gram(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1178). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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6-Oxo-6-phenyl-6-phospha-3,9-dithiabicyclo[9.4.0]pentadeca-1(11),12,14-triene

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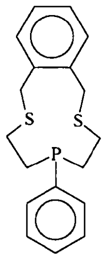
Abstract

The title molecule, 6-phenyl-6-phospha-3,9-dithiabicyclo-[9.4.0]pentadeca-1(11),12,14-triene 6-oxide, $C_{18}H_{21}OPS_2$, has an exodentate conformation, with the S and P atoms oriented away from the centre of the macrocyclic cavity.

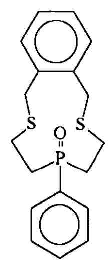
Comment

Tricoordinated P atom-containing macrocycles are of potential use as ligands in catalysis and ion-selective transport (Caminade & Majoral, 1994). It has been reported that the introduction of S donor atoms into these systems could modulate their complexing abilities towards transition metal ions (Kyba, Clubb, Larson, Schueler & Davis, 1985). These mixed macrocycles containing phosphorus and sulfur can be easily transformed into their phosphane or sulfoxide equivalents which are useful in molecular recognition and the complexation of anions (Izatt, Pawlak, Brandshaw & Bruening, 1991).

We have reported recently that $S_2P({=}O)$-containing macrocycles show good selectivity properties as neutral carriers in ion-selective electrodes (Casabó *et al.*, 1996). In this context and in order to clarify the relationships between the molecular conformations and selectivity properties, we report here the synthesis of the S_2P-containing macrocycle 6-phenyl-6-phospha-3,9-dithiabicyclo[9.4.0]pentadeca-1(11),12,14-triene, (1), and its phosphine oxide derivative, (2), together with the crystal structure determination of the latter.



(1)



(2)

The bond lengths and angles in compound (2) (Fig. 1) are normal. A comparison of the torsion angles of (2) with those of the 6-S derivative reveals only minor differences (at most 10°) and thus, the conformations of the two compounds are essentially similar (Lockhart *et al.*, 1992). Also, the intramolecular distances between the heavy atoms are almost the same. The longest S···S distance is 5.795 (1) Å in (2) and 5.772 (1) Å in the 6-S

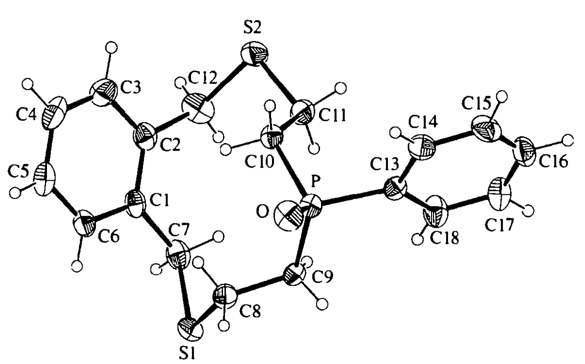


Fig. 1. The molecular structure of the title compound showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

compound. The S· · ·P distances in (2) are 4.342 (1) and 4.474 (1) Å, while the comparable short S· · ·S distances in the 6-S derivative are 4.398 (1) and 4.421 (1) Å, respectively. These results indicate that the influence of the S and P═O groups on the conformations of these macrocycles are almost the same.

The title compound and the corresponding 6-O substituted compound display considerable differences in their ring conformations (Kivekäs *et al.*, 1994), for example, in the latter compound, the S· · ·S distance is only 4.501 (1) Å compared with the long S· · ·S distance of 5.795 (1) Å in (2).

The crystal packing shows two C—H· · ·O hydrogen bonds, which are from H9*A* and H11*A* to the O atom. The C9· · ·O^{i} and C11· · ·O^{i} [symmetry code: (i) $x-1, y, z$] distances are 3.329 (4) and 3.293 (5) Å, respectively. The C—H· · ·O angles are almost linear, C9—H9*A*· · ·O^{i} being 173 (3) and C11—H11*A*· · ·O^{i} being 175 (3)°.

