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Dimethyl 6-[1,2-bis(methoxycarbonyl)-2-(triphenyl-λ^5-phosphanylidene)-ethylideneamino]-2-methylsulfanyl-3,4-pyridinedicarboxylate forms a chain of hydrogen-bonded rings

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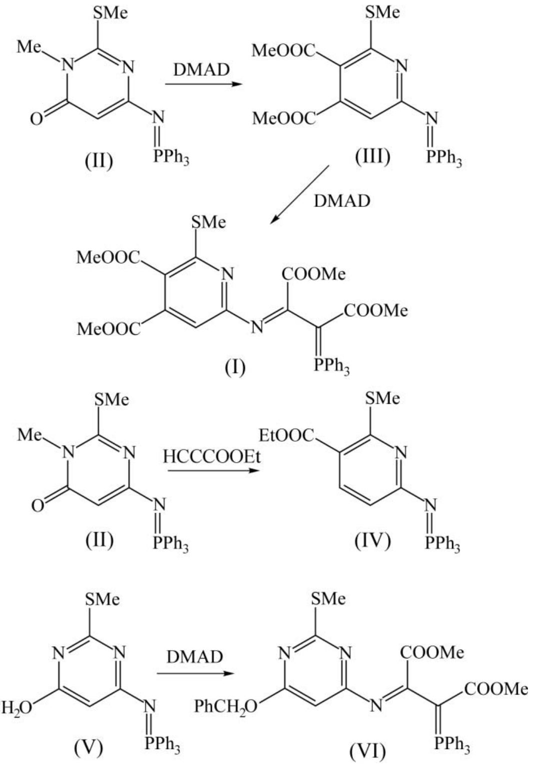
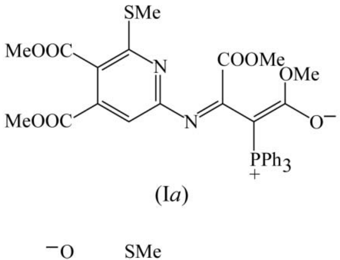
In the title compound, $C_{34}H_{31}N_2O_8PS$, the intramolecular distances provide evidence for polarization of the molecular–electronic structure. The molecules are linked into complex chains of rings by three independent C—H⋯O hydrogen bonds. The significance of this study lies in its finding that two of the four carbonyl O atoms play no role in the hydrogen bonding, despite the large excess of potential hydrogen-bond donors present.

Comment

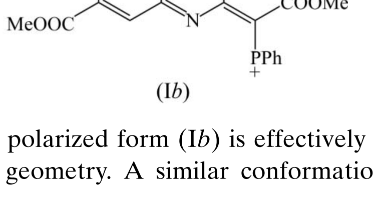
The triphenylphosphoranylidene unit (Ph_3P═N) has proven to be an effective protecting group for the amino substituent in aminopyrimidines and aminopyrimidinones, which are themselves useful precursors for the synthesis of substituted 2-aminopyridines (Cobo *et al.*, 1994). We report here the synthesis and structure of the title compound, (I) (Fig. 1), prepared by reaction of dimethyl acetylenedicarboxylate (DMAD) with the protected 6-aminopyrimidin-4(3*H*)-one (II), presumably *via* the intermediate (III). The first step, *viz*. conversion of (II) to (III) *via* a Diels–Alder addition followed by a retro Diels–Alder elimination, finds a precedent in the conversion of (II) to the pyridine (IV) (Cobo *et al.*, 2008), while the second step, also involving cycloaddition followed by cycloreversion, is closely analogous to the conversion of (V) to (VI) (Cobo *et al.*, 1999).

The Ph_3P═N fragment of the molecule of (I) has very approximate C_3 local symmetry, as indicated by the relevant torsion angles (Table 1), while the methylsulfanyl substituent is nearly coplanar with the pyridine ring; the displacement of atom C21 from this plane is only 0.347 (3) Å. The two methoxycarbonyl substituents on the pyridine ring are significantly rotated out of the plane of the ring, with dihedral angles between the pyridine ring and the C*x*/C*x*1/O*x*1/O*x*2 planes (*x* = 3 or 4, see Fig. 1) of 37.8 (2) and 44.6 (2)° when *x* = 3 and 4, respectively. Such similarity of conformation is not mimicked by the other pair of carboxylate substituents; the N6—C7—C8—P9 fragment is markedly nonplanar and the torsion angles C8—C7—C71—O71 and C7—C8—C81—O81 differ by well over 20° (Table 1). Associated with this difference in conformation is a significant difference between the C7—C71 and C8—C81 bond lengths of 0.73 (3) Å, whereas C3—C31 and C4—C41 differ by only 0.022 (3) Å. These observations taken together indicate a modest contribution to the overall molecular–electronic structure of the polarized form (I*a*) (see scheme below) involving short-range charge separation, but the long-range polarized form (I*b*) is effectively ruled out by the molecular geometry. A similar conformational arrange-





