

***N,N',N''*-Tris(*p*-methoxyphenyl)-
phosphoric triamide**Chenguang Li,^a Daniel J. Dyer,^a Nigam P. Rath^b and
Paul D. Robinson^{c*}^aDepartment of Chemistry and Biochemistry, Southern Illinois University at Carbondale, Carbondale, IL 62901-4409, USA, ^bDepartment of Chemistry and Biochemistry, University of Missouri – St Louis, 8001 Natural Bridge Road, St Louis, MO 63121, USA, and ^cDepartment of Geology, Southern Illinois University at Carbondale, Carbondale, IL 62901-4324, USA
Correspondence e-mail: robinson@geo.siu.edu

Received 28 September 2005

Accepted 5 October 2005

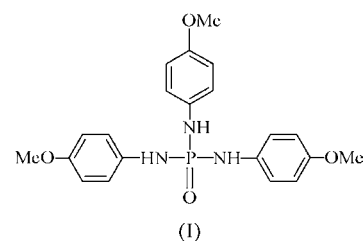
Online 22 October 2005

The title compound, C₂₁H₂₄N₃O₄P, is a self-complementary hydrogen-bond (HB) building unit, with (P=O) as the primary HB acceptor and N–H as the HB donor. Each of the four crystallographically distinct and nearly parallel molecules of the unit cell has a net dipole moment along the P=O bond direction and all of the dipoles are directed in the same general crystallographic direction. Head-to-tail N–H...O=P double-HB strands stack adjacent molecules into one-dimensional infinite polar columns. Each polar column is a 2₁ helix and all columns are essentially parallel, resulting in polar order throughout the entire crystal.

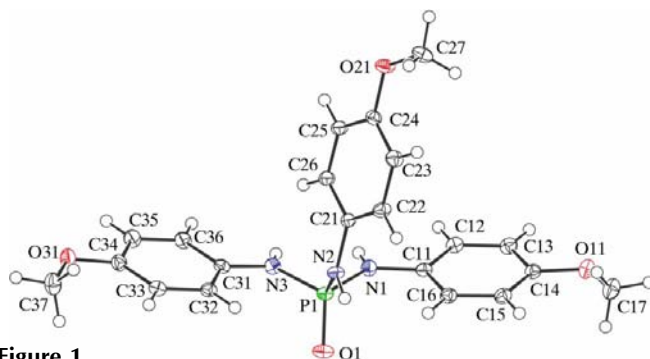
Comment

Realising polar order in organic systems has long been a goal in organic and material chemistry, due to applications that utilize non-linear optics, or piezo-, ferro- and pyroelectricity (Glaser & Kaszynski, 2001). Approaches to polar organic materials include the self-assembly of host–guest molecules (Hulliger *et al.*, 1997), electric field poling of polymer films (Burland *et al.*, 1994), Langmuir–Blodgett film multilayers (Ashwell, 1999) and grafted polymer brushes (Jaworek *et al.*, 1998). However, spontaneous polar self-assembly potentially provides a pathway to the creation of polar order in thin organic films with a minimum number of processing steps (Stupp *et al.*, 1997). By embracing supramolecular synthons as the critical design element for generating new organic materials (Desiraju, 1995), our efforts (Dyer *et al.*, 2003) and those of others (Bushey *et al.*, 2004; Facchetti *et al.*, 2004) utilize hydrogen bond (HB) forces to direct spontaneous polar self-assembly, which requires the design of non-centrosymmetric building blocks with HB donors and acceptors incorporated in a single molecule. Such designed intermolecular HB interactions should favour head-to-tail molecular stacking and generate sheets, columns and three-dimensional polar domains. Nevertheless, nature's propensity

for centrosymmetric aggregation of molecular dipole moments looms as a challenge for the design of polar order in organic materials (Hollingsworth, 2002). This communication details the crystal structure of *N,N',N''*-tris(*p*-methoxyphenyl)phosphoric triamide, (I), which represents one of our attempts at polar order through HB-directed spontaneous polar assembly. *N,N',N''*-Tris(*p*-methoxyphenyl)phosphoric triamide has long been known (Audrieth & Toy, 1942). However, structural elucidation has been hindered by solvent inclusion (Cameron *et al.*, 1976). Thus, our work represents the first crystal structure elucidation of an *N,N',N''*-triarylphosphoric triamide.



