

and the oxygen-hydrogen van der Waals contact distances are listed in Table 6 and shown in Fig. 6. C-H bond lengths and O-C-H, C-C-H and H-C-H bond angles are in conformity with the C-H bond length of 1.09 ± 0.01 Å (Pauling, 1960) and the tetrahedral angle of 109.5° when the error limit of $\pm 2\sigma$ is considered, except for C(3)-H(4): 0.86 (0.07) Å and O(1)-C(2)-H(2): 97 (4)°. For the former the lengthening of the bond distance and for the latter the widening of the bond angle both by about 3σ are necessary so that H(4) and H(2) atoms will occupy expected reasonable positions. The distances between oxygen and hydrogen atoms, O(1)-H(4): 2.45 (0.07), O(1)-H(5): 2.70 (0.11), O(2)-H(9): 2.62 (0.10) and O(2)-H(10): 2.73 (0.12) Å, are in conformity with the sum of the van der Waals radii of oxygen and hydrogen atoms, 2.6 Å.

The numerical calculations were performed on the FACOM 270-30 computer of this Institute with the universal crystallographic computation program system UNICS (Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967).

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The Crystal Structure of Potassium *O,O*-Dibenzylphosphorodithioate $\text{KS}_2\text{P}(\text{O}-\text{CH}_2-\text{C}_6\text{H}_5)_2$

BY J. P. HAZEL AND R. L. COLLIN

Department of Radiation Biology and Biophysics, School of Medicine and Dentistry, The University of Rochester, Rochester, New York 14642, U.S.A.

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The crystal structure of potassium *O,O*-dibenzylphosphorodithioate [$\text{KS}_2\text{P}(\text{O}-\text{CH}_2-\text{C}_6\text{H}_5)_2$] has been determined with diffractometer data. The space group is triclinic, *PT*, and the unit cell contains two formula units. The unit-cell dimensions at 23°C are $a = 11.468$ (6), $b = 11.735$ (6), $c = 6.542$ (4) Å, $\alpha = 99.48$ (4), $\beta = 98.50$ (3), $\gamma = 69.09$ (2)°. The intensities were measured by the 2θ -scan method with Mo $K\alpha$ radiation. The structure was solved using symbolic addition procedures and refined by block-diagonal least-squares methods to an *R* value of 0.043. The K^+ ion is coordinated to four sulfur atoms at an average distance of 3.319 Å and to three oxygen atoms at an average distance of 2.971 Å. The P-O distances are both 1.619 (3) Å and the average P-S distance is 1.957 Å. The conformation of the ester groups with respect to the phosphorodithioate group is synclinal, and antiperiplanar.

Introduction

The phosphorodithioate anion is an analog of the phosphate ion in which two oxygen atoms have been replaced by sulfur. Both simple and extended Hückel calculations on the π -bonding system in phosphate diesters that uses the $3d$ orbitals on phosphorus suggest that the conformation stabilized most by π bonding is one in which the ester groups are rotated 90° about the P-O bond out of the plane of the phosphorus and esterified oxygen atoms (Collin, 1966, 1969).

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The same stable conformation would be predicted for the analogous *O,O*-diester phosphorodithioate ion in which the π bonding should be similar to that in the phosphate diester.

The crystal structure of potassium *O,O*-dimethylphosphorodithioate, $\text{KPS}_2(\text{O}-\text{CH}_3)_2$, has been solved by Coppens, MacGillavry, Hovenkamp & Douwes (1962), and the conformation does agree closely with that expected from the Hückel calculations (Collin, 1966). However, the large thermal motion of the carbon and oxygen atoms, together with an anomalously

long C–O bond distance of 1.58 Å, suggest that the positions of the carbon atoms have not been accurately located. The crystal structure analysis of the dibenzyl ester was carried out in the hope that thermal disorder in the ester group would be reduced and a more precise location of the carbon atoms bonded to oxygen would be obtained, resulting in a more precise determination of the conformation for this type of anion.

