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Orthorhombic and monoclinic polymorphs of 1,3,5-triphenylperhydro-1,3,5-triazine-2,4,6-trione at 120 K: chains and sheets formed by C—H$\cdots\pi$(arene) hydrogen bonds

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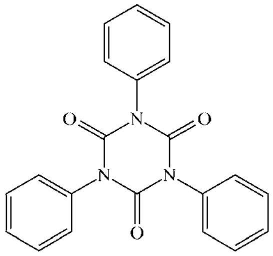
The title compound, $C_{21}H_{15}N_3O_3$, crystallizes in two polymorphic forms. In the orthorhombic polymorph, (I), in space group *Fdd*2 with $Z' = 1$, the molecules lie in general positions, while in the monoclinic polymorph, (II), in space group *C*2/*c* with $Z' = \frac{1}{2}$, the molecules lie across twofold rotation axes. In each polymorph, the molecules are linked by a single C—H$\cdots\pi$(arene) hydrogen bond, forming chains in polymorph (I) and sheets in (II).

Comment

We report here the molecular and supramolecular structures at 120 K of two polymorphic forms of 1,3,5-triphenyl-1,3,5-perhydrotriazine-2,4,6-trione, the cyclic trimer of phenyl isocyanate, PhNCO. The orthorhombic polymorph, (I) (Fig. 1), crystallizes in space group *Fdd*2 with $Z' = 1$, and the monoclinic polymorph, (II) (Fig. 2), crystallizes in space group *C*2/*c*, with $Z' = \frac{1}{2}$. The molecules in (II) lie across twofold rotation axes, with the reference molecule lying across the axis along $(\frac{1}{2}, y, \frac{1}{4})$. The structure of (II) was reported from ambient-temperature data some years ago (Usanmaz, 1979) and it is clear from the cell dimensions and space group that this earlier structure was of the same phase as (II), thus suggesting that the monoclinic phase does not undergo any temperature-dependent change, at least within the range 120–300 K.

The bond lengths and angles in (I) and (II) (Tables 1 and 3) are very similar, and the distances show evidence of strong bond fixation. Within the heterocyclic rings, the internal bond angles at the N atoms are consistently some 10° larger than the internal angles at the C atoms. In polymorph (II), the heterocyclic ring is slightly puckered. The ring-puckering parameters (Cremer & Pople, 1975) for the atom sequence N1—C2—N3—C4—N3^{i}—C2^{i} [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$] of $\theta = 90.0\,(7)^\circ$ and $\varphi = 270.0\,(6)^\circ$ indicate a twist-boat ring conformation (Boeyens, 1978), although the puckering amplitude Q is fairly small, at 0.104 (2) Å. The conformations defined by the phenyl rings (Figs. 1 and 2, and Tables 1 and 3) are very similar.



(I) *Fdd*2, $Z'=1$
(II) *C*2/*c*, $Z'=\frac{1}{2}$

In the crystal structure of (I), there are no C—H$\cdots$O or C—H$\cdots$N hydrogen bonds and no aromatic π–π stacking interactions. However, the molecules are linked into chains by a single C—H$\cdots\pi$(arene) interaction (Table 2). Aromatic atom C14 in the molecule at (x, y, z) acts as hydrogen-bond donor to phenyl ring C31–C36 in the molecule at $(\frac{5}{4} - x, y - \frac{1}{4}, \frac{3}{4} + z)$, while atom C14 at $(\frac{5}{4} - x, y - \frac{1}{4}, \frac{3}{4} + z)$ in turn acts as donor to the C31–C36 ring at $(x, y - \frac{1}{2}, \frac{3}{2} + z)$, so producing a chain running parallel to the $[0\bar{1}3]$ direction and generated by the *d*-glide plane at $x = \frac{5}{8}$ (Fig. 3). There are no direction-specific interactions between adjacent chains.

