

Ethyl 2-methoxy-6-[(triphenylphosphoranylidene)amino]nicotinate and ethyl 2-methylsulfanyl-6-[(triphenylphosphoranylidene)amino]nicotinate

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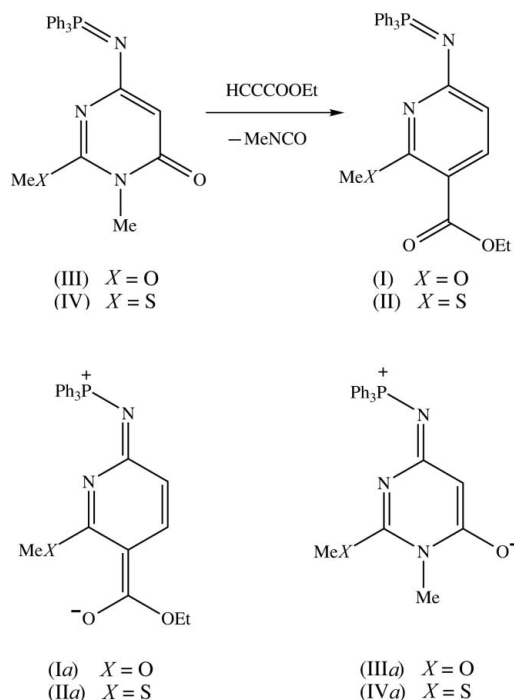
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The molecules of ethyl 2-methoxy-6-[(triphenylphosphoranylidene)amino]nicotinate, $C_{27}H_{25}N_2O_3P$, (I), and ethyl 2-methylsulfanyl-6-[(triphenylphosphoranylidene)amino]nicotinate, $C_{27}H_{25}N_2O_2PS$, (II), have almost identical bond lengths and molecular conformations, and both show evidence for polarized electronic structures. However, the crystal structures, as illustrated by the weak hydrogen bonds linking the molecules, are significantly different. The significance of this study lies in the observation that two compounds which are almost identical in constitution, configuration and conformation nonetheless adopt different crystal structures.

Comment

2-Aminopyridines are an important class of heterocyclic compounds with applications in the agrochemical and pharmaceutical sectors (Vijn *et al.*, 1993), and an effective route to substituted 2-aminopyridines has been developed (Cobo *et al.*, 1994) based on tandem Diels–Alder/retro-Diels–Alder reactions of 6-aminopyrimidin-4(3*H*)-ones with acetylenic esters. The structures of two such products have been reported (Low *et al.*, 1996). The triphenylphosphoranylidene unit is an effective protecting group for the 6-amino substituent (Wamhoff *et al.*, 1986), and this is readily introduced by reaction of the aminopyrimidine precursor with triphenylphosphine in the presence of hexachloroethane (Wamhoff *et al.*, 1986). The structures of the protected precursors, (III) and (IV) (see scheme), were reported several years ago (Low *et al.*, 1998), and we report here the structures of the title compounds, (I) and (II), derived from (III) and (IV), respectively, using their reactions with ethyl propiolate (ethyl acetylenemonocarboxylate) conducted under microwave irradiation.

While the molecular structures of compounds (I) and (II) are almost identical, their crystal structures differ considerably.



Compounds (I) and (II) both crystallize in the $P\bar{1}$ space group and the repeat vectors of the two unit cells are extremely similar, with the maximum difference, in *c*, being less than 1%. However, the cell angles in (II) are all close to the supplementary values in (I), *i.e.* each angle θ ($\theta = \alpha, \beta$ or γ) in (II) corresponds rather closely to $(180^\circ - \theta)$ in (I), such that no transformation can interconvert the two unit cells.

The molecular structures of (I) and (II) (Figs. 1 and 2) are very similar. The conformations, as defined by the leading torsion angles (Table 1), are almost identical, with the $\text{Ph}_3\text{P}=\text{N}$ fragments adopting approximate local threefold rotational symmetry, while the chain-extended ester fragment is, in both compounds, directed away from the MeX ($X = \text{O}$ or S) substituent at C2. In each compound, there is a reasonably short intramolecular $\text{C}—\text{H} \cdots \text{N}$ hydrogen bond, with almost identical dimensions in the two compounds (Table 2), and these interactions may be of significance in influencing the overall molecular conformations. No such contacts are apparent in the structures of (III) and (IV) (Low *et al.*, 1998).

