

An Eight-Membered Ring Containing Two Phosphorus Atoms. *trans* Isomer of 2,6-Dimethyl-1,3-dioxa-2,6-diphosphacyclooctane 2,6-Disulphide

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Abstract

$C_6H_{14}O_2P_2S_2$ is monoclinic, $P2_1/n$, with $Z = 4$, $a = 9.954(2)$, $b = 9.632(1)$, $c = 12.165(1)$ Å, $\beta = 102.31(1)^\circ$, $D_c = 1.42$, $D_m = 1.40(2)$ Mg m $^{-3}$. 2012 independent reflexions were collected on a Syntex computer-automated diffractometer. The structure was solved by direct methods using the *MULTAN* system. A final R value of 0.037 was obtained for 1770 reflexions with $I > 2.5\sigma(I)$. The eight-membered ring adopts an asymmetric boat–chair conformation. The bond lengths and bond angles are compared to those obtained on cyclic 2-methyl-2-thioxo-1,3-dioxa compounds of various ring size.

Introduction

Phosphorus heterocycles with ring size larger than six are still rare and there exist only a few data concerning their stereochemistry in the solid state or in solution (Gallagher, 1977). Among the rarely studied phosphorus heterocycles are the eight-membered rings in which the heteroatoms are located in positions 1, 2, 3 and 6. This class of molecules provides interesting models for studying transannular interactions, as for example in 1,3-dioxa-6-aza-2-phosphacyclooctanes (Kalinin, Andrianov & Struchkov, 1975; Sharma, Sampath & Vaidyanathaswamy, 1980; Devillers,

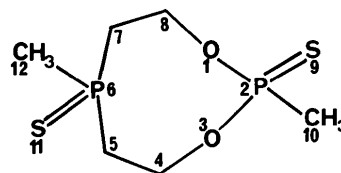


Fig. 1. The molecule showing atom numbering.

Houalla, Bonnet & Wolf, 1980), 1,3,6-trioxa-2-phosphacyclooctanes (Dutasta & Robert, 1978) and 1,3,6-trithia-2-phosphacyclooctanes (Martin & Robert, 1979). Another interest in the study of these molecules is their possible use in coordination chemistry (Pradat, Riess, Bondoux, Mentzen, Tkatchenko & Houalla, 1979). In addition, the low-temperature NMR study of these heterocyclic eight-membered rings, combined with their solid-state molecular structure, may provide information concerning the geometrical dependence of the ^{31}P NMR parameters.

We report here the molecular structure of the *trans* isomer of 2,6-dimethyl-1,3-dioxa-2,6-diphosphacyclooctane 2,6-disulphide (Fig. 1). This is the first structural analysis of a 1,3-dioxa-2,6-diphosphacyclooctane.

Experimental – structural data

Addition of elemental sulphur to a solution containing the *cis* and *trans* isomers of 2,6-dimethyl-1,3-dioxa-2,6-diphosphacyclooctane leads to a mixture of the corresponding 2,6-dithioxo (*i.e.* disulphide) compounds (Dutasta, Jurkschat & Robert, 1981). The *cis* and *trans* isomers are separated by successive crystallizations in

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benzene. Single crystals of the title compound (m.p. 389 K) were grown from a benzene solution.

2012 reflexions were collected on a Syntex diffractometer using graphite-monochromatized Mo K α ($\lambda = 0.71069 \text{ \AA}$) radiation and the ω scan technique to $2\theta = 50^\circ$. 1770 reflexions had $I > 2.5\sigma(I)$ and these were used in the final refinement. The structure was solved by direct methods using the MULTAN 78 computer system (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). The refinement was carried out by the program SHELX (Sheldrick, 1976) with anisotropic thermal parameters for the non-hydrogen atoms. The positions of the H atoms were calculated using the program SHELX. The final conventional R value was 0.037.