The molecule of (I) is composed of three aryloxy units bonded to the P atom *via* amide linkages, as shown in Fig. 1. Importantly, the amide H atoms should be capable of hydrogen bonding with neighbouring P=O bonds in order to bias the orientation and induce polar order. Geometric parameters of interest are listed in Table 1. The P1–O1 bond length in (I) is slightly longer than those in triphenylphosphine oxide [(C₆H₅)₃P=O = 1.487 Å; Thomas & Hamor, 1993] and tri-*tert*-butylphosphoric triamide [(*t*-BuNH)₃P=O = 1.474 Å, hereinafter abbreviated as TBPA; Chivers *et al.*, 2003]. This elongation reflects the generation of a more polar P⁺–O[−] bond. The N3–P1–N1 angle in (I) is in good agreement with the N–P–N' angle (99.5°) in the crystal structure of trianilino-phosphine, (C₆H₅NH)₃P, which consists of a trigonal arrangement of aniline groups around a central P atom in a C₃ molecular symmetry (Tarassoli *et al.*, 1982). It is noteworthy that both N1–H1 and N3–H3 point away from the P1–O1 bond vector, while N2–H2 is nearly parallel to it, in contrast with the three N–H bonds all directed below the N1–N2–N3 plane in (C₆H₅NH)₃P (Tarassoli *et al.*, 1982). This upward twisting of N2–H2 probably minimizes the molecule dipole moment, a feature also observed in the structure of

**Figure 1**

The molecular structure and atom-numbering scheme for (I), with displacement ellipsoids drawn at the 50% probability level.

(C₆H₅NH)₃P=Se, a homologue of (I) without HB interactions (Chivers *et al.*, 2003).

Since each molecule of (I) contains both HB donors and acceptors it is not surprising that significant HB interactions occur. Fig. 2 shows that each molecule acts as both donor and acceptor, atoms N1 and N3 acting as H-atom donors to the same atom O1 of an adjacent molecule at $(-x, 1 - y, \frac{1}{2} + z)$, and atom N2 twisting to donate its H atom to atom O21 of a second adjacent molecule at $(x, y, z - 1)$. Simultaneously, atom O1 acts as an H-atom acceptor from atoms N1 and N3 of a third molecule at $(-x, 1 - y, z - \frac{1}{2})$, and atom O21 accepts a HB from atom N2 of a fourth adjacent molecule at $(x, y, 1 + z)$. Thus, each molecule is hydrogen bonded to four surrounding molecules. Details of the HB geometry are given in Table 2.

The resultant molecular chain is stacked in a head-to-tail manner and forms a one-dimensional columnar suprastructure parallel to the *c* axis. Within the column, double-HB strands exist as a result of the N1/N3–O(=P) interactions. There is a slight zigzag character to the column, due to the fact that the P=O bond is at an angle of 5.23 (5)° to the *c* axis, and the