With the exception of the parameters involving the MeX substituents, the corresponding bond distances in (I) and (II) are also very similar. The distances and angles around the P atoms are similar to the corresponding parameters in the precursor compounds (III) and (IV) (Low *et al.*, 1998). In particular, all of (I)–(IV) exhibit wide angles at N6 and all exhibit a range of *ca* 10° in the bond angles at P6. Within each pyridine ring, the N1–C2 bond is significantly shorter than N1–C6, while C4–C5 is significantly shorter than all of the other C–C bonds in this ring. In addition, the C3–C31 bond is somewhat short for its type (mean value 1.487 Å; Allen *et al.*, 1987), while C31–O31 is somewhat long (mean value

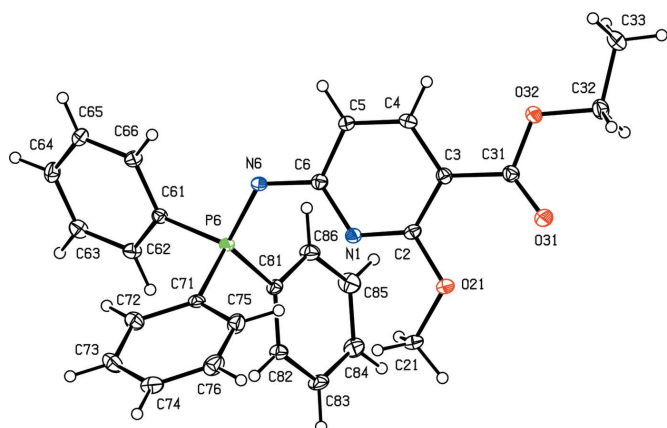


Figure 1
The molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

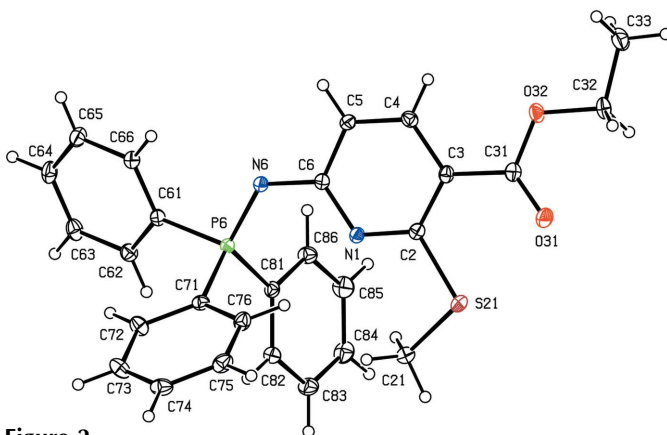


Figure 2
The molecular structure of compound (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

1.196 Å). These observations, taken all together, support a degree of quinonoidal bond fixation within the pyridine rings, corresponding to the polarized forms (Ia) and (IIa) (see scheme). The bond distances in the precursor compounds (III) and (IV) similarly show clear evidence for polarization of the molecular–electronic structures, with the short exocyclic C–N bonds, the long carbonyl C–O bonds and the similarity of the two C–C distances in the polarized fragments all pointing towards the significance of forms (IIIa) and (IVa) in addition to the classical forms (III) and (IV).

The molecules of (I) are linked, albeit rather weakly, by three C–H...O hydrogen bonds, all involving the polarized carbonyl atom O31 as acceptor. Atoms C64 and C65 in the molecule at (*x*, *y*, *z*) both act as hydrogen-bond donors to atom O31 in the molecule at (−1 + *x*, *y*, 1 + *z*), so forming a $C(12)C(13)[R_2^1(5)]$ (Bernstein *et al.*, 1995) chain of rings running parallel to the [10 $\bar{1}$] direction. Antiparallel pairs of such chains are linked by the third C–H...O hydrogen bond to form a more complex chain containing three types of ring, with alternating centrosymmetric $R_2^2(26)$ and $R_4^2(24)$ rings and pairs of $R_2^1(5)$ rings flanking the $R_4^2(24)$ rings (Fig. 3).