The original report (Usanmaz, 1979) on the monoclinic phase, (II), did not identify any direction-specific interactions between the molecules. However, the intermolecular interac-

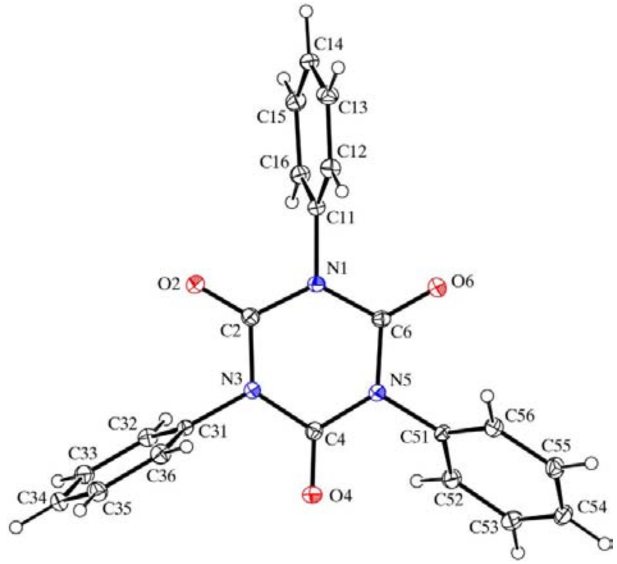


Figure 1
The molecule in the orthorhombic polymorph, (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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tions present in (II) are, in fact, very similar to those in orthorhombic phase (I). While C—H$\cdots$O and C—H$\cdots$N hydrogen bonds and aromatic π–π stacking interactions are all absent, the molecules are linked by a single C—H$\cdots\pi$(arene) hydrogen bond (Table 4), but now forming sheets as opposed to the simple chain in (I). The ring containing atom C11, which lies across a twofold rotation axis, acts as a double acceptor of C—H$\cdots\pi$(arene) hydrogen bonds, one on each face. This ring in the reference molecule accepts such hydrogen bonds from atoms C33 at $(x-\frac{1}{2}, \frac{1}{2}+y, z-1)$ and $(\frac{3}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z)$, while atoms C33 at (x, y, z) and $(1-x, y, \frac{1}{2}-z)$ in the reference molecule act as donors to the ring faces at $(\frac{3}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z)$ and $(x-\frac{1}{2}, y-\frac{1}{2}, z-1)$, respectively. Thus, with the reference molecule lying across the axis along $(\frac{1}{2}, y, \frac{1}{4})$, the donor and acceptor molecules lie across the axes $(0, y, -\frac{3}{4})$ and $(1, y, \frac{5}{4})$, so that each molecule is linked to four others, forming a $(\overline{2}01)$ sheet (Fig. 4).

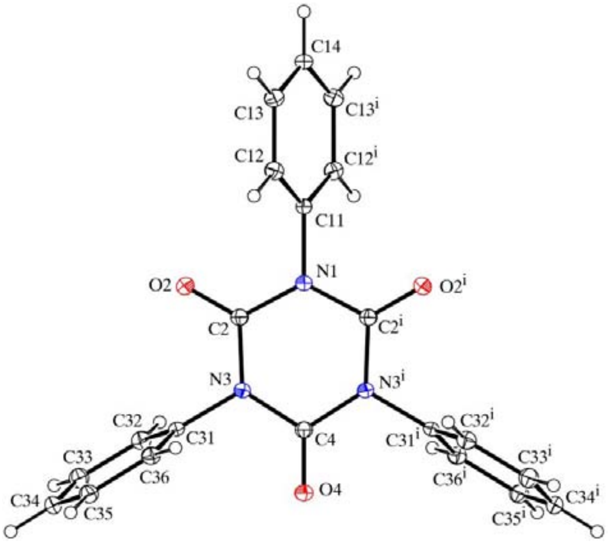

Figure 2
The molecule in the monoclinic polymorph, (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $1-x, y, \frac{1}{2}-z$.]