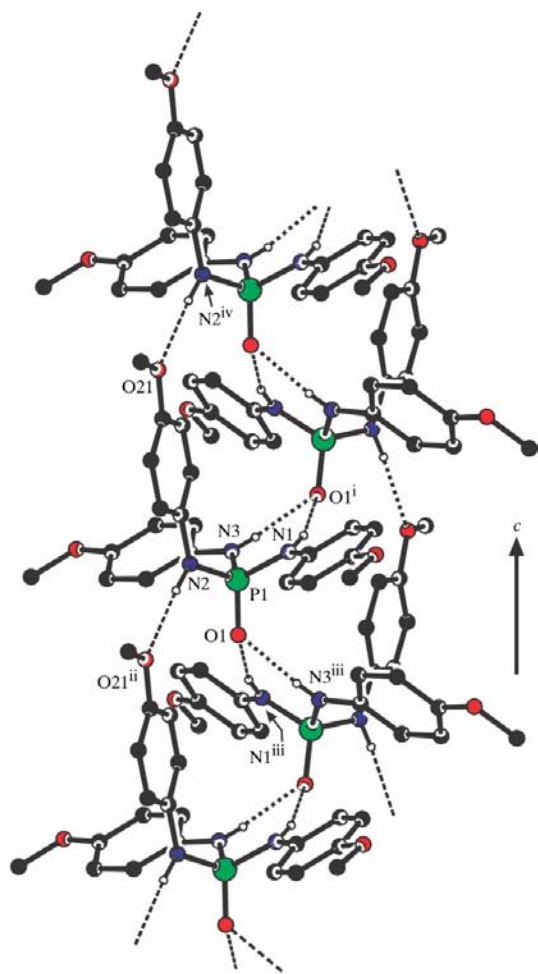


Figure 2

The hydrogen bonding in (I) (dashed lines). The three crystallographically distinct hydrogen bonds generate one-dimensional molecular chains parallel to the *c* axis. [Symmetry codes: (i) $-x, 1 - y, \frac{1}{2} + z$; (ii) $x, y, z - 1$; (iii) $-x, 1 - y, z - \frac{1}{2}$; (iv) $x, y, 1 + z$.]

column is symmetrically disposed about a twofold screw axis. It is important to note that all P=O bonds are oriented in the same general direction; thus, the column is polar. Each polar column can be described as a 2₁ helix. Space-group symmetry generates additional parallel columns (Fig. 3) which are all oriented identically with respect to their polar axes, resulting in polar order and a net dipole moment along the *c* axis.

When compared with TBPA, the double-HB *D*···*A* distances in (I) are much shorter and the HB angles are significantly straighter. This indicates appreciably stronger HB interactions in (I) than in TBPA, the tripodal HB geometry of which is controlled by large steric factors (Chivers *et al.*, 2003).

The N2–H2···O21 interaction seems fairly weak; however, the *D*–H···*A* bond is quite linear. A consequence of the upward twisting is that the N2–H2···O21 interaction reinforces the hydrogen-bonded molecular stacking inside a single column, and the upward-twisted benzene ring encapsulates the double-HB strands inside the columnar core to avoid the formation of interpenetrating HBs. Concurrently, the encapsulation should also decrease the inter-columnar dipole interactions, therefore favouring the formation of polar order. Calculations indicate no intra- or intermolecular π – π or C–H··· π (arene) interactions. The polar structure could be a consequence of the helical character of the columnar suprastructure.