By contrast, the molecules of (II) are linked by one C–H...O hydrogen bond and one C–H... π (pyridyl) hydrogen

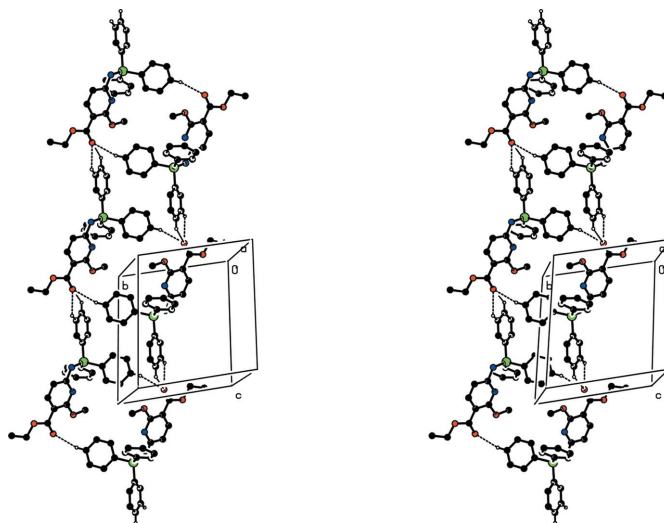


Figure 3
A stereoview of part of the crystal structure of compound (I), showing the formation of a chain of rings along [10 $\bar{1}$], built from C–H...O hydrogen bonds only. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

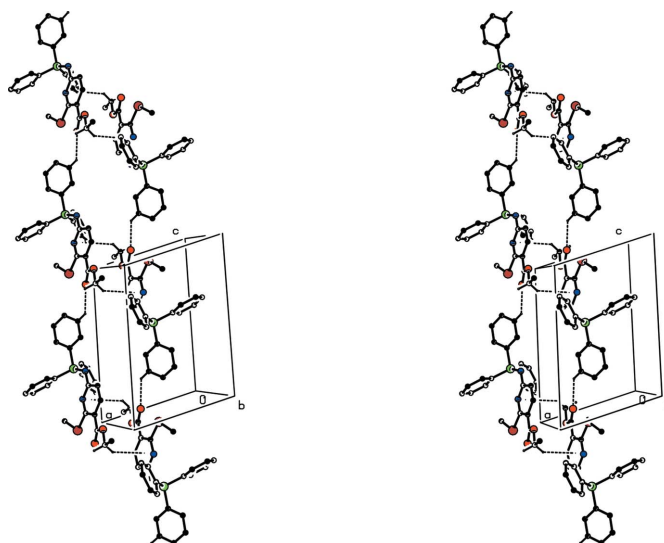
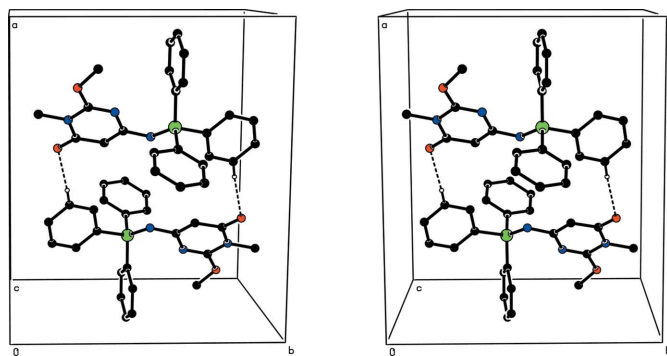


