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Key indicators

Single-crystal X-ray study

T = 100 K

Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$

R factor = 0.038

wR factor = 0.089

Data-to-parameter ratio = 14.8

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Ethyl *N,N'*-bis(3,4,5-trimethoxyphenyl)-
phosphorodiamidate

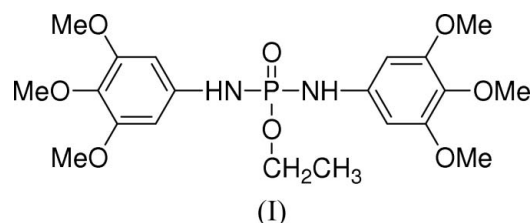
Hydrogen-bond interactions in the title compound, $\text{C}_{20}\text{H}_{29}\text{N}_2\text{O}_8\text{P}$, generate infinite ribbons consisting of alternating centrosymmetric $R_2^2(8)$ and $R_2^2(16)$ rings. Within the ribbons, the $\text{P}=\text{O}$ bonds are antiparallel, making the crystal structure non-polar.

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Comment

The title compound, (I), is a by-product in the preparation of *N,N',N''*-tris[(3,4,5-trimethoxy)phenyl] phosphoric triamide, in our ongoing project aimed at the realisation of spontaneous polar self-assembly through columnar head-to-tail molecular packing (Li *et al.*, 2005).



The P atom of (I) is in a tetrahedral coordination with two N atoms of amide groups, one O atom of the ester group and one double-bonded O atom, as shown in Fig. 1. Selected bond lengths and angles are listed in Table 1. In particular, the $\text{P1}=\text{O8}$ bond is shorter than the equivalent bond in *N,N',N''*-tris(*p*-methoxyphenyl) phosphoric triamide, hereinafter TPPA [1.4898 (14) Å; Li *et al.*, 2005], suggesting that stronger hydrogen-bonding interactions in TPPA polarize the $\text{P}=\text{O}$ bond, causing bond elongation. Because the smaller ester group causes less steric hindrance, atoms N1, N2, and O7 are able to assume reasonably good tetrahedral positions with respect to the $\text{P}=\text{O}$ bond (Table 1).

Fig. 2 shows the hydrogen-bonding scheme. Atom N1 of the molecule at (x, y, z) acts as a hydrogen-bond donor through atom H1 to atom O8ⁱ of the molecule at $(-x, -y, 1 - z)$. Inversion of this interaction across $(0, 0, \frac{1}{2})$ produces an $R_2^2(8)$ ring (Bernstein *et al.* 1995). Atom N2 of the molecule at (x, y, z) acts as a hydrogen-bond donor through atom H2 to atom O3ⁱⁱ of the molecule at $(1 - x, 1 - y, 1 - z)$. Inversion of this interaction across $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ produces an $R_2^2(16)$ ring. These two ring systems then propagate by inversion along $[110]$, producing the infinite ribbon shown in Fig. 2. Apparent π - π stacking at the center of the unit cell is discounted because the offset value indicates no ring overlap. PLATON (Spek, 2003) calculations suggest that the ribbons may be weakly cross-linked through $\text{C}-\text{H}\cdots\text{O}$ interactions involving methyl

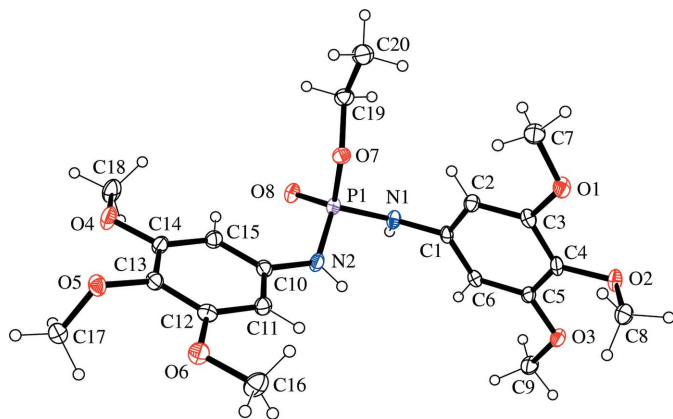


Figure 1

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

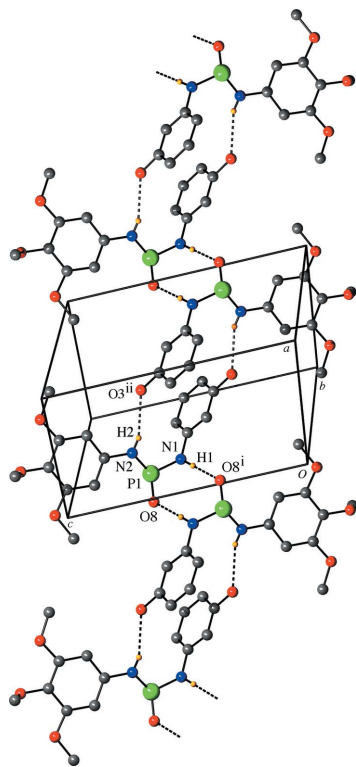


Figure 2

The hydrogen-bonded molecular ribbon in (I), propagating in the [110] direction. Dashed lines represent hydrogen bonds. H atoms and selected C and O atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$].

groups (Table 2, entries 3–5). There are no significant intramolecular interactions.