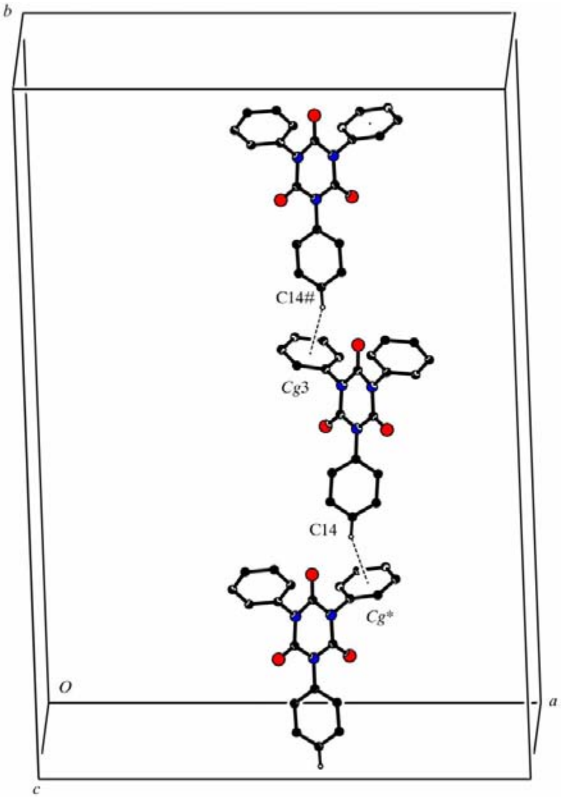

Figure 3
Part of the crystal structure of polymorph (I), showing a hydrogen-bonded chain running along the $[0\overline{1}3]$ direction. For the sake of clarity, H atoms not involved in the motif shown have been omitted. *Cg*3 is the centroid of ring C31–C36. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{5}{4}-x, y-\frac{1}{4}, \frac{3}{4}+z)$ and $(\frac{5}{4}-x, \frac{1}{4}+y, z-\frac{3}{4})$, respectively.

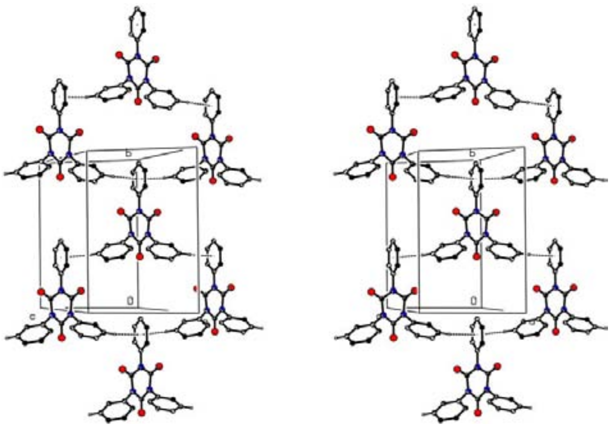

Figure 4
A stereoview of part of the crystal structure of polymorph (II), showing a hydrogen-bonded $(\overline{2}01)$ sheet. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

We have not investigated the relative thermodynamic stability of the two polymorphs. Their densities are almost identical, so that no useful deductions concerning stability (Burger & Ramberger, 1979) can be made here.

Experimental

The orthorhombic polymorph, (I), was obtained as an adventitious product from the attempted preparation of the heterocumulene $Ph_3P{=}C{=}C{=}O$ *via* reaction of $Ph_3P{=}CHCOOCH_2CH_3$ with *n*-butyllithium and excess phenyl isocyanate (m.p. 544–545 K). The monoclinic polymorph, (II), was obtained from a methanol solution containing (I) and uranyl nitrate hexahydrate [m.p. > 550 K; literature m.p. for (II): 553–555 K (Usanmaz, 1979)]. However, similar crystallization from a methanol solution containing mercury(II) chloride gave polymorph (I) rather than polymorph (II).

Polymorph (I)

Crystal data

$C_{21}H_{15}N_3O_3$
$M_r = 357.36$
Orthorhombic, *Fdd*2
$a = 23.3764$ (8) Å
$b = 37.1079$ (12) Å
$c = 7.7091$ (2) Å
$V = 6687.3$ (4) Å^3
$Z = 16$
$D_x = 1.420$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 2065 reflections
$\theta = 3.2$–27.6°
$\mu = 0.10$ mm^{-1}
$T = 120$ (2) K
Block, yellow
$0.50 \times 0.24 \times 0.10$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min}$ = 0.966, $T_{\max}$ = 0.990
22 356 measured reflections

2065 independent reflections
1859 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.045
$\theta_{\max}$ = 27.6°
$h = -30 \rightarrow 29$
$k = -48 \rightarrow 48$
$l = -9 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.082$
$S = 1.08$
2065 reflections
244 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 2.7798P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.17$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for orthorhombic polymorph (I).

