

hydrogen-bond distances lie between 1.88 and 1.97 Å. These are longer than in the crystal structure of ethanol (Jönsson, 1976) where the hydrogen bonding forms infinite chains with corrected H...O distances of 1.75 Å. In order to form the closed loop, two of the four O—H...O angles are less than the theoretical value of 163° for the most probable temperature-dependent O—H...O angle (Newton, Jeffrey & Takagi, 1978).

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A Twelve-Membered-Ring Organophosphorus Compound: *cis*-2,8-Dithio-2,5,5,8,11,11-hexamethyl-1,3,7,9-tetraoxa-2,8-diphosphacyclododecane

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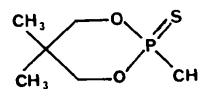
(Received 30 May 1978; accepted 22 August 1978)

Abstract. $C_{12}H_{26}O_4P_2S_2$, $M_r = 360.41$, triclinic $P\bar{1}$, $a = 6.422$ (1), $b = 9.155$ (1), $c = 16.738$ (1) Å, $\alpha = 84.64$ (2), $\beta = 89.87$ (1), $\gamma = 70.30$ (2)°, $V = 922$ Å³, $D_x = 1.299$ Mg m⁻³, $Z = 2$. The structure was refined to $R = 0.073$ for 2227 observed data. The twelve-membered ring adopts a square conformation close to that found for cyclododecane. The substituted C and the P atoms are placed in the corner positions. The O—P—O and the P—O—C ring angles are larger than in the corresponding monomer.

Introduction. It has been established that cyclic phosphonite molecules of various ring sizes, e.g. five-membered 1,3,2-dioxaphospholanes, six-membered 1,3,2-dioxaphosphorinanes, seven-membered 1,3,2-dioxaphosphhepanes and eight-membered 1,3,6,2-trioxaphosphocanes, can dimerize in solution to give ten- (Dutasta, Guimaraes, Martin & Robert, 1975), twelve- (Albrand, Dutasta & Robert, 1974), fourteen- (Dutasta, Guimaraes & Robert, 1977), and sixteen- (Dutasta & Robert, 1978) membered rings respectively. The structural study of these medium-ring compounds, which are stable when the P atom is tetra-coordinate (thiophosphonate), offers several points of interest. By keeping the same substituents attached to the P atom, and by changing the ring size, one may

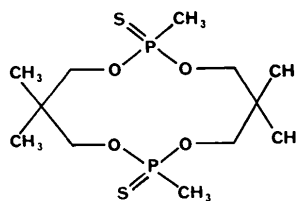
follow the gradual modification of the chemical shift, δ , and hyperfine coupling constant, J , with the changes in bond angles and lengths. Also, knowledge of the solid-state conformation of these ring compounds when combined with NMR studies in solution (¹H, ¹³C, ³¹P) will help towards a better understanding of the ring conformation in solution.

The structure of the monomer (I) has already been reported (Dutasta, Grand & Robert, 1974; Grand & Robert, 1978). We now report the structure of the *cis* isomer (II) which is obtained from the dimerization and sulphurization of (I) (Albrand, Dutasta & Robert,



(I)

2-Thio-2,5,5-trimethyl-1,3,2-dioxaphosphorinane



(II)

2,8-Dithio-2,5,5,8,11,11-hexamethyl-1,3,7,9-tetraoxa-2,8-diphosphacyclododecane

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1974). The crystals were obtained from hot *o*-dichlorobenzene.

Cell parameters were determined by least-squares calculations from the positions of 25 reflexions measured on an automatic Nonius CAD-4 diffractometer, with Ni-filtered Cu K α radiation.

The intensities of 3547 reflexions ($3 < \theta < 70^\circ$) were collected. Three check reflexions were recorded periodically and showed no fall in intensity. The intensities were corrected for Lorentz and polarization factors, but not for absorption ($\mu = 42.22 \text{ cm}^{-1}$). 2227 reflexions were judged observed [$I > 3\sigma(I)$].

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). An *E* map based on 200 reflexions with $E > 1.84$ allowed the location of all non-hydrogen atoms. The intensity statistics indicated space group *P*1. Least-squares refinement of non-hydrogen atoms with *ORFLS* (Busing & Levy, 1959) reached $R = \sum |F_o - F_c| / \sum |F_o| = 0.073$ and $R_w = \sum w(F_o - F_c)^2 / \sum wF_o^2 = 0.086$.