It is also clear from Fig. 2 that there are two distinct orientations of the P=O bond within the unit cell resulting from the centrosymmetric nature of the $R_2^2(8)$ ring. Since the two bond directions are anti-parallel, the net dipole moment is zero within the ribbon. The P=O bond vector is nearly parallel to [010]. Compared with TPPA, whose molecular packing results in macroscopic polar order, the structure of (I)

highlights the need for steric hindrance within achiral molecules in order to form a noncentrosymmetric architecture in the bulk (Link *et al.*, 1997).

Experimental

Compound (I) is a by-product in the preparation of N,N',N'' -tris[(3,4,5-trimethoxy)phenyl] phosphoric triamide, following the literature procedure of Audrieth & Toy (1942), and it was separated as a pure compound *via* column chromatography. The mechanism is still unknown. Single crystals of (I) were obtained by slow room-temperature evaporation of a dilute EtOH solution (m.p. 434–436 K). NMR data are available in the archived CIF.

Crystal data

$C_{20}H_{29}N_2O_8P$	$V = 1068.10 (11) \text{ \AA}^3$
$M_r = 456.42$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.419 \text{ Mg m}^{-3}$
$a = 10.0994 (5) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.1542 (5) \text{ \AA}$	$\mu = 0.18 \text{ mm}^{-1}$
$c = 11.9800 (9) \text{ \AA}$	$T = 100 (2) \text{ K}$
$\alpha = 93.596 (3)^\circ$	Irregular fragment, colorless
$\beta = 98.968 (3)^\circ$	$0.26 \times 0.20 \times 0.20 \text{ mm}$
$\gamma = 117.066 (2)^\circ$	

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer	31960 measured reflections
φ and ω scans	4358 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 2005)	3628 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.862, T_{\max} = 0.965$	$R_{\text{int}} = 0.039$
	$\theta_{\max} = 26.4^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0355P)^2 + 0.7048P]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.089$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.03$	$\Delta\rho_{\max} = 0.38 \text{ e \AA}^{-3}$
4358 reflections	$\Delta\rho_{\min} = -0.44 \text{ e \AA}^{-3}$
295 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

P1–O8	1.4757 (11)	P1–N1	1.6308 (14)
P1–O7	1.5765 (12)	P1–N2	1.6451 (15)
O8–P1–O7	112.74 (6)	O8–P1–N2	114.49 (7)
O8–P1–N1	110.68 (7)	O7–P1–N2	102.90 (7)
O7–P1–N1	108.58 (7)	N1–P1–N2	106.96 (7)

Table 2

Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H1 \cdots O8 ⁱ	0.85 (2)	1.94 (2)	2.7904 (18)	179 (3)
N2–H2 \cdots O3 ⁱⁱ	0.81 (2)	2.33 (2)	3.099 (2)	160 (2)
C8–H8B \cdots O1 ⁱⁱⁱ	0.98	2.49	3.470 (2)	175
C9–H9B \cdots O6 ^{iv}	0.98	2.50	3.270 (2)	135
C16–H16B \cdots O7 ^v	0.98	2.60	3.459 (2)	147

Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y + 2, -z + 1$; (iv) $x, y, z - 1$; (v) $-x + 1, -y + 1, -z + 2$.

The rotational orientations of the methyl H atoms were refined by the circular Fourier method available in *SHELXL97* (Sheldrick, 1997). With the exception of the nitrogen-bound H atoms, which were refined isotropically, the H atoms were treated as riding, with C–H distances ranging from 0.95 to 0.99 Å and with $U_{\text{iso}}(\text{H}) = 1.5$ (methyl H atoms) or 1.2 times (all other H atoms) U_{eq} of the parent atom.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINTE* (Bruker, 2005); data reduction: *SAINTE* and *SADABS* (Bruker, 2005); program(s) used to solve structure: *SIR92* (Burla *et al.*, 1989); program(s) used to refine structure: *LS* in *TEXSAN* (Molecular Structure Corporation, 1997) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *SHELXTL* (Bruker, 2005); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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