Experimental

Potassium *O,O*-dibenzylphosphorodithioate, $\text{KS}_2\text{P}(\text{O}-\text{CH}_2-\text{C}_6\text{H}_5)_2$, was prepared by the general procedure for phosphorodithioate esters of Fletcher, Hamilton, Hechenbleikner, Hoegberg, Sertl & Cassaday (1950). Benzyl alcohol was refluxed with phosphorus pentasulfide and the resulting precipitate was treated with alcoholic potassium hydroxide. An elemental analysis gave: K, 11.48; S, 18.29; P, 9.00; C, 48.48; H, 3.7%. (Calculated: K, 11.22; S, 18.40; P, 8.89; C, 48.25; H, 4.05%.) Single crystals were grown by dissolving the compound in a 1:1 mixture of amyl acetate and ethyl acetate and allowing the solvents to evaporate completely at room temperature.

Lattice constants were determined by a least-squares fit of measurements at 23°C on 12 high angle reflections with Mo $K\alpha_1$ radiation, a target take-off angle of 0.8° and a narrow receiving slit. Intensity data were collected at room temperature on a Picker 4-circle diffractometer using zirconium filtered molybdenum radiation and the 2θ -scan method. The first crystal on which intensity measurement was begun was approximately cylindrical with a radius of 0.05 mm and a height of 0.2 mm. Because of a slow decomposition, data collection was discontinued at $2\theta = 35^\circ$. A second nearly cylindrical crystal of radius 0.075 mm and height of 0.375 mm was used to continue the intensity measurements to $2\theta = 50^\circ$. The data from the two crystals were put on a common scale by measuring ten reflections in various zones common to both. Decline in in-

tensities due to decomposition or other factors was compensated for by scale factors derived from the measurement of three standard reflections after approximately every four hours of data collection. The maximum decline in the standard intensities for both crystals was about 10%. Within the range over which data were collected, there were 2098 observed and 744 unobserved reflections according to the criterion that an observed reflection must have a net intensity equal to or greater than 2.5 times its standard deviation.

With a solid of twenty-two faces as an approximation to a cylinder, the absorption correction program of Ahmed, Hall, Pippy & Saunderson (1966) showed that absorption effects were negligible for both crystals, and hence no correction for absorption was used on the data. Lorentz and polarization factors were applied and a set of observed structure factors were produced (Table 1).

Crystal data

$\text{KS}_2\text{P}(\text{O}-\text{CH}_2-\text{C}_6\text{H}_5)_2$, M.W. 348.5; triclinic; $P\bar{1}$.
 $a = 11.468$ (6), $b = 11.735$ (6), $c = 6.542$ (4) Å,
 $\alpha = 99.48$ (4), $\beta = 98.50$ (3), $\gamma = 69.09$ (2)°.
 $V = 807.39$ Å³, $D_m = 1.47$ g.cm⁻³ (floatation).
 $D_c = 1.47$ g.cm⁻³, $Z = 2$, $F(000) = 360$,
 Mo $K\alpha_1$ ($\lambda = 0.70926$ Å), $\mu = 6.63$ cm⁻¹.

The lack of a piezoelectric effect, the intensity statistics and the final structure refinement all suggest $P\bar{1}$ as the correct space group.

Structure determination and refinement

The symbolic addition programs of Ahmed *et al.* (1966) were used to assign phases to 392 reflections, from which an E map was computed. This revealed the positions of potassium, sulfur, phosphorus and oxygen and these atomic positions were used to calculate phases for all 2098 observed reflections. A Fourier map calculated with these phases showed the location of the two methylene carbon atoms and the carbon