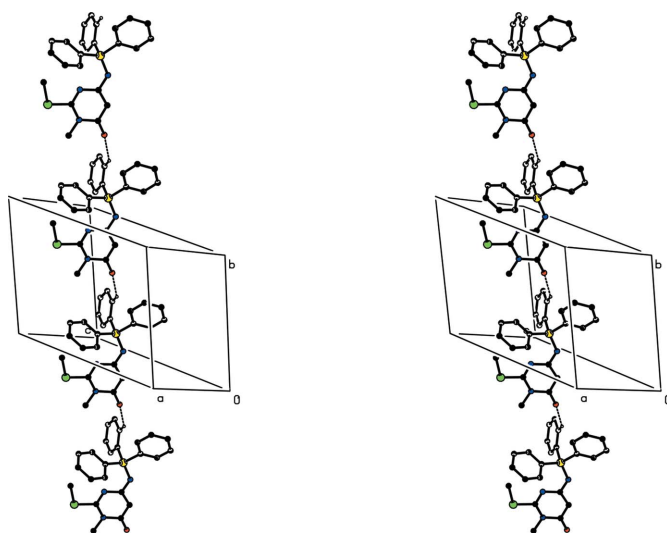
Figure 4
A stereoview of part of the crystal structure of compound (II), showing the formation of a chain of rings along [001], built from C–H...O and C–H... π (pyridyl) hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms not involved in the motifs shown have been omitted.

bond (Table 2), with the former generating $C(12)$ chains running parallel to the [001] direction and the latter linking antiparallel pairs of such chains into a chain of edge-fused centrosymmetric rings (Fig. 4). Hence, despite the almost identical intramolecular geometries of (I) and (II), their patterns of supramolecular aggregation are different. Such a contrast between the similarity in molecular structures and the difference in crystal structures could provide an interesting test for methods for crystal structure prediction from first principles.

The original report on the structures of the precursor compounds (III) and (IV) did not discuss the intermolecular interactions (Low *et al.*, 1998). Analysis using the original atom

**Figure 5**

A stereoview of part of the crystal structure of compound (III), showing the formation of a hydrogen-bonded $R_2^2(20)$ dimer. The original atom coordinates (Low *et al.*, 1998) have been used and, for the sake of clarity, H atoms not involved in the motif shown have been omitted.

**Figure 6**

A stereoview of part of the crystal structure of compound (IV), showing the formation of a hydrogen-bonded $C(9)$ chain along $[010]$. The original atom coordinates (Low *et al.*, 1998) have been used and, for the sake of clarity, H atoms not involved in the motif shown have been omitted.

coordinates shows that the molecules of (III) are linked by paired $C-H \cdots O$ hydrogen bonds to form a centrosymmetric $R_2^2(20)$ dimer (Fig. 5), while in (IV) a single $C-H \cdots O$ hydrogen bond links molecules related by translation into a $C(9)$ chain (Fig. 6).

Experimental

For the synthesis of compounds (I) and (II), mixtures of the precursors (III) or (IV) (0.5 mmol), respectively, and ethyl propiolate (2.5 mmol) in dry acetonitrile (0.9 ml) were subjected to microwave irradiation (100 W for 0.5 h) in sealed tubes under magnetic stirring. The resulting mixtures were evaporated to dryness under reduced pressure, and the products were purified by chromatography on silica using dichloromethane–acetone (98:2 *v/v*) as eluent. After removal of the solvent, crystallization from ethanol gave samples of (I) and (II) suitable for single-crystal X-ray diffraction. Compound (I): yellow blocks, m.p. 483–484 K, yield 54%; compound (II): yellow blocks, m.p. 492 K, yield 18%.

Compound (I)

Crystal data

$C_{27}H_{25}N_2O_3P$
 $M_r = 456.46$
 Triclinic, $P\bar{1}$
 $a = 8.5336$ (18) Å
 $b = 11.063$ (3) Å
 $c = 13.426$ (3) Å
 $\alpha = 73.722$ (18)°
 $\beta = 72.389$ (16)°

$\gamma = 85.93$ (2)°
 $V = 1159.5$ (5) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.15$ mm⁻¹
 $T = 120$ (2) K
 $0.22 \times 0.20 \times 0.15$ mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.972$, $T_{\max} = 0.978$

30925 measured reflections
 5321 independent reflections
 3750 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.080$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.120$
 $S = 1.08$
 5321 reflections