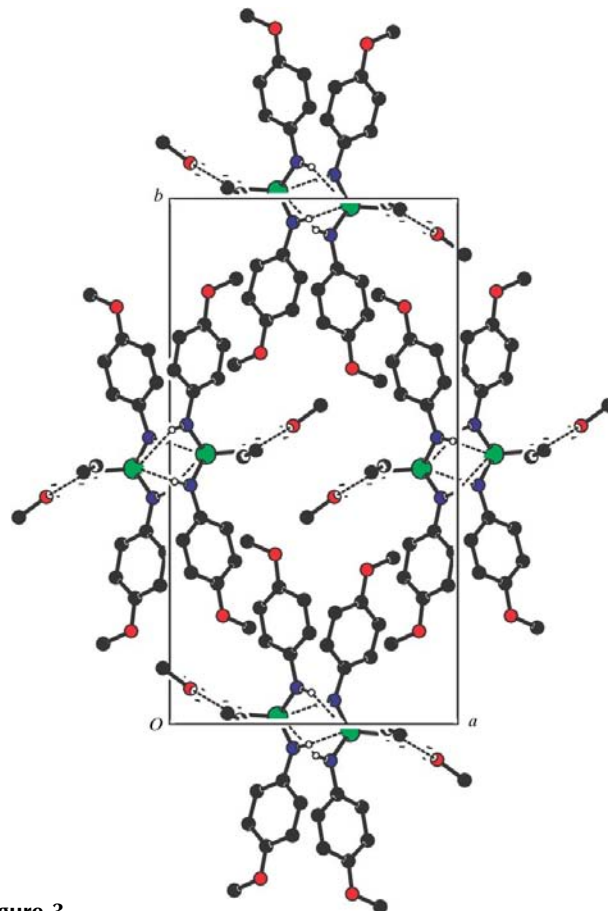


Figure 3

The molecular packing in (I), viewed down [001], providing an end-on view of the one-dimensional molecular chains symmetrically disposed about twofold screw axes. Dashed lines represent hydrogen bonds.

Experimental

Compound (I) was synthesized according to the literature procedure of Audrieth & Toy (1942). Rod-like single crystals of (I) were obtained by slow room-temperature evaporation of a dilute EtOH solution (m.p. 454.8 K). TLC: $R_F = 0.30$ (95:5, $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$); ^1H NMR (300 MHz, CDCl_3): δ 7.50 (*d*, $J = 9.6$ Hz, 1H), 7.10 (*d*, $J = 8.7$ Hz, 2H), 6.76 (*d*, $J = 9.0$ Hz, 2H), 3.67 (*s*, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 154.00, 136.02, 119.41, 114.75, 55.90.

Crystal data

$\text{C}_{21}\text{H}_{24}\text{N}_3\text{O}_4\text{P}$ Mo $K\alpha$ radiation
 $M_r = 413.40$ Cell parameters from 7209 reflections
 Orthorhombic, $Pna2_1$ $\theta = 2.5\text{--}34.0^\circ$
 $a = 11.930$ (2) Å $\mu = 0.17$ mm $^{-1}$
 $b = 21.790$ (4) Å $T = 100$ (2) K
 $c = 7.7700$ (16) Å Tabular, colourless
 $V = 2019.9$ (7) Å 3 $0.26 \times 0.24 \times 0.16$ mm
 $Z = 4$
 $D_x = 1.359$ Mg m $^{-3}$

Data collection

Bruker Kappa-APEX-II CCD area-detector diffractometer 6527 independent reflections
 5686 reflections with $I > 2\sigma(I)$
 ω and φ scans $R_{\text{int}} = 0.035$
 Absorption correction: multi-scan (*SADABS*; Bruker, 2005) $\theta_{\text{max}} = 34.1^\circ$
 $T_{\text{min}} = 0.755$, $T_{\text{max}} = 0.973$ $h = -18 \rightarrow 17$
 13717 measured reflections $k = -30 \rightarrow 34$
 $l = -10 \rightarrow 11$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.058P)^2]$
 $R[F^2 > 2\sigma(F^2)] = 0.040$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.100$ $(\Delta/\sigma)_{\text{max}} = 0.001$
 $S = 1.02$ $\Delta\rho_{\text{max}} = 0.39$ e Å $^{-3}$
 6527 reflections $\Delta\rho_{\text{min}} = -0.28$ e Å $^{-3}$
 277 parameters Absolute structure: Flack (1983),
 H atoms treated by a mixture of with 2277 Friedel pairs
 independent and constrained refinement Flack parameter: 0.03 (7)

Table 1 Selected geometric parameters (Å, °).

