organic papers

4-Phenyl-14,18-dithia-4-phosphatricyclo-[18.4.0.0^{7,12}]tetracosa-2,5-dien-4-one benzene hemisolvate

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The asymmetric unit of the title compound, $C_{27}H_{27}OPS_2 \cdot 0.5C_6H_6$, is composed of a heterocyclic molecule and one half-benzene ring, the solvent molecule being located on a centre of inversion. The 16-membered ring has an irregular $-ap$, $-ap$, $+sp$, $+ac$, $-sc$, $+ap$, $-ap$, $-sc$, $+ap$, $-ap$, $+sc$, $+sp$, $-ap$, $+ap$, $+sp$, $-ac$ conformation. The phosphorus tetrahedron exhibits its usual deformation, with C—P—C angles smaller than the usual tetrahedral value of 109.5° and O—P—C angles greater than this value. In the structure, there is a stacking interaction between the P-bonded benzene rings. Furthermore, there is a weak intermolecular C—H···O hydrogen bond. In this way, a hydrogen-bonded chain is created along the crystallographic a axis.

Comment

The design of cation-binding compounds for biological, environmental or recycling purposes is of crucial importance (Bashall *et al.*, 1994). The development of new technologies, based on the binding of cations, is constrained by the properties of the ligands used. Thus, compounds like crown ethers (Pedersen, 1967), podands or cryptands (Lehn, 1978; Mathieu *et al.*, 1978) have recently been widely studied (Hancock *et al.*, 1996; Lukes *et al.*, 2001). The main disadvantage of podands is their low selectivity (Pujo-Bouteille *et al.*, 1998).

(I)
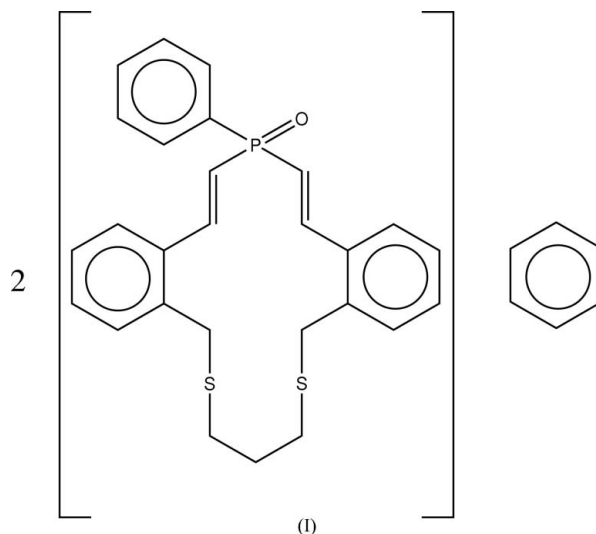
Crown ethers and cryptands selectively and specifically bind different cations. For example, [2.2.2]-cryptand (trade name Kryptofix) selectively binds K$^+$ cations, whereas [2.2.1]-cryptand selectively binds Na$^+$ cations and PNP-5-ethers bind only alkaline earth metals without preferring any of them (Krus-
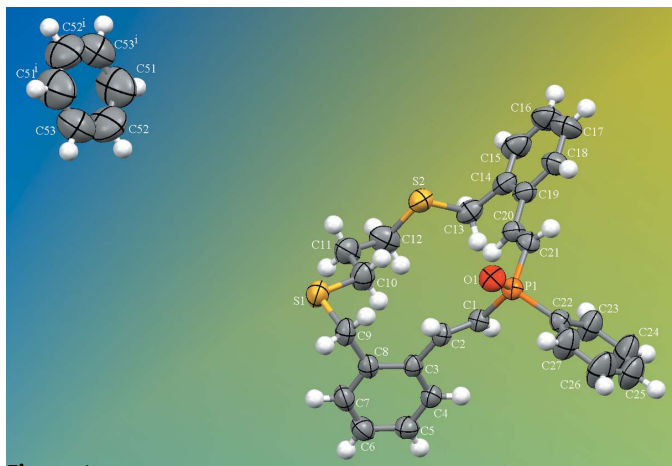
Figure 1
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x + 1, -y, -z$.]
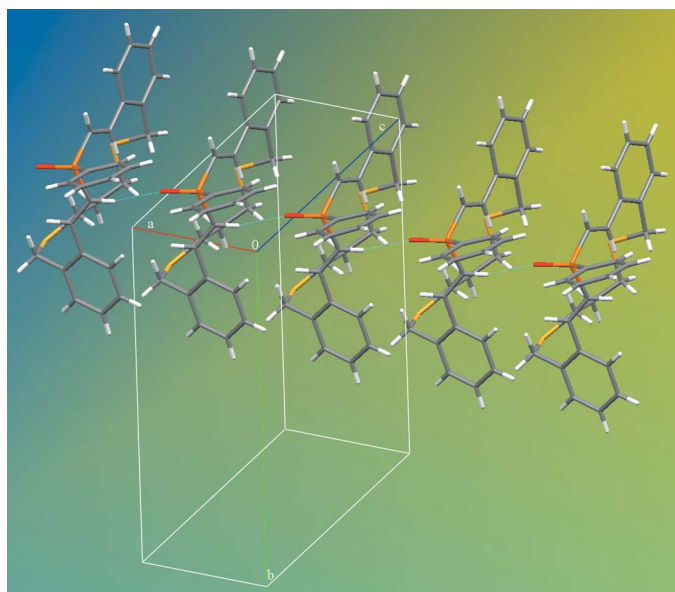