The fractional atomic coordinates are listed in Table 1, following the numbering given in Fig. 2 which represents a stereoview of the molecule. Tables 2 and 3

Table 1. Fractional atomic coordinates ($\times 10^4$) and B_{eq} values

$$B_{eq} = \frac{8}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq} (\text{\AA}^2)$
O(1)	8793 (2)	3798 (2)	5147 (2)	3.29
P(2)	7691 (1)	3931 (1)	3991 (1)	3.06
O(3)	6925 (2)	2474 (2)	3841 (1)	3.41
C(4)	5830 (2)	2140 (3)	4410 (2)	3.47
C(5)	6277 (2)	2116 (2)	5684 (2)	3.05
P(6)	7680 (1)	943 (1)	6277 (1)	2.90
C(7)	9310 (3)	1876 (3)	6438 (2)	3.96
C(8)	9620 (3)	2539 (3)	5392 (3)	3.98
S(9)	6564 (1)	5541 (1)	4018 (1)	4.53
C(10)	8611 (4)	3863 (3)	2875 (3)	5.32
S(11)	7612 (1)	-806 (1)	5453 (1)	4.30
C(12)	7536 (4)	746 (3)	7719 (3)	4.63

Table 2. Bond lengths (\AA)

O(1)—P(2)	1.594 (2)	C(4)—C(5)	1.519 (3)
O(1)—C(8)	1.460 (3)	C(5)—P(6)	1.821 (2)
P(2)—O(3)	1.589 (2)	P(6)—C(7)	1.828 (2)
P(2)—S(9)	1.918 (1)	P(6)—S(11)	1.954 (1)
P(2)—C(10)	1.793 (3)	P(6)—C(12)	1.800 (3)
O(3)—C(4)	1.446 (3)	C(7)—C(8)	1.513 (4)

Table 3. Bond angles ($^\circ$)

P(2)—O(1)—C(8)	119.9 (2)	C(4)—C(5)—P(6)	116.5 (2)
O(1)—P(2)—O(3)	104.7 (1)	C(5)—P(6)—C(7)	109.0 (1)
O(1)—P(2)—S(9)	110.2 (1)	C(5)—P(6)—S(11)	113.1 (1)
O(1)—P(2)—C(10)	107.4 (1)	C(5)—P(6)—C(12)	103.8 (1)
O(3)—P(2)—S(9)	116.6 (1)	C(7)—P(6)—S(11)	114.3 (1)
O(3)—P(2)—C(10)	101.0 (1)	C(7)—P(6)—C(12)	101.6 (1)
S(9)—P(2)—C(10)	115.9 (1)	S(11)—P(6)—C(12)	114.1 (1)
P(2)—O(3)—C(4)	122.3 (2)	P(6)—C(7)—C(8)	116.9 (2)
O(3)—C(4)—C(5)	113.9 (2)	O(1)—C(8)—C(7)	108.4 (2)

Table 4. Torsion angles ($^\circ$) ($\langle \sigma \rangle < 0.5^\circ$)

C(8)—O(1)—P(2)—O(3)	44.2	O(3)—C(4)—C(5)—P(6)	-57.0
C(8)—O(1)—P(2)—S(9)	170.3	C(4)—C(5)—P(6)—C(7)	91.1
C(8)—O(1)—P(2)—C(10)	-62.6	C(4)—C(5)—P(6)—S(11)	-37.2
P(2)—O(1)—C(8)—C(7)	-118.5	C(4)—C(5)—P(6)—C(12)	-161.3
O(1)—P(2)—O(3)—C(4)	81.0	C(5)—P(6)—C(7)—C(8)	-56.4
S(9)—P(2)—O(3)—C(4)	-41.0	S(11)—P(6)—C(7)—C(8)	71.1
C(10)—P(2)—O(3)—C(4)	-167.6	C(12)—P(6)—C(7)—C(8)	-165.6
P(2)—O(3)—C(4)—C(5)	-63.2	P(6)—C(7)—C(8)—O(1)	75.9

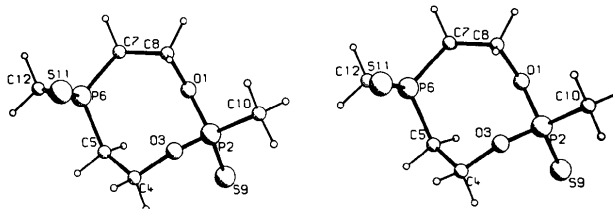


Fig. 2. Stereoscopic view of the solid-state molecular structure of the *trans* isomer of 2,6-dimethyl-1,3-dioxo-2,6-diphosphacyclooctane 2,6-disulphide.