P1—O1	1.4886 (13)	P1—N3	1.6381 (13)
P1—N1	1.6514 (13)	P1—N2	1.6552 (12)
O1—P1—N3	114.83 (7)	O1—P1—N1	116.54 (7)
O1—P1—N2	107.10 (6)	N3—P1—N1	99.17 (7)
N3—P1—N2	109.97 (7)	N1—P1—N2	108.98 (6)

Table 2 Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O1 ⁱ	0.79 (2)	2.44 (2)	3.1678 (18)	155 (2)
N3—H3...O1 ⁱ	0.78 (2)	2.06 (2)	2.8400 (18)	172 (2)
N2—H2...O21 ⁱⁱ	0.92 (2)	2.57 (2)	3.4774 (18)	171 (2)

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

The three N-bound H atoms were refined isotropically. All other H atoms were treated as riding, with C—H distances ranging from 0.95 to 0.98 Å and with $U_{\text{iso}}(\text{H})$ values equal to 1.5 (methyl H atoms) or 1.2 (aromatic H atoms) times U_{eq} of the parent atom. The rotational orientations of the methyl H atoms were refined by the circular Fourier method available in *SHELXTL* (Bruker, 2005). Refinement of the N2 H atom improved the geometry of the N2—H2...O21 hydrogen bond significantly. The correct orientation of the structure with respect to the polar axis (Jones, 1986) in (I) was established from the value of 0.03 (7) for the Flack (1983) parameter.

Data collection: *APEXII* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* and *SHELXTL* (Bruker, 2005); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL* and *PLATON*.

Funding was provided by the NSF under grant No. CHE-0094195 and by the Materials Technology Center at SIUC. NMR characterization was supported by NSF grant No. CHE-90421012.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1875). Services for accessing these data are described at the back of the journal.

References

Ashwell, G. J. (1999). *J. Mater. Chem.* **9**, 1991–2003.
 Audrieth, L. F. & Toy, A. D. F. (1942). *J. Am. Chem. Soc.* **64**, 1553–1555.
 Bruker (2005). *SADABS* (Version 2.10), *SAINT* (Version 7.1), *SHELXTL* (Version 6.10) and *APEXII* (Version RC13). Bruker AXS Inc., Madison, Wisconsin, USA.
 Burland, D. M., Miller, R. D. & Walsh, C. A. (1994). *Chem. Rev.* **94**, 31–75.
 Bushey, M. L., Nguyen, T.-Q., Zhang, W., Horoszewski, D. & Nuckolls, C. (2004). *Angew. Chem. Int. Ed.* **43**, 5446–5453.
 Cameron, T. S., Magee, M. G. & McLean, S. (1976). *Z. Naturforsch. Teil B*, **31**, 1295–1296.
 Chivers, T., Krahn, M., Schatte, G. & Parvez, M. (2003). *Inorg. Chem.* **42**, 3994–4005.
 Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2311–2327.
 Dyer, D. J., Wolf, J., Li, C., Landorf, C., Brown, B., Maas, J., Conlin, E. & Zhao, T. (2003). *Polym. Prepr.* **44**, 578–579.
 Facchetti, A., Annoni, E., Beverina, L., Morone, M., Zhu, P., Marks, T. J. & Panani, G. A. (2004). *Nature Mater.* **3**, 910–917.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Glaser, R. & Kaszynski, P. (2001). American Chemical Society Symposium Series No. 798, Washington, DC: American Chemical Society.
 Hollingsworth, M. D. (2002). *Science*, **295**, 2410–2413.
 Hulliger, J., Rogin, P., Quintel, A., Rechsteiner, P., Konig, O. & Wubbenhorst, M. (1997). *Adv. Mater.* **9**, 677–680.
 Jaworek, T., Neher, D., Wegner, G., Wieringa, R. H. & Schouten, A. J. (1998). *Science*, **279**, 57–60.
 Jones, P. G. (1986). *Acta Cryst.* **A42**, 57.
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
 Stupp, S. I., LeBonheur, V., Walker, K., Li, L. S., Huggins, K. E., Keser, M. & Amstutz, A. (1997). *Science*, **276**, 384–389.
 Tarassoli, A., Haltiwanger, R. C. & Norman, A. D. (1982). *Inorg. Chem.* **21**, 2684–2690.
 Thomas, J. A. & Hamor, T. A. (1993). *Acta Cryst.* **C49**, 355–357.