N1—C2	1.389 (3)	N1—C11	1.448 (2)
C2—N3	1.388 (2)	N3—C31	1.448 (3)
N3—C4	1.395 (2)	N5—C51	1.452 (2)
C4—N5	1.395 (3)	C2—O2	1.208 (2)
N5—C6	1.394 (2)	C4—O4	1.204 (2)
C6—N1	1.389 (2)	C6—O6	1.210 (2)
C6—N1—C2	125.11 (16)	N1—C2—N3	115.05 (16)
C2—N3—C4	124.97 (17)	N3—C4—N5	115.01 (16)
C4—N5—C6	124.38 (16)	N5—C6—N1	115.19 (17)
C2—N1—C11—C12	103.9 (2)	C6—N5—C51—C52	−119.9 (2)
C4—N3—C31—C32	−101.5 (2)		

Table 2
Hydrogen-bonding geometry (Å, °) for orthorhombic polymorph (I).

*Cg*3 is the centroid of ring C31–C36.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C14—H14$\cdots Cg3^{\rm i}$	0.95	2.71	3.541 (2)	146

Symmetry code: (i) $\frac{5}{4} - x, y - \frac{1}{4}, \frac{3}{4} + z$.

Polymorph (II)

Crystal data

$C_{21}H_{15}N_3O_3$
$M_r = 357.36$
Monoclinic, *C*2/*c*
$a = 15.6526$ (3) Å
$b = 13.6819$ (3) Å
$c = 9.6454$ (2) Å
$\beta = 126.035$ (2)°
$V = 1670.39$ (7) Å^3
$Z = 4$

$D_x = 1.421$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1927 reflections
θ = 3.2–27.5°
$\mu = 0.10$ mm^{-1}
$T = 120$ (2) K
Block, yellow
0.50 × 0.40 × 0.12 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min}$ = 0.945, $T_{\max}$ = 0.988
13 735 measured reflections

1927 independent reflections
1620 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.031
$\theta_{\max}$ = 27.5°
$h = -20 \rightarrow 20$
$k = -17 \rightarrow 17$
$l = -11 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.124$
$S = 1.17$
1927 reflections
126 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.073P)^2 + 0.412P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.60$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.034 (3)

Table 3
Selected geometric parameters (Å, °) for monoclinic polymorph (II).

N1—C2	1.3940 (13)	N3—C31	1.4516 (14)
C2—N3	1.3949 (16)	C2—O2	1.2035 (14)
N3—C4	1.3914 (13)	C4—O4	1.204 (2)
N1—C11	1.455 (2)		
C2$^{\rm i}$—N1—C2	124.59 (14)	N1—C2—N3	114.92 (10)
C2—N3—C4	124.80 (10)	N3—C4—N3$^{\rm i}$	114.86 (14)
C2—N1—C11—C12	69.56 (8)	C4—N3—C31—C32	−100.07 (12)

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Table 4
Hydrogen-bonding geometry (Å, °) for monoclinic polymorph (II).

*Cg*2 is the centroid of ring C11–C14/C13$^{\rm i}$/C12$^{\rm i}$.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C33—H33$\cdots Cg2^{\rm ii}$	0.95	2.95	3.678 (2)	134

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

For polymorph (I), the space group *Fdd*2 was uniquely assigned from the systematic absences. For polymorph (II), the systematic absences permitted *C*2/*c* or *Cc* as possible space groups; *C*2/*c* was selected and confirmed by the systematic absences. All H atoms were located from difference maps and then treated as riding atoms, with C—H distances of 0.95 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). In the absence of significant anomalous scattering, the Flack (1983) parameter for (I) was indeterminate (Flack & Bernardinelli, 1999, 2000). Accordingly, the Friedel-equivalent reflections were merged prior to the final refinements. It was thus not possible to establish the correct orientation of the structure of (I) relative to the polar-axis direction (Jones, 1986).

For both polymorphs, data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1750). Services for accessing these data are described at the back of the journal.

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