Experimental

Dehydrated and deoxygenated THF was used in the synthesis. Dilithium 3-phenyl-3-phosphapentane-1,5-dithiolate was obtained as described by Muñoz, Escriche, Casabó, Kivekäs & Sillanpää (1996). The macrocycle (1) was synthesized, under high dilution conditions, by mixing a solution of dilithium 3-phenyl-3-phosphapentane-1,5-dithiolate (4.40 g, 18.1 mmol) in THF (100 ml) with a solution of α,α'-dichloro-*o*-xylene (3.17 g, 18.1 mmol) in THF (100 ml) over THF (500 ml) at a rate of 20 ml h^{-1}. After addition was complete, the reaction mixture was stirred at room temperature for 48 h and then evaporated to dryness. The resulting oily material was treated with diethyl ether (50 ml), affording a white solid (LiCl) which was filtered off. The ether solution was then evaporated to 25 ml and cyclohexane (20 ml) was added. A white solid of (1) appeared which was filtered off and vacuum dried. Yield: 1.40 g (23%). Analysis calculated for $C_{18}H_{21}PS_2$: C 65.03, H 6.37, S 19.29%; found: C 64.7, H 6.1, S 18.9%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.61 (*t*, 4H, $^{3}J_{HH}$ = 7.5 Hz, SCH_2C), 2.66 (*m*, 4H, CCH_2P), 3.85 (*d*, 2H, $^{3}J_{HH}$ = 14.4 Hz, SCH_2Ph), 4.00 (*d*, 2H, $^{3}J_{HH}$ = 14.4 Hz, SCH_2Ph), 7.25–7.50 (*m*, 9H, Ph). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 27.47, 27.72, 32.26 ($PhCH_2SCH_2CH_2P$), 127.49, 128.21, 128.39, 130.55, 131.37, 136.93, 138.33 (Ph). $^{31}P\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ −21.49. The macrocycle (1) was dissolved in dichloromethane and this solution was left in an open vessel for 48 h. After this time, colourless prismatic crystals of 6-oxo-6-phenyl-6-phospha-3,9-dithiabicyclo[9.4.0]-pentadeca-1(11),12,14-triene, (2), appeared. This material was suitable for X-ray diffraction analysis. Analysis calculated for $C_{18}H_{21}OPS_2$: C 61.98, H 6.02, S 18.36%; found: C 61.5, H 6.0, S 18.3%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01 (*m*, 4H), 2.64 (*m*, 4H), 3.92 (*d*, $^{2}J_{HH}$ = 15 Hz, 2H), 4.10 (*d*, $^{2}J_{HH}$ = 15 Hz), 7.3 (*m*, 9H, Ph). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 27.26 (*d*, $^{1}J_{PC}$ = 5.98 Hz) 27.87, (*d*, $^{2}J_{PC}$ = 7.84 Hz), 32.34 (*s*), 127–138 (Ph). $^{31}P\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 41.

Crystal data

$C_{18}H_{21}OPS_2$
M_r = 348.44
Monoclinic
$P2_1/c$
a = 5.644 (2) Å
b = 13.624 (2) Å
c = 22.617 (1) Å
β = 95.31 (1)°
V = 1731.6 (7) Å^3
Z = 4
D_x = 1.337 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 13.2–17.6°
μ = 0.399 mm^{-1}
T = 293 (2) K
Prism
0.38 × 0.30 × 0.22 mm
Colourless

Data collection

Rigaku AFC-5*S* diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.880, T_{max} = 0.916
3622 measured reflections
3544 independent reflections

1960 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0370
θ_{max} = 25°
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 16$
$l = -27 \rightarrow 27$
3 standard reflections monitored every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.0425
$wR(F^2)$ = 0.1620
S = 1.041
3034 reflections
262 parameters
$w = 1/[\sigma^2(F_o^2) + 1.1268P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.002

$\Delta\rho_{max}$ = 0.264 e Å^{-3}
$\Delta\rho_{min}$ = −0.296 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S1	0.1671 (2)	0.86625 (7)	0.50311 (4)	0.0533 (3)
S2	−0.0123 (2)	0.73363 (8)	0.25963 (4)	0.0559 (3)
P	0.49263 (15)	0.62949 (7)	0.41079 (4)	0.0389 (2)
O	0.7520 (4)	0.6439 (2)	0.42218 (11)	0.0598 (7)
C1	0.1382 (6)	0.9316 (2)	0.3840 (2)	0.0433 (9)
C2	0.0863 (6)	0.9092 (3)	0.3236 (2)	0.0467 (9)
C3	0.2187 (8)	0.9546 (3)	0.2825 (2)	0.0610 (11)
C4	0.3988 (9)	1.0192 (3)	0.2992 (2)	0.0687 (13)
C5	0.4504 (8)	1.0417 (3)	0.3580 (2)	0.0617 (12)
C6	0.3206 (7)	0.9984 (3)	0.3997 (2)	0.0512 (10)
C7	0.0022 (7)	0.8858 (3)	0.4316 (2)	0.0503 (10)
C8	0.4005 (6)	0.7870 (3)	0.4814 (2)	0.0464 (9)
C9	0.3231 (6)	0.6814 (3)	0.4672 (2)	0.0386 (8)
C10	0.3762 (6)	0.6878 (3)	0.3421 (2)	0.0412 (8)
C11	0.1250 (7)	0.6576 (3)	0.3188 (2)	0.0480 (9)
C12	−0.1058 (7)	0.8387 (3)	0.3004 (2)	0.0636 (12)
C13	0.4085 (6)	0.5025 (2)	0.40216 (15)	0.0397 (8)
C14	0.5488 (7)	0.4426 (3)	0.3703 (2)	0.0530 (10)
C15	0.4893 (9)	0.3455 (3)	0.3594 (2)	0.0633 (12)
C16	0.2912 (8)	0.3067 (3)	0.3804 (2)	0.0576 (11)
C17	0.1547 (7)	0.3638 (3)	0.4134 (2)	0.0602 (11)
C18	0.2097 (7)	0.4614 (3)	0.4236 (2)	0.0566 (11)