(I*a*)



(I*b*)

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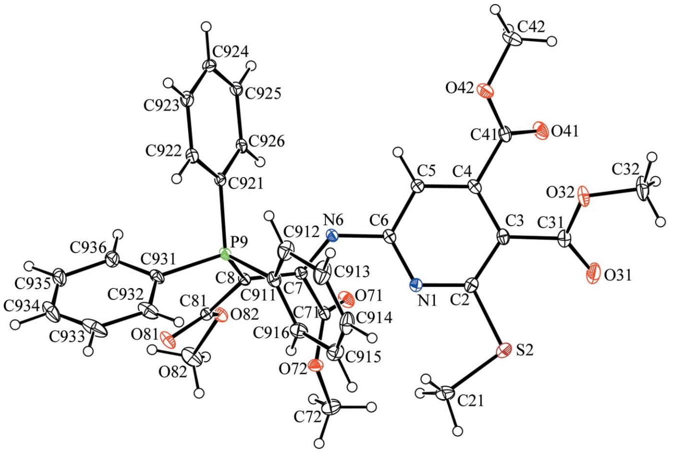

Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

ment of the two ester groups was observed in the structure of (VI) (Cobo *et al.*, 1999). Although the intramolecular distances in (VI) were not discussed in the original report, scrutiny of the geometry of (VI) in fact indicates electronic delocalization precisely analogous to that in (I*a*)

The molecules of (I) are linked by three independent C—H···O hydrogen bonds (Table 2). Aryl atoms C922 and C934 in the molecule at (x, y, z) act as hydrogen-bond donors, respectively, to carbonyl atoms O41 and O71, both in the molecule at (x, $y - 1$, z), so forming $C(12)$ and $C(10)$ (Bernstein *et al.*, 1995) chains, respectively, generated by translation. In addition, aryl atom C924 at (x, y, z) acts as a hydrogen-bond donor to carbonyl atom O71 in the molecule at ($-x + \frac{1}{2}$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$), so linking molecules related by the 2_1 screw axis along ($\frac{1}{4}$, y, $\frac{1}{4}$) to form another $C(10)$ chain. The combination of these three hydrogen bonds then forms a complex chain of rings running parallel to the [010] direction and containing rings of $R_2^2(18)$, $R_3^2(22)$ and $R_3^3(24)$ types (Fig. 2). Two chains of this type pass through each unit cell, but there are no direction-specific interactions between the chains. In particular, despite the number of aromatic rings within the molecule, there are no C—H···π hydrogen bonds and no π–π stacking interactions.

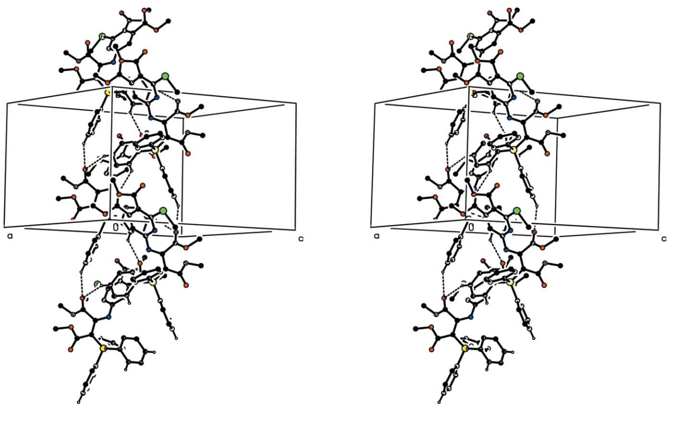

Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded chain of rings parallel to [010]. For the sake of clarity, H atoms not involved in the interactions shown have been omitted.