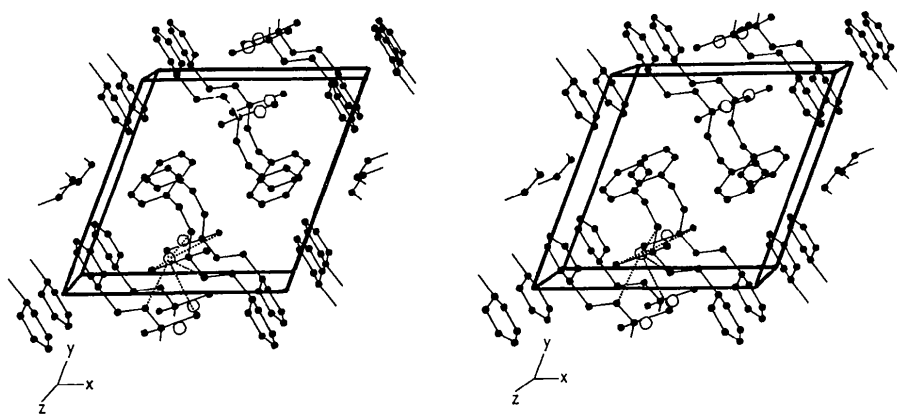


Fig. 1. Stereoscopic view looking approximately down the column axis. The potassium ions are indicated by open circles and the coordination of one potassium ion is shown by dotted lines.

Table 1. Observed and calculated structure factors (x 10),

An * indicates an unobserved reflection and the observed amplitude is replaced by the value calculated from an estimate of the minimum observable intensity.

Table with multiple columns of numerical data representing structure factors. The columns are organized into groups, each with a header like 'L FO FC' and 'L FU FC'. The data points are arranged in rows, with some rows starting with an asterisk to denote unobserved reflections. The values range from approximately -100 to 100.

atom connected to them on each benzene ring. A Fourier map phased with the new positions of potassium, sulfur, phosphorus, oxygen and the four carbon atoms showed the positions of the remaining carbon atoms. Several cycles of block-diagonal least-squares

refinement, omitting unobserved reflections and with anisotropic temperature factors, caused the R index for the observed reflections, defined as $R = \sum |F_o - F_c| / \sum |F_o|$, to converge to 0.07. The weighting scheme used during this stage of refinement was $w = |F_o|/25$ for

Table 1 (cont.)

Table with multiple columns of numerical data representing reflection intensities and indices. The columns are organized into groups, each with a header like 'L FO FC' and 'L FU FC'. The data consists of rows of numbers, some with signs, representing the intensity of various reflections.

$|F_o| \leq 25$ or $\sqrt{w} = 25/|F_o|$ for $|F_o| > 25$ and the function minimized was $\sum w(F_o - F_c)^2$.

A difference Fourier map using observed reflections with $\sin^2 \theta \leq 0.08$ showed 13 of the 14 hydrogen atoms. After several cycles of least-squares refinement with

Table 2. Final fractional coordinates and their estimated standard deviations

	x	y	z
K+	0.4137 (1)	0.1431 (1)	0.8094 (1)
P	0.5130 (1)	0.1968 (1)	0.3302 (1)
S(1)	0.5895 (1)	0.2476 (1)	0.5986 (2)
S(2)	0.3709 (1)	0.1381 (1)	0.3165 (2)
O(1)	0.6124 (3)	0.0895 (2)	0.1908 (4)
O(2)	0.4792 (3)	0.3015 (2)	0.1764 (4)
C(1)	0.7304 (4)	0.1022 (4)	0.1578 (8)
C(2)	0.8366 (4)	-0.0166 (4)	0.1892 (7)
C(3)	0.9054 (6)	-0.0830 (6)	0.0305 (9)
C(4)	1.0096 (6)	-0.1898 (6)	0.0704 (11)
C(5)	1.0397 (5)	-0.2238 (6)	0.2622 (11)
C(6)	0.9684 (7)	-0.1617 (6)	0.4166 (11)
C(7)	0.8683 (6)	-0.0572 (5)	0.3805 (9)
C(8)	0.3855 (5)	0.4219 (4)	0.2347 (7)
C(9)	0.3013 (4)	0.4615 (4)	0.0416 (6)
C(10)	0.2030 (5)	0.4178 (5)	-0.0236 (9)
C(11)	0.1322 (6)	0.4483 (6)	-0.2069 (10)
C(12)	0.1566 (5)	0.5212 (5)	-0.3274 (8)
C(13)	0.2514 (5)	0.5682 (4)	-0.2618 (7)
C(14)	0.3227 (4)	0.5389 (4)	-0.0762 (7)
H(1a)	0.719 (5)	0.129 (4)	0.019 (1)
H(1b)	0.748 (4)	0.173 (4)	0.274 (7)
H(3)	0.884 (5)	-0.055 (5)	-0.094 (8)
H(4)	1.043 (5)	-0.223 (5)	-0.044 (9)
H(5)	1.115 (5)	-0.287 (5)	0.296 (9)
H(6)	0.987 (6)	-0.190 (6)	0.584 (9)
H(7)	0.812 (5)	-0.010 (5)	0.494 (8)
H(8a)	0.432 (4)	0.476 (4)	0.291 (7)
H(8b)	0.338 (4)	0.414 (4)	0.341 (7)
H(10)	0.189 (5)	0.366 (5)	0.071 (8)
H(11)	0.071 (5)	0.419 (5)	-0.246 (8)
H(12)	0.105 (5)	0.546 (5)	-0.454 (8)
H(13)	0.272 (4)	0.623 (4)	-0.347 (7)
H(14)	0.386 (4)	0.575 (4)	-0.030 (7)