Positional parameters are listed in Table 1, bond distances and angles in Table 2.*

Discussion. The bond lengths agree well with average values found for 1,3,2-dioxaphosphorinanes (Corbridge, 1974). The corresponding bond lengths in each of the four P—O—C—C parts of the molecule are equal within the error limit (3σ). The bond angles show some interesting features when compared with the values

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33842 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	8269 (10)	10326 (7)	1179 (4)
P(2)	10153 (4)	8676 (3)	1282 (1)
O(3)	10371 (10)	8151 (7)	2221 (3)
C(4)	9003 (15)	7318 (10)	2601 (5)
C(5)	9456 (13)	7159 (9)	3512 (5)
C(6)	8701 (13)	8782 (9)	3830 (5)
O(7)	6276 (9)	9450 (6)	3725 (4)
P(8)	5031 (4)	11261 (3)	3706 (1)
O(9)	5876 (9)	12052 (7)	2957 (3)
C(10)	4809 (15)	12264 (11)	2158 (5)
C(11)	6205 (16)	12890 (10)	1564 (5)
C(12)	8508 (15)	11700 (10)	1502 (5)
C(13)	12761 (15)	9006 (12)	1104 (6)
S(14)	9440 (4)	7267 (3)	638 (1)
S(15)	1896 (4)	11671 (3)	3707 (2)
C(16)	6191 (15)	11947 (11)	4513 (5)
C(17)	8196 (16)	6128 (10)	3905 (6)
C(18)	11988 (14)	6409 (11)	3709 (6)
C(19)	6525 (20)	14384 (10)	1831 (5)
C(20)	4886 (18)	13244 (12)	734 (5)

E.s.d.'s in parentheses refer to the last digit.

Table 2. Bond distances (\AA) and angles ($^\circ$) and their e.s.d.'s

P(2)—O(1)	1.579 (5)	P(2)—O(3)	1.592 (6)
P(8)—O(7)	1.577 (6)	P(8)—O(9)	1.576 (6)
O(1)—C(12)	1.468 (12)	O(3)—C(4)	1.455 (12)
O(9)—C(10)	1.471 (10)	O(7)—C(6)	1.473 (9)
C(11)—C(12)	1.523 (11)	C(5)—C(4)	1.538 (11)
C(11)—C(10)	1.535 (14)	C(5)—C(6)	1.544 (11)
P(2)—S(14)	1.923 (4)	P(8)—S(15)	1.920 (3)
P(2)—C(13)	1.818 (11)	P(8)—C(16)	1.803 (10)
C(11)—C(19)	1.554 (15)	C(5)—C(17)	1.541 (14)
C(11)—C(20)	1.578 (13)	C(5)—C(18)	1.559 (14)
O(1)—P(2)—O(3)	105.6 (3)	O(7)—P(8)—O(9)	106.8 (3)
P(2)—O(1)—C(12)	122.3 (5)	P(2)—O(3)—C(4)	121.4 (5)
P(8)—O(9)—C(10)	121.2 (5)	P(8)—O(7)—C(6)	121.1 (6)
O(1)—C(12)—C(11)	108.1 (7)	O(3)—C(4)—C(5)	107.5 (7)
O(9)—C(10)—C(11)	107.1 (7)	O(7)—C(6)—C(5)	107.8 (7)
C(10)—C(11)—C(12)	111.4 (6)	C(4)—C(5)—C(6)	110.4 (6)
O(1)—P(2)—S(14)	110.1 (3)	O(3)—P(2)—S(14)	114.5 (3)
O(9)—P(8)—S(15)	115.1 (2)	O(7)—P(8)—S(15)	109.4 (3)
O(1)—P(2)—C(13)	106.9 (4)	O(3)—P(2)—C(13)	101.4 (4)
O(9)—P(8)—C(16)	100.6 (4)	O(7)—P(8)—C(16)	107.5 (3)
C(13)—P(2)—S(14)	117.4 (3)	C(16)—P(8)—S(15)	116.7 (2)
C(12)—C(11)—C(19)	106.8 (8)	C(10)—C(11)—C(19)	111.5 (7)
C(12)—C(11)—C(20)	110.9 (7)	C(10)—C(11)—C(20)	105.3 (7)
C(4)—C(5)—C(17)	107.4 (8)	C(6)—C(5)—C(17)	111.4 (7)
C(4)—C(5)—C(18)	110.3 (8)	C(6)—C(5)—C(18)	106.7 (7)
C(19)—C(11)—C(20)	111.2 (7)	C(17)—C(5)—C(18)	110.7 (7)

observed in rings of smaller size and which have the same groups attached to the P atom. By comparing a five- (Grand, unpublished), a six- (Dutasta, Grand & Robert, 1974), and a seven-membered ring (Grand & Robert, 1978) with the twelve-membered (II), it is found that the O—P—O ring angles are 97.6 , 103.5 , 105.1 and 106.2° respectively. Thus, one observes an increase of the O—P—O bond angle with an increase in ring size. The largest difference is between the five- and six-membered rings.