Figure 2
Part of the molecular packing of the title compound, showing intermolecular hydrogen bonds creating a chain along the crystallographic a axis. Hydrogen bonds are indicated by dashed lines.

zynski & Wieczorek, 2004). There is a great need of agents that interact with specific cations. Increasing selectivity can be imposed by the introduction of geometric constraints. Complexation depends not only on an appropriate topography, but also on neutralizing the charge of the ion or on possessing electron lone pairs. Thus, introducing —P=O or —P=S groups should affect the selectivity of the compound (Kruszynski & Wieczorek, 2004). We have designed and synthesized a compound containing a 16-membered heteroatom ring, with geometrical constraints induced by double bonds, and three structural units capable of binding cations; the π-electron clouds of aromatic rings and the electron lone pairs of S and O atoms.

A perspective view of the title compound, (I), together with the atom-numbering scheme is shown in Fig. 1. The asym-metric unit is composed of a heterocyclic molecule and one half-benzene ring; the solvent molecule is located on a centre of inversion. The solvent benzene molecule shows signs of disorder, as evidenced by relatively large displacement parameters. This is the first structure of a 16-membered heteroatom ring containing one P and two S atoms in positions 1, 7 and 11. The 16-membered ring has an irregular $-ap$, $-ap$, $+sp$, $+ac$, $-sc$, $+ap$, $-ap$, $-sc$, $+ap$, $-ap$, $+sc$, $+sp$, $-ap$, $+ap$, $+sp$, $-ac$ conformation (beginning with P1—C1—C2—C3 and following with C1—C2—C3—C8). The tetrahedrally coordi-nated P atom exhibits its usual deformation, with C—P—C angles smaller than 109.5° and O—P—C angles greater than 109.5° (Table 1). The macrocyclic-fused benzene rings are inclined by 88.28 (10)° with respect to each other, and make angles of 77.85 (13) and 84.21 (10)° with the phenyl ring bonded to P. In the structure, a stacking interaction can be found between the P-bonded benzene rings [second ring generated by $(-x + 1, -y + 1, -z + 2)$; the distance between ring centroids is 4.229 (6) Å, the perpendicular distance between the rings is 3.682 (6) Å, and the angle between the vector linking the ring centroids and the normal to one of the planes is 29.4 (4)°]. In addition, there is one intermolecular C—H···O contact (Table 2 and Fig. 2) which, according to Desiraju & Steiner (1999), can be classified as a weak hydrogen bond. In this way, a hydrogen-bonded chain is created along the crystallographic a axis. There are no further unusual intermolecular short contacts.