isotropic thermal parameters for the hydrogen atoms and a weighting scheme with $\sqrt{w} = \{1 + [(F_o - 40)/50]^4\}^{-1/2}$, a second difference map was prepared, from which the position of the remaining hydrogen atom was determined. Since the least-squares refinement caused the isotropic thermal parameters of some of the hydrogen atoms to be unreasonably small, the temperature factors of all hydrogen atoms were held constant in subsequent least-squares cycles at the value of the equivalent isotropic temperature factor (Hamilton, 1959) of the carbon to which each was bonded. Refinement was continued to a final R index of 0.043, at which point all parameters had shifted by less than $\frac{1}{4}$ of their standard deviations. The mean value of $w(\Delta F)^2$ showed a variation of a factor of about 2 over the entire range of $|F_o|$. Of the 743 unobserved reflections, only two showed an $|F_c|$ greater than twice the estimated threshold value.

A correction for anomalous dispersion was applied to the potassium, sulfur and phosphorus atoms at this point using the $\Delta f'$ and $\Delta f''$ values of Cromer & Liberman (1970), but least-squares refinement resulted in only small shifts of the thermal parameters of these atoms and no change in the R index. The atomic form factors for K^+ , S, O, P, C, H were taken from *International Tables for X-ray Crystallography* (1962). The calculated and observed structure factors are listed in Table 1 and the atomic coordinates and thermal parameters are given in Table 2 and Table 3.

Results and discussion

The structure can be visualized as being made up of columns of composition $[K(C_7H_7)_2PS_2O_2]_n$, with an approximately parallelogram cross section, running parallel to the c axis. The potassium ions are imbedded in the interior of the columns and one pair of column faces is made up entirely of benzyl groups while the other pair of faces is made up of both benzyl groups and exposed ester oxygen atoms. This can be seen in

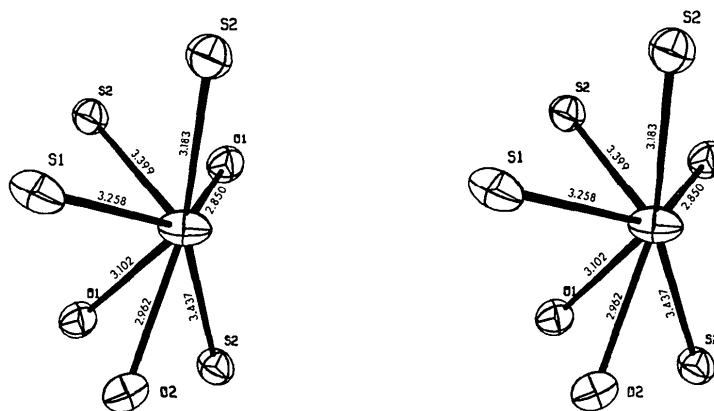


Fig. 2. Bond distances in the coordination sphere of the potassium ion. The standard deviation of the $K^+ - O$ distances is 0.003 Å and that of the $K^+ - S$ distances is 0.002 Å.

Fig. 1 where a view is shown looking approximately down the column axis.