In the same rings as those mentioned above the P—O—C angles increase regularly with the ring size. The mean values are 111.3 , 115.7 , 119.9 and 121.5° respectively, and show a shift of the O atom hybridization from sp^3 towards sp^2 . This flexing of the alkoxy O atom bond angle has been termed the 'hinge effect' (Verkade, 1974) and may have some interesting consequences concerning the complexing properties of these large rings.

The conformation of the twelve-membered ring of (II) (Fig. 1) is close to the square conformation found for cyclododecane (Dunitz & Shearer, 1960) where the following sequence of C—C—C torsion angles is observed in the ring: 70 , -161 , 69 , 68 , -155 , 67 , 70 , -163 , 69 , 68 , -155 , 67° . This sequence may be compared with the values for (II): 87.4 , -173.8 , 64.3 , 65.8 , -159.2 , 62.5 , 87.6 , -173.7 , 64.8 , 63.3 , -160.2 , 65.2° (Fig. 2).

In cyclododecanes, the introduction of *gem*-dimethyl substituents does not perturb the conformation, but the substituted C atoms are restricted to corner positions in

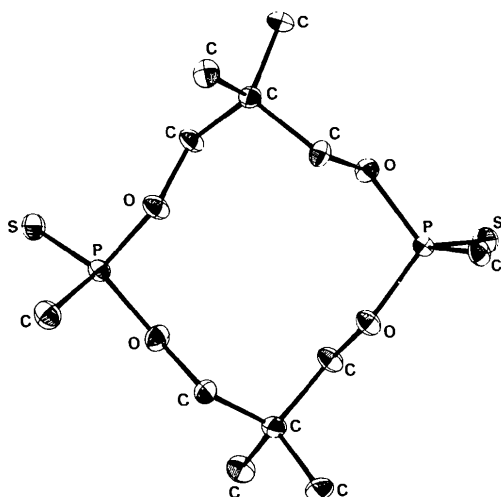


Fig. 1. *cis*-2,8-Dithioxo-2,5,5,8,11,11-hexamethyl-1,3,7,9-tetraoxa-2,8-diphosphacyclododecane.

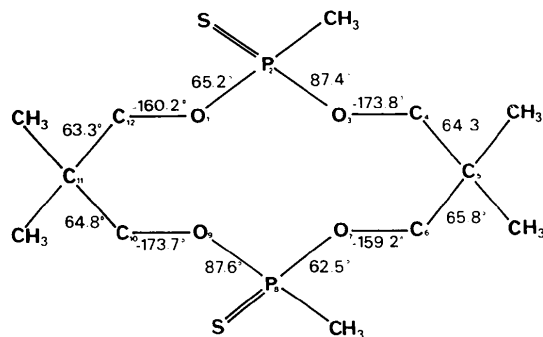


Fig. 2. Torsion angles across the ring.

the ring as a result of steric requirements (Dale, 1973). Similarly, 1,3,7,9-tetraoxacyclododecane adopts the same conformation with the O atoms placed across the corners, as found by NMR for 1,3,7,9-tetraoxacyclododecane (Borgen & Dale, 1974), and for 2,2,8,8-tetramethyl-1,3,7,9-tetraoxacyclododecane (Borgen, 1975).

In (II), the P and the *gem*-dimethyl C atoms are situated at the corners. This conformation satisfies the steric requirements due to the P substituents and the preferred *gauche*(±), *gauche*(±) conformation around the P—O bond (Van der Veken & Herman, 1977).

At room temperature, the ¹H NMR spectrum of (II) shows the two coupling constants ³J(POCH) to be nearly equal (5.5 and 6.5 Hz respectively). Such a value corresponds to a POCH dihedral angle close to 60° (Dutasta, Grand, Robert & Taieb, 1974), in agreement with the conformation observed in the solid state.

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Structure of Diethylammonium Diethyldithiocarbamate

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Abstract. [(CH₃CH₂)₂NH₂]⁺[(CH₃CH₂)₂NCS₂]⁻, C₉H₂₂N₂S₂, monoclinic, *P*2₁/*c*, *a* = 11.175 (2), *b* = 7.755 (1), *c* = 15.605 (2) Å, β = 90.53 (1)°, *Z* = 4,

V = 1352.3 Å³, *D_m* = 1.094, *D_x* = 1.092 Mg m⁻³, m.p. 354–355 K. The structure has been refined to *R*(*F*²) = 0.048 for 1546 reflexions and 206 varied parameters. It