Experimental

The title compound was synthesized according to the method of Pietrusiewicz (2000). Elemental analysis for C, H, O, P, S (calculated/found): 71.83/71.91, 6.03/5.99, 3.19/3.14, 6.17/6.01, 12.78/12.66%. IR (KBr, cm^{-1}): 3120 (s, νC—H, ar), 3055 (m, νC—H, CH), 2910 (s, νC—H, CH$_2$), 2870 (s, νC—H, CH$_2$), 1670 (m, νC=C), 1600 (s, νC=C), 1525 (s, νC=C), 1455 (v, νC—H, CH$_2$), 1263 (m, νP=O), 705 (m, νC(—S). FABs–MS $[M+H]^+$: 79, 463.

Crystal data

$C_{27}H_{27}OPS_2 \cdot 0.5C_6H_6$	$Z = 2$
$M_r = 501.67$	$D_x = 1.243$ Mg m^{-3}
Triclinic, $P\bar{1}$	Cu $K\alpha$ radiation
$a = 5.492$ (1) Å	Cell parameters from 25
$b = 14.098$ (1) Å	reflections
$c = 18.056$ (1) Å	$\theta = 5.0$–25.0°
$\alpha = 101.92$ (1)°	$\mu = 2.51$ mm^{-1}
$\beta = 91.52$ (1)°	$T = 291.3$ (3) K
$\gamma = 100.83$ (1)°	Prism, colourless
$V = 1340.4$ (3) Å^3	$0.35 \times 0.33 \times 0.31$ mm

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.059$
diffractometer	$\theta_{max} = 75.0$°
ω–2θ scans	$h = 0 \rightarrow 6$
Absorption correction: numerical	$k = -17 \rightarrow 17$
(X-RED32; Stoe & Cie, 1999)	$l = -22 \rightarrow 22$
$T_{min} = 0.473$, $T_{max} = 0.507$	3 standard reflections
6116 measured reflections	frequency: 60 min
5512 independent reflections	intensity decay: 11.3%
5155 reflections with $I > 2\sigma(I)$	

Refinement

Table 1
Selected geometric parameters (Å, °).

P1—O1	1.4859 (17)	S1—C9	1.813 (3)
P1—C21	1.777 (3)	S1—C10	1.819 (3)
P1—C1	1.781 (2)	S2—C13	1.803 (3)
P1—C22	1.805 (3)	S2—C12	1.814 (4)
O1—P1—C21	113.51 (12)	C21—P1—C22	106.03 (12)
O1—P1—C1	113.10 (11)	C1—P1—C22	103.80 (11)
C21—P1—C1	107.95 (11)	C9—S1—C10	99.52 (13)
O1—P1—C22	111.75 (12)	C13—S2—C12	100.59 (17)
P1—C1—C2—C3	−171.50 (17)	C11—C12—S2—C13	155.6 (2)
C1—C2—C3—C8	−152.8 (2)	C12—S2—C13—C14	−177.01 (19)
C2—C3—C8—C9	8.4 (4)	S2—C13—C14—C19	75.7 (3)
C3—C8—C9—S1	103.1 (3)	C13—C14—C19—C20	3.9 (4)
C8—C9—S1—C10	−56.4 (2)	C14—C19—C20—C21	−176.9 (3)
C9—S1—C10—C11	168.0 (3)	C19—C20—C21—P1	177.0 (2)
S1—C10—C11—C12	−175.2 (3)	C20—C21—P1—C1	7.2 (3)
C10—C11—C12—S2	−68.6 (4)	C21—P1—C1—C2	−130.6 (2)

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
C1—H1$\cdots$O1^i	0.96	2.18	3.094 (3)	159

Symmetry code: (i) $x - 1, y, z$.

H atoms were placed in calculated positions and refined as riding on their parent atoms [aromatic C—H = 0.93 Å, CH$_2$ C—H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$].

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CAD-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *MERCURY* (Version 1.4; Bruno *et al.*, 2002) and *ORTEP3* (Windows Version 1.062; Farrugia 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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