On the two sides that pack together by benzyl-benzyl interactions, the closest carbon-carbon approach is 3.49 Å between atom C(3) and its equivalent in an adjacent molecule related by a center of symmetry. All other carbon-carbon non-bonded contacts are greater than 3.67 Å. On the other two sides of the column, intermolecular approaches occur between benzyl groups and oxygen and sulfur atoms with the closest occurring between an oxygen atom in one column and a carbon atom in another column which are 3.6 Å apart.

The potassium ions in the column interiors are surrounded by four sulfur and three oxygen atoms in an irregular sevenfold coordination shown both in Fig. 1 and in Fig. 2. The mean potassium-oxygen distance is 2.971 Å while the mean potassium-sulfur distance is 3.319 Å. These are reasonable distances for this type of bonding.

The potassium ion is not surrounded completely by

oxygen and sulfur atoms, but rather it occupies a position close to a face of the coordination polyhedron which points toward benzyl groups. The potassium-carbon distances ranging from 3.39 Å [for K⁺-C(10)] to 4.4 Å are not especially short, but the geometry does suggest a moderately strong interaction between the potassium ion and the benzyl groups. A similar situation exists in potassium L-tyrosine-*O*-sulfate dihydrate (Fries & Sundaralingam, 1971) where potassium is five-coordinated to oxygen with an open face occupied by an aromatic ring giving a potassium-carbon approach of 3.53 Å.

The potassium ion is not directly centered over the aromatic ring, but is offset from a line passing perpendicular to the ring and through its center by 2.0 Å with ring C(9)-C(14) and by 2.2 Å with ring C(2)-C(7). The potassium ion is at an appreciable distance from the planes of the aromatic rings [3.3 Å from ring C(9)-C(14) and 3.5 Å from C(2)-C(7)] and there is unlikely to be any specific interaction with the overall π -bond cloud of the rings. The interaction may be be-

Table 3. *Thermal parameters and their estimated standard deviations*

The values are $\times 10^4$.

The temperature factor = $\exp[-2\pi^2(U_{11}h^2a^2 + U_{22}k^2b^2 + U_{33}l^2c^2 + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K ⁺	903 (8)	530 (5)	390 (5)	29 (4)	65 (5)	-272 (5)
P	503 (6)	404 (5)	376 (5)	32 (4)	17 (4)	-146 (4)
S(1)	828 (9)	634 (7)	437 (6)	40 (5)	-88 (6)	-363 (6)
S(2)	549 (6)	614 (7)	451 (6)	51 (5)	37 (5)	-270 (5)
O(1)	506 (17)	427 (15)	560 (17)	9 (13)	88 (13)	-117 (13)
O(2)	599 (17)	395 (14)	423 (15)	86 (12)	109 (13)	-63 (13)
C(1)	585 (30)	559 (29)	899 (37)	155 (29)	239 (26)	126 (24)
C(2)	482 (25)	470 (25)	728 (30)	37 (21)	112 (22)	-151 (21)
C(3)	776 (39)	932 (43)	861 (40)	78 (33)	279 (32)	-154 (33)
C(4)	826 (43)	888 (44)	1276 (55)	-104 (38)	562 (40)	-62 (34)
C(5)	555 (33)	759 (40)	1540 (61)	229 (39)	57 (36)	-87 (29)
C(6)	1100 (54)	933 (47)	1023 (49)	232 (38)	-22 (41)	-21 (40)
C(7)	1015 (46)	717 (37)	750 (38)	78 (29)	115 (33)	18 (33)
C(8)	733 (32)	420 (24)	542 (26)	59 (20)	92 (23)	-72 (18)
C(9)	491 (25)	360 (22)	570 (26)	34 (18)	94 (20)	-52 (18)
C(10)	656 (33)	710 (34)	1004 (41)	271 (30)	-17 (29)	-299 (28)
C(11)	723 (38)	951 (45)	1273 (52)	302 (39)	-320 (36)	-446 (35)
C(12)	819 (39)	663 (34)	785 (36)	158 (28)	-203 (30)	-190 (29)
C(13)	669 (31)	517 (27)	617 (29)	93 (22)	56 (24)	-92 (23)
C(14)	547 (26)	400 (23)	630 (28)	50 (20)	65 (22)	-100 (20)