list the interatomic bond distances and bond angles. Table 4 gives the torsion angles.*

Discussion

The eight-membered ring adopts an asymmetric conformation which is best characterized by the torsion angles shown in Table 4. Although the standard nomenclature used to define the canonical conformations of the cyclooctane (Anet & Krane, 1973) cannot be applied here, the ring shape can be described as a boat-chair conformation (BC) with the pseudo-mirror passing through O(3) and C(7). Only a few structures of eight-membered-ring organophosphorus compounds containing heteroatoms other than phosphorus in positions 1, 3 and 6 have been reported. 2-Methyl-6-phenyl-1,3-dioxo-6-aza-2-phosphacyclooctane 2-oxide (Kalinin *et al.*, 1975) adopts a symmetric crown conformation. Conversely, 2,2'-[*tert*-butylaminobis(ethyleneoxy)]bis(6-*tert*-butyl-1,3-dioxo-6-aza-2-phosphacyclooctane) (Devillers *et al.*, 1980) and 2-*tert*-butyl-1,3,6-trithia-2-phosphacyclooctane (Martin & Robert, 1979) show an asymmetric conformation.

The corresponding bond lengths of the two P—C—C—O—P fragments are equal within the limits of error. The bond angles show significant differences, as for example O(1)—C(8)—C(7) [$108.4(2)^\circ$] and O(3)—

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36718 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C(4)–C(5) [113.9 (2)°]. In the phosphonate moiety, P(2), the angles around the phosphorus indicate a significant deviation from local C_3 symmetry. Similarly, large differences between the corresponding S–P–O and C–P–O bond angles are observed in the twelve-membered ring 2,5,5,8,11,11-hexamethyl-1,3,7,9-tetraoxa-2,8-diphosphacyclododecane 2,8-disulphide (*cis* isomer) (Dutasta, Grand & Robert, 1978).

X-ray structure analyses have been reported for several cyclic 2-methyl-2-thioxo-1,3-dioxo-2-phosphorane rings of ring size equal to five (Grand, 1979), six, seven (Grand & Robert, 1978), eight (Dutasta, 1980) and twelve (Dutasta, Grand & Robert, 1978). The most significant features of these structures are the smaller O–P–O bond angle in the five-membered ring than in the others and the increase of P–O–C bond angle with ring size. The P–O–C values of the compound under study are close to those observed in a twelve-membered ring (121.4, 122.3°) (Dutasta, Grand & Robert, 1978) and illustrate the shift of the oxygen hybridization from sp^3 to sp^2 as the ring size increases. This flexibility of the alkoxy O-atom bond angles has been termed the hinge effect (Verkade, 1974).

The P(6)–S(11) bond length is comparable to the value reported for S=P(CH₃)₃ (Eller & Corfield, 1971), S=P(C₆H₁₁)₃ (Kerr, Boorman, Misener & Van Roode, 1977) and various substituted phosphorinane sulphides (Quin, McPhail, Lee & Onan, 1974; Onan, 1975) but significantly longer than the value found in S=P(C₂H₅)₃ (Van Meerssche & Léonard, 1959). The P=S bond length is shorter in the phosphonate moiety than in the phosphane one. This may be explained by the fact that the presence of the electronegative O atoms increases the *s* character of the P=S bond which will thus be shortened. Such a result is in line with the shortening of the P=S bond length in 2-*R*-1,3,2-dioxaphosphorinane 2-sulphide when the *R* group is electronegative (Van Nuffel, Lenstra & Geise, 1981; Wiczorek, Sheldrick, Karolak-Wojciechowska, Mikołajczyk & Ziemnicka, 1979).

The crystal packing of the molecules in the unit cell shows that the intermolecular distances are larger than the sum of the corresponding van der Waals radii (Pauling, 1960).

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