300 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.32$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.40$ e Å⁻³

Compound (II)

Crystal data

$C_{27}H_{25}N_2O_2PS$
 $M_r = 472.52$
 Triclinic, $P\bar{1}$
 $a = 8.5671$ (14) Å
 $b = 11.0617$ (6) Å
 $c = 13.547$ (2) Å
 $\alpha = 102.987$ (8)°
 $\beta = 106.417$ (12)°

$\gamma = 94.596$ (10)°
 $V = 1185.7$ (3) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.23$ mm⁻¹
 $T = 120$ (2) K
 $0.46 \times 0.31 \times 0.29$ mm

Table 1

Selected geometric parameters (Å, °) for compounds (I) and (II).

	(I)	(II)
N1–C2	1.319 (3)	1.335 (2)
C2–C3	1.406 (3)	1.403 (2)
C3–C4	1.401 (3)	1.403 (2)
C4–C5	1.365 (3)	1.369 (2)
C5–C6	1.413 (3)	1.410 (2)
C6–N1	1.359 (3)	1.3581 (19)
C3–C31	1.466 (3)	1.470 (2)
C31–O31	1.207 (3)	1.212 (2)
C6–N6	1.359 (3)	1.3637 (19)
N6–P6	1.5975 (18)	1.5944 (13)
P6–C61	1.792 (2)	1.7959 (16)
P6–C71	1.814 (2)	1.8148 (17)
P6–C81	1.807 (2)	1.8050 (16)
C6–N6–P6	124.01 (15)	124.59 (11)
N6–P6–C61	105.47 (10)	104.98 (7)
N6–P6–C71	115.46 (10)	115.61 (7)
N6–P6–C81	114.99 (10)	115.68 (7)
C61–P6–C71	105.61 (10)	106.30 (7)
C71–P6–C81	107.39 (10)	106.87 (7)
C81–P6–C61	107.20 (10)	106.65 (7)
N6–P6–C61–C62	158.42 (18)	156.65 (13)
N6–P6–C71–C72	124.57(19)	128.28 (14)
N6–P6–C81–C82	136.53 (19)	141.77 (13)
P6–N6–C6–N1	–11.1 (3)	–7.7 (2)
N1–C2–X21–C21†	4.8 (3)	11.65 (14)
C2–C3–C31–O32	165.7 (2)	165.35 (14)
C3–C31–O32–C32	–176.17 (19)	–176.39 (13)
C31–O32–C32–C33	–177.9 (2)	–179.24 (15)

† The X21 site represents atom O21 in compound (I) and S21 in compound (II).

Table 2

Hydrogen bonds and short intramolecular contacts (Å, °) for compounds (I) and (II).

Cg represents the centroid of the N1/C2–C6 ring.

	<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>
(I)	C76—H76...N1	0.95	2.48	3.284 (3)	142
	C64—H64...O31 ⁱ	0.95	2.55	3.138 (3)	120
	C65—H65...O31 ⁱ	0.95	2.46	3.096 (3)	124
	C74—H74...O31 ⁱⁱ	0.95	2.54	3.466 (3)	164
(II)	C76—H76...N1	0.95	2.43	3.246 (3)	143
	C65—H65...O31 ⁱⁱⁱ	0.95	2.50	3.170 (2)	128
	C33—H33B...Cg ^{iv}	0.99	2.73	3.560 (2)	141

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

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.901$, $T_{\max} = 0.936$
24840 measured reflections
5400 independent reflections
4362 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.098$
 $S = 1.06$
5400 reflections
300 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.36 \text{ e } \text{\AA}^{-3}$

Crystals of (I) and (II) are triclinic. For each, the $P\bar{1}$ space group was selected and confirmed by the structure analysis. All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C—H = 0.95 (aromatic and heteroaromatic), 0.98 (CH₃) or 0.99 Å (CH₂), and $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{C})$, where $k = 1.5$ for the methyl groups and 1.2 for all other H atoms.

For both compounds, data collection: *COLLECT* (Nonius, 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: SK3213). Services for accessing these data are described at the back of the journal.

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