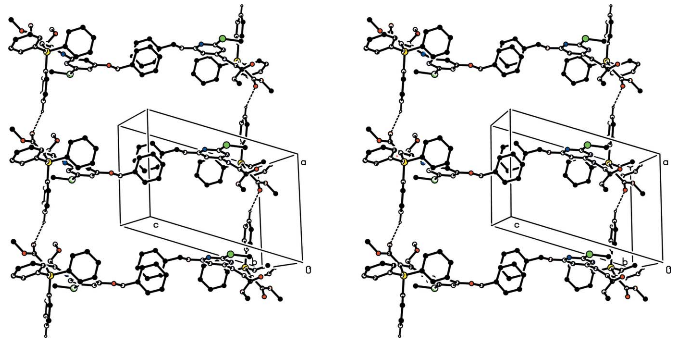

Figure 3
A stereoview of part of the crystal structure of (VI), showing the formation of a molecular ladder parallel to the [100] direction in the form of a π-stacked pair of hydrogen-bonded chains. The original atomic coordinates (Cobo *et al.*, 1999) have been used and, for the sake of clarity, H atoms not involved in the motif shown have been omitted.

It is notable that, although there are four independent carbonyl O atoms present in the molecule of (I) (O31, O41, O71 and O81), two of them play no part in the hydrogen bonding, despite the large excess of potential hydrogen-bond donors present, while O71 acts as a double acceptor. By contrast, in the structure of the related compound (VI), there is only one C—H···O hydrogen bond, utilizing the carbonyl O atom closest to the P atom to form a $C(9)$ chain (Cobo *et al.*, 1999). Further analysis of the crystal structure of (VI) now shows that, in addition, pairs of these chains are linked by a single aromatic π–π stacking interaction between the aryl groups of the benzyl substituents in centrosymmetrically related molecules to form a molecular ladder running parallel to the [100] direction (Fig. 3).

Experimental

A mixture of 3-methyl-2-methylsulfanyl-6-(triphenyl-λ^5-phosphanylideneamino)pyrimidin-4(3*H*)-one, (II) (0.5 mmol), and dimethyl acetylenedicarboxylate (1.1 mmol) with dry acetonitrile (0.9 ml) was subjected to microwave radiation in a CEM monomode microwave reactor in a sealed tube under magnetic stirring for 12 min (323 K and 100 W maximum power), the progress of the reaction being monitored by thin-layer chromatography. After the mixture had been cooled to ambient temperature, the solvent was removed under reduced pressure. The crude product was purified by chromatography on silica gel using a mixture of dichloromethane and acetone (96:4 *v*/*v*) as eluant to give the title compound, which was then crystallized from dry ethanol to give crystals suitable for single-crystal X-ray diffraction (yellow blocks, 67% yield, m.p. 444 K). MS *m*/*z* (abundance %): 658 (M^+, 59), 599 (100), 472 (15), 383 (11), 313 (11), 299 (10), 262 (46), 216 (19), 183 (54), 108 (24), 59 (16), 44 (11).

Crystal data

$C_{34}H_{31}N_2O_8PS$
$M_r = 658.64$
Monoclinic, $P2_1/n$
$a = 14.8046$ (12) Å
$b = 12.0095$ (12) Å
$c = 18.9720$ (16) Å
$\beta = 109.499$ (8)°
$V = 3179.7$ (5) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.21$ mm^{-1}
$T = 120$ (2) K
0.32 × 0.21 × 0.10 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.942$, $T_{\max} = 0.979$

68029 measured reflections
7297 independent reflections
4859 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.075$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.104$
$S = 1.09$
7297 reflections

420 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C3—C31	1.483 (3)	C7—C71	1.528 (3)
C4—C41	1.505 (3)	C8—C81	1.455 (3)
C4—C3—C31—O31	−144.5 (3)	N6—C7—C8—P9	−22.3 (3)
C5—C4—C41—O41	−130.7 (3)	C8—P9—C911—C912	151.8 (2)
C8—C7—C71—O71	123.8 (3)	C8—P9—C921—C922	163.91 (17)
C7—C8—C81—O81	147.6 (2)	C8—P9—C931—C932	116.1 (2)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C922—H922$\cdots$O41$^{\rm i}$	0.95	2.50	3.225 (3)	133
C924—H924$\cdots$O71$^{\rm ii}$	0.95	2.43	3.315 (3)	155
C934—H934$\cdots$O71$^{\rm i}$	0.95	2.42	3.272 (3)	149

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

The space group $P2_1/n$ was uniquely assigned from the systematic absences. All H atoms were located in difference maps and then treated as riding atoms, with C—H distances of 0.95 (arene and pyridine) or 0.98 Å (methyl), and with $U_{\rm iso}({\rm H}) = kU_{\rm iso}({\rm C})$, where k = 1.5 for the methyl groups and k = 1.2 for the other H atoms.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3237). Services for accessing these data are described at the back of the journal.

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