Refinement

Refinement on F^2
$R(F) = 0.0457$
$wR(F^2) = 0.1332$
$S = 1.071$
4980 reflections
633 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0719P)^2 + 0.4343P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.078$
$\Delta\rho_{\max} = 0.233$ e Å^{-3}
$\Delta\rho_{\min} = -0.208$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0015 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—O2	1.428 (2)	S1′—O2′	1.423 (2)
S1—O1	1.429 (2)	S1′—O1′	1.430 (2)
S1—N1	1.670 (2)	S1′—N1′	1.684 (2)
S1—C16	1.751 (3)	S1′—C16′	1.756 (3)
N1—C8	1.430 (3)	N1′—C8′	1.426 (3)
N1—C5	1.447 (3)	N1′—C5′	1.455 (3)
O2—S1—O1	120.19 (12)	O2′—S1′—O1′	119.33 (12)
O2—S1—N1	106.45 (11)	O2′—S1′—N1′	107.01 (12)
O1—S1—N1	106.03 (11)	O1′—S1′—N1′	107.18 (11)
O2—S1—C16	108.58 (13)	O2′—S1′—C16′	108.86 (12)
O1—S1—C16	108.81 (12)	O1′—S1′—C16′	110.07 (12)
N1—S1—C16	105.87 (12)	N1′—S1′—C16′	103.11 (11)
C8—N1—C5	106.8 (2)	C8′—N1′—C5′	106.1 (2)
C8—N1—S1	123.7 (2)	C8′—N1′—S1′	121.0 (2)
C5—N1—S1	126.0 (2)	C5′—N1′—S1′	118.4 (2)

Data collection: *P*3 *Software* (Siemens, 1991). Cell refinement: *P*3 *Software*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*92 (Vickovic, 1994). Software used to prepare material for publication: *SHELXL*93 and *PARST*95 (Nardelli, 1983).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: VJ1042). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Tricyclic Phosphorus(V)–Hydrazine System with Twist Conformation of the Central Heterocycle

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Abstract

The compound 9-oxo-2-phenoxy-1,3,8,10-tetraaza-2λ^5-phosphatricyclo[8.4.0.0^{3,8}]tetradecane 2-sulfide, $C_{15}H_{21}N_4O_2PS$, was synthesized from bis(hexahydropyridazido)thiophosphoric acid *O*-phenyl ester and bis(trichloromethyl)carbonate trisphosgene in the presence of triethylamine. The molecular structure of the tricyclic system consists of a central six-membered ring with a twist conformation, the two anellated hexahydropyridazine rings revealing 'normal' chair conformations. Bond distances are N—N 1.429 (3) and 1.420 (3), P—N 1.647 (2) and 1.663 (2), and P—S 1.913 (1) Å.

Comment

Inorganic six-membered rings containing phosphorus(V) and two hydrazine fragments as building blocks reveal, in many cases, an unusual twist conformation. The 'normal' chair conformation is destabilized by short N—N bond lengths, substituents at the four N atoms and large heteroatoms in the ring (Engelhardt, Bünger & Viertel, 1984; Engelhardt & Stromburg, 1985, 1987, 1992, 1993; Engelhardt & Giersdorf, 1986; Engelhardt & Simon, 1992*a*,*b*, 1993; Engelhardt, Stromburg & Simon, 1994; Engelhardt & Rosefid, 1994; Diefenbach, Stromburg & Engelhardt, 1995). In fused saturated ring systems, there are examples of the central P^V–hydrazine heterocycle having a chair conformation or a twist conformation depending on the configuration at the P^V atoms in opposite positions of the ring: a *cis* configuration of the large S-atom substituents at the two P atoms in these positions leads to a twist conformation, whereas a *trans* configuration of these substituents gives a normal chair form of the

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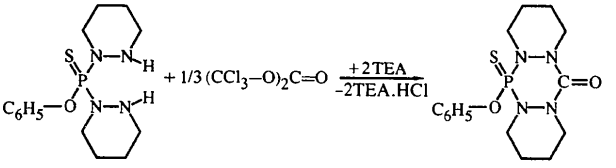
central heterocycle. The anellated organic six-membered rings linked to the N atoms always have normal chair conformations (Engelhardt & Stromburg, 1989). For the title compound, (I), a twist conformation of the central heterocycle was expected, since the carbonyl moiety adjoining the N atoms should induce an sp^2-hybridization of the latter and therefore rather short N—N bond lengths.