Table 4. *Bond angles within the anion*

O(1)-P-O(2)	96.6 (2)°	C(4)-C(5)-C(6)	120.7 (6)°
S(1)-P-S(2)	120.0 (1)	C(5)-C(6)-C(7)	119.4 (7)
O(1)-P-S(1)	112.9 (1)	P-O(2)-C(8)	118.1 (3)
O(1)-P-S(2)	104.2 (1)	O(2)-C(8)-C(9)	107.6 (4)
O(2)-P-S(1)	110.4 (1)	C(8)-C(9)-C(10)	119.8 (4)
O(2)-P-S(2)	110.0 (1)	C(8)-C(9)-C(14)	120.9 (4)
P-O(1)-C(1)	120.4 (3)	C(9)-C(10)-C(11)	119.1 (5)
O(1)-C(1)-C(2)	109.3 (4)	C(10)-C(11)-C(12)	121.5 (6)
C(1)-C(2)-C(3)	121.0 (5)	C(11)-C(12)-C(13)	120.1 (5)
C(1)-C(2)-C(7)	120.4 (5)	C(12)-C(13)-C(14)	118.9 (5)
C(2)-C(3)-C(4)	119.1 (6)	C(13)-C(14)-C(9)	121.0 (4)
C(2)-C(7)-C(6)	121.8 (6)	C(10)-C(9)-C(14)	119.3 (4)
C(3)-C(4)-C(5)	120.2 (6)		
C(3)-C(2)-C(7)	118.6 (5)		

tween the positively charged potassium ion and the C-H bond dipoles of the aromatic rings. Calculations

based on a bond moment of 0.4 Debyes for $\overset{-}{\text{C}}-\overset{+}{\text{H}}$ (Orgel, Cottrell, Dick & Sutton, 1951) show that such an interaction, at distances between 3 and 4 Å from the plane of the aromatic ring, is attractive with a broad minimum centered on the aromatic ring's sixfold axis. The energy minimum is so broad that considerable attractive force would exist for deviation of the potassium ion by even 4 Å from the sixfold axis. The thermal motion of the potassium ion is highly anisotropic and its largest amplitude is in a direction nearly perpendicular to the open face of the coordination polyhedron and toward the benzyl groups.

Bond distances and the conformation of the phosphorodithioate ion are shown in Fig. 3 and the bond angles are given in Table 4. The carbon-hydrogen bond distances range from 0.86 to 1.16 Å with an average value of 0.98 Å. The two P-O bond distances are identical at 1.619 Å and close to the corresponding distances in other diester phosphorodithioates (Coppens *et al.*, 1962; Kastalsky & McConnell, 1969; McConnell & Kastalsky, 1967; Shetty & Fernando, 1970; Lawton & Kokotailo, 1969; Ito, Igarashi & Hagihara, 1969).

The two phosphorus-sulfur bond lengths [P-S(1) = 1.945 Å and P-S(2) = 1.969 Å] appear to be significantly different but both are close to those found in other studies. An analysis of the thermal motion based on the sulfur and oxygen atoms riding on the phosphorus, using the program *ORFFE* of Busing, Martin & Levy (1964), decreased the difference between these two distances somewhat to give P-S(1) = 1.960 Å and P-S(2) = 1.976 Å. If the thermal vibrations of phosphorus and sulfur are assumed independent, then the P-S(1) and P-S(2) distances become 2.008 and 2.017 Å.

The esterified O-P-O angle of 96.6° is smaller than the tetrahedral angle of 109.5°, while the non-esterified S-P-S angle of 120.0° is larger. This distortion from

regular tetrahedral angles has also been observed in other phosphorodithioate structures and a similar angular variation exists in phosphate diesters. In potassium dimethyl phosphorodithioate (Coppens *et al.*, 1962), the O-P-O angle is 85.6° and the S-P-S angle is 118°.