Table 2. *Selected geometric parameters (Å, °)*

S1—C8	1.806 (4)	P—O	1.476 (3)
S1—C7	1.809 (4)	P—C13	1.800 (3)
S2—C12	1.808 (4)	P—C9	1.808 (3)
S2—C11	1.808 (4)	P—C10	1.813 (4)

C8—S1—C7	100.0 (2)	C1—C7—S1	116.3 (3)
C12—S2—C11	101.6 (2)	C9—C8—S1	114.7 (3)
O—P—C13	113.20 (15)	C8—C9—P	110.9 (3)
O—P—C9	114.0 (2)	C11—C10—P	115.5 (3)
C13—P—C9	107.5 (2)	C10—C11—S2	115.1 (3)
O—P—C10	111.5 (2)	C2—C12—S2	116.6 (3)
C13—P—C10	104.9 (2)	C18—C13—P	124.5 (3)
C9—P—C10	105.0 (2)	C14—C13—P	117.7 (3)
C7—C1—C2—C12	−0.1 (5)	C9—P—C10—C11	−70.0 (3)
C2—C1—C7—S1	148.3 (3)	P—C10—C11—S2	167.7 (2)
C8—S1—C7—C1	−59.0 (3)	C12—S2—C11—C10	−79.0 (3)
C7—S1—C8—C9	−74.7 (3)	C1—C2—C12—S2	−120.3 (4)
S1—C8—C9—P	148.5 (2)	C11—S2—C12—C2	75.0 (4)
C10—P—C9—C8	−73.9 (3)		

H atoms were located from $\Delta\rho$ maps and refined with U_{eq} fixed to $1.2U_{eq}$ of the host atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1995). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1413). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diguanidinium Hexafluorosilicate

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Abstract

The crystal structure of diguanidinium hexafuorosilicate, $[C(NH_2)_3]_2SiF_6$, consists of regular octahedral SiF_6^{2-} anions linked through a system of hydrogen bonds to the guanidinium cations, which have a planar conformation. The striking feature of the structure is the high degree of hydrogen bonding. All H atoms of the guanidinium units are involved in hydrogen bonds of the type N—H···F of length 2.901 (2), 2.908 (2) and 2.891 (1) Å. Unlike other materials belonging to the family of compounds of general formula $R_x(NH_{4-x})_2MX_3$, the crystals of the present compound do not display ferroelectric/ferroelastic properties.

Comment

This paper is a continuation of earlier reports on structural studies of the complex compounds of metal halogenides with various N-atom containing organic ligands (*e.g.* Morimoto & Lingafelter, 1970; Adams & Small, 1974; Waśkowska, Czapla & Janczak, 1993). The general formula is $R_x(NH_{4-x})MX_3$ and $(R_xNH_{4-x})_2MX_4$, where *R* is an aliphatic or aromatic hydrocarbon, *M* is a metal atom and *X* is Cl, Br, I or F. Most of these compounds show phase transitions of ferroelectric or ferroelastic character which are related to the dynamics of the constituent organic or inorganic subunits (Doudin & Chapuis, 1988; Miyazaki, Irokawa, Komukae, Osaka & Makita, 1991; Katrusiak & Szafranski, 1994). The title compound could be a candidate for behaviour of this type, but our specific heat measurements by differential scanning calorimetry (DSC), performed in the temperature range 106–410 K, showed no anomalies which could be related to a phase transition. The X-ray diffraction study of the title crystal structure, (I), has been undertaken in order to try to provide a structural explanation for the distinct physical properties of this