained to be similar.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1078). Services for accessing these data are described at the back of the journal.

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