(I)

The X-ray structure analysis was undertaken to prove the above assumption. The asymmetric unit contains one molecule (Fig. 1). The central inorganic six-membered ring apparently has a somewhat distorted twist conformation; according to Cremer & Pople (1975), the conformation can be described in more detail by the parameters Q = 0.607 (2) (ring-folding parameter), θ = 100.7 (2)° (ring-conformation parameter) and φ = 255.2 (2)° (pseudo-rotation parameter). The values of these parameters can be interpreted as follows: the conformation is flattened compared with a normal saturated organic six-membered ring, which can also be seen by comparing the torsion angles around the bonds in the ring in Table 1; the conformation is distorted from a twist–boat conformation in the direction of a chair form; the actual conformation lies almost exactly between a pure boat form and a pure twist conformation in the so-called pseudo-rotation cycle comprising all possible twist and boat conformations of the ring. The outer hexahydropyridazine rings show almost ideal normal chair conformations. The N—N distances, 1.429 (3) and 1.420 (3) Å, compare well with other values in non-planar hydrazine rings with sp^2-N atoms (Engelhardt & Hartl, 1975, 1976), but are about 0.03 Å longer than in the corresponding N-carboxyethyl-substituted compounds (Engelhardt & Simon, 1992a,b). Only the N8 atom has an almost trigonal planar configuration [sum of bond angles 357.5 (3)°]. The deviation from planarity is somewhat larger at the other N atoms [sum of bond angles: N1 349.2 (3), N3 351.9 (3) and N10 346.6 (3)°]. Interestingly, the contact distance P2···C9 across the ring, 3.075 (3) Å, is even shorter than in the molecules with ethoxycarbonyl substituents at the N atoms, 3.104 (3) and 3.102 (3) Å (Engelhardt & Simon, 1992a,b), and as in these and other cases, much shorter than the sum of the van der Waals radii of phosphorus and carbon (3.50 Å; Bondi, 1964). This short contact distance also favours a twist conformation as discussed in previous papers (Engelhardt & Simon, 1992a,b, 1993; Viertel & Engelhardt, 1984). There are no particularly short intermolecular contact distances in the structure.

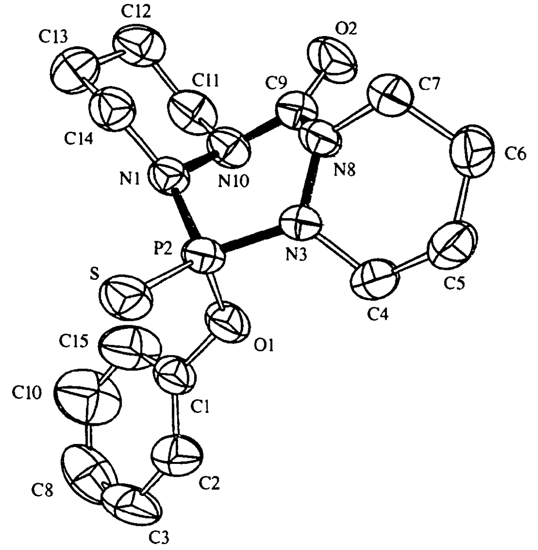


Fig. 1. The molecular structure of (I) with displacement ellipsoids at the 50% probability level. H atoms have been omitted.