There is considerable variation in carbon-carbon bond lengths within the aromatic rings. One ring in particular contains a C-C distance of 1.338 Å and another of 1.418 Å. Mean plane calculations (Table 5) also show deviations from planarity of up to 0.02 Å in the aromatic rings and deviations of 0.1 Å for the methylene carbon atom from the mean plane of the six-membered rings. Deviations of aromatic carbon atoms from a plane, greatly in excess of what would be expected from the standard deviations calculated by the block-diagonal least-squares method, were also found in dibenzyl phosphoric acid (Dunitz & Rollett, 1956) and were attributed to an underestimation of standard deviations by the block-diagonal method when thermal motion was large. The same situation probably applies to the K dibenzylphosphorodithioate structure. Some of the benzyl carbon atoms, the ones farthest from the methylene groups in particular, have large amplitudes of thermal vibration, as can be seen in Fig. 3. The ring, C(2)-C(7), which has much larger thermal motion for some atoms is also the one where the bond distance variations and mean plane deviations are larger.

Table 5. Deviations of atoms from mean plane of benzene rings

	Deviation		Deviation
C(2)	-0.014 (5) Å	C(9)	0.017 (4) Å
C(3)	0.010 (6)	C(10)	-0.007 (5)
C(4)	0.008 (7)	C(11)	-0.008 (6)
C(5)	-0.022 (6)	C(12)	0.013 (5)
C(6)	0.018 (8)	C(13)	-0.003 (5)
C(7)	0.001 (7)	C(14)	-0.012 (4)
C(1)*	-0.109 (5)	C(8)*	0.116 (4)

* Not included in least-squares derivation of mean plane.

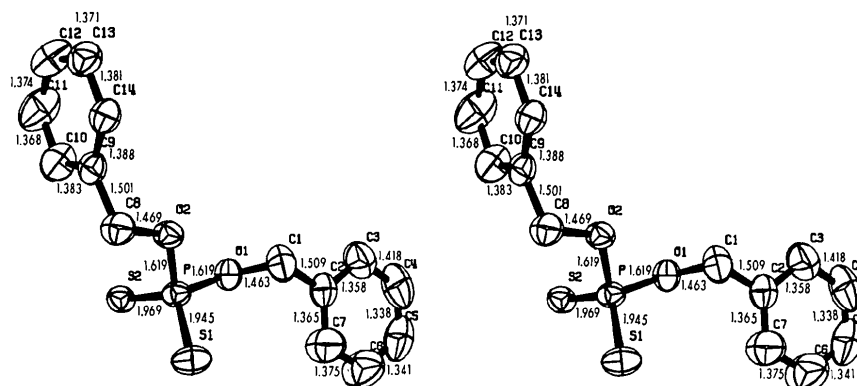


Fig. 3. Bond distances within the dibenzylphosphorodithioate anion. The hydrogen atoms have been omitted. The standard deviations are as follows: P-O, 0.003; P-S, 0.002; C-O, 0.006; C-C, 0.008 Å.

A rigid body analysis of the thermal motion was carried out for each ester group with the *MGTL* program of Schomaker & Trueblood (1968) and the bond distances corrected for rigid-body motion are shown in Table 6. The calculations for the more regular ring result in changes in carbon-carbon bond lengths which are not usually more than one standard deviation. In the case of the other ring, however, bond length shifts are often greater than twice the standard deviation of the bond distance. An estimate of the correctness of the rigid body assumption may be obtained by comparing the values of the anisotropic thermal parameters, U_{ij} , derived from the least-squares refinement, and those calculated on the basis of the rigid-body analysis. The r.m.s. difference for the aromatic rings, C(2)-C(7) and C(9)-C(14), are 0.0028 and 0.0016 Å. The mean corrected C-C bond distance in the C(2)-C(7) ring is 1.390 Å and the mean C-C bond distance in the C(9)-C(14) ring is 1.379 Å, both reasonable values.