Experimental

To a solution of 1.0 g (0.003 mol) of bis(hexahydropyridazido)thiophosphoric acid O-phenyl ester and 2.66 ml (0.019 mol) triethylamine (50% excess) in 150 ml THF, a solution of 0.63 g (0.002 mol) of bis(trichloromethyl)carbonate in 100 ml THF was added dropwise over a period of 2 h. The mixture was stirred at room temperature overnight. The precipitate of triethylamine hydrochloride was removed by filtration. The filtrate was evaporated to dryness under vacuum. The yellow solid residue was recrystallized from dry diethyl ether to give colourless needles [yield 0.75 g (70%); m.p. 385 K].

Crystal data

$C_{15}H_{21}N_4O_2PS$
M_r = 352.14
Monoclinic
$P2_1/n$
a = 8.002 (5) Å
b = 12.286 (2) Å
c = 17.380 (4) Å
β = 91.10 (2)°
V = 1708 (1) Å^3
Z = 4
D_x = 1.371 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 23 reflections
θ = 7–14°
μ = 0.29 mm^{-1}
T = 293 K
Needle
0.55 × 0.25 × 0.15 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scan
Absorption correction: none
3241 measured reflections
3008 independent reflections
2378 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.020
$\theta_{\rm max}$ = 25°
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 20$
2 standard reflections every 100 reflections intensity decay: 3%

Refinement

Refinement on F
$R = 0.048$
$wR = 0.029$
$S = 2.80$
2760 reflections
293 parameters
H atoms refined isotropically
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{\max} = 0.017$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}
Extinction correction: Larson (1967)
Extinction coefficient: 0.29 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S—P2	1.913 (1)	N3—N8	1.420 (3)
P2—O1	1.594 (2)	O2—C9	1.218 (3)
P2—N1	1.647 (2)	N8—C9	1.370 (3)
P2—N3	1.663 (2)	N10—C9	1.390 (3)
N1—N10	1.429 (3)		
S—P2—O1	114.94 (7)	P2—N3—C4	123.3 (2)
S—P2—N1	114.67 (8)	N8—N3—C4	112.0 (2)
S—P2—N3	118.67 (8)	N3—N8—C7	113.9 (2)
O1—P2—N1	106.32 (1)	N3—N8—C9	122.0 (2)
O1—P2—N3	98.6 (1)	C7—N8—C9	121.6 (2)
N1—P2—N3	101.6 (1)	N1—N10—C9	117.6 (2)
P2—O1—C1	125.2 (2)	N1—N10—C11	111.0 (2)
P2—N1—N10	111.2 (2)	C9—N10—C11	118.0 (2)
P2—N1—C14	124.7 (2)	O2—C9—N8	124.0 (2)
N10—N1—C14	113.3 (2)	O2—C9—N10	123.3 (2)
P2—N3—N8	116.6 (2)	N8—C9—N10	112.7 (2)
N3—P2—N1—N10	42.4 (2)	N10—C9—N8—N3	29.1 (3)
P2—N1—N10—C9	−66.0 (2)	C9—N8—N3—P2	−44.9 (3)
N1—N10—C9—N8	28.4 (3)	N8—N3—P2—N1	5.6 (2)

Reflections with $F_o^2 < 2\sigma(F_o^2)$ and $F_o > F_c$ were included in the refinement. Atomic form factors for non-H atoms are from Cromer & Mann (1968), and for H atoms from Stewart, Davidson & Simpson (1965).

Data collection: *CAD*-4 *Express* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *Express*. Data reduction: *CAD*-4 *Express*. Program(s) used to solve structure: *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Program(s) used to refine structure: *Xtal*3.0 (Hall & Stewart, 1990). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: CF1146). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3,4-Dimethoxybenzaldehyde Isonicotinoylhydrazone†

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Abstract

Hydrogen bonds between the N2 and O1 atoms [2.879 (3) Å] link molecules of the title Schiff base, $C_{15}H_{15}N_3O_3$, into a zigzag chain along the *c* axis.

Comment

Conjugated organic molecules have attracted a great deal of interest in recent years because of their large optical non-linearities (Cheng, Tam, Stevenson & Meredith, 1991). Non-linear optical molecules must possess

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† Alternative name: *N*-(3,4-dimethoxybenzylideneamino)isonicotinamide.