Table 6. *Results of rigid body analysis of aromatic rings*

Bond	Uncorrected distance	Corrected distance
C(1)-C(2)	1.509 (7) Å	1.509 Å
C(2)-C(3)	1.358 (8)	1.380
C(3)-C(4)	1.419 (9)	1.452
C(4)-C(5)	1.339 (10)	1.358
C(5)-C(6)	1.340 (10)	1.361
C(6)-C(7)	1.374 (10)	1.406
C(7)-C(2)	1.365 (7)	1.384
C(8)-C(9)	1.502 (6)	1.507
C(9)-C(10)	1.384 (8)	1.380
C(10)-C(11)	1.368 (9)	1.373
C(11)-C(12)	1.375 (8)	1.374
C(12)-C(13)	1.371 (8)	1.371
C(13)-C(14)	1.380 (7)	1.406
C(9)-C(14)	1.388 (6)	1.372

The P-O-C angles are 118.09 and 120.44°, both within the normal range. The C-O bond distances of 1.469 and 1.463 Å appear normal as do the C-C bond distances between the methylene carbon atom and the aromatic ring of 1.501 and 1.509 Å.

The conformation of the ester groups with respect to the O-P-O bond system can be described by the dihedral angle between the COP and OPO planes in a manner discussed by Sundaralingam (1969). In the potassium salt of dimethyl phosphorodithioate (Coppens *et al.*, 1962), this dihedral angle is 88.3° for both ester groups (the molecule has a twofold symmetry axis) and this corresponds to a rotation of the ester group about the P-O bond by 88.3° away from the OPO plane. Using the conformational nomenclature of Klyne & Prelog (1960), this is a synclinal, synclinal (sc, sc) conformation with $\omega = \omega' = 88.3^\circ$. In the dibenzyl ester, C(8) is rotated 178.5° out of the O(1)-P-O(2) plane so that it lies inside the S(1)-P-S(2) angle. The other ester carbon, C(1), is rotated 65.4° out of the C(1)-P-O(2) plane and lies inside the O(2)-P-S(1) angle. This corresponds to a synclinal, antiperiplanar (sc, ap) conformation with $\omega = 65.4^\circ$ and $\omega' = 178.5^\circ$.

Comprehensive reviews of phosphate ester structures have been made by Sundaralingam (1969) and by Shefter, Barlow, Sparks & Trueblood (1969) and among structures that have no obvious steric hindrance, the preferred conformations are sc,sc and sc,ap. In the phosphorodithioate esters that have been studied, some of which involve strong coordination between the sulfur atoms and metal atoms such as nickel, zinc and cadmium (Lawton & Kokotailo, 1969; Ito *et al.*, 1969; Kastalsky *et al.*, 1969; McConnell *et al.*, 1967; Shetty *et al.*, 1970), the conformations are much more varied and indeed the ap,ap conformation, considered by Sundaralingam (1969) to be not preferred for the phosphate esters, appears in the two nickel complexes studied by Kastalsky *et al.* (1969) and McConnell *et al.* (1967).

It is not clear to us why the potassium dibenzyl and dimethyl phosphorodithioate esters should have different conformations, but we suspect that our success in reducing the thermal motion of the ester groups was achieved at the expense of introducing strong intermolecular forces.

Computer programs

In addition to the programs mentioned in the text, Fourier, least-squares and mean-plane calculations were carried out with the *NRC* crystallographic programs of Ahmed, Hall, Pippy & Saunderson (1966). The stereoscopic views were drawn with the *ORTEP* program of Johnson (1965).

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The Crystal Structure of [2.2.2](1,3,5)Cyclophane-1,9,17-triene

BY A. W. HANSON AND M. RÖHRL*

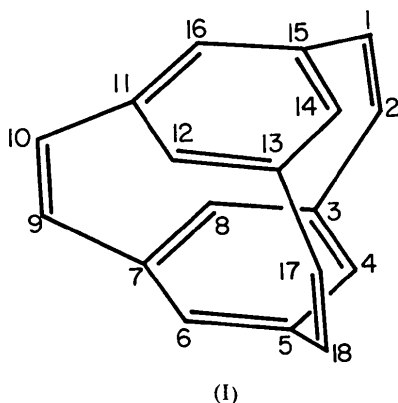
Biochemistry Laboratory, National Research Council of Canada, Ottawa, Canada K1A 0R6

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Crystals of the title compound, $C_{18}H_{12}$, are triclinic $P\bar{1}$, with $a = 7.332(5)$, $b = 11.663(10)$, $c = 7.224(5)$ Å, $\alpha = 87.73(5)$, $\beta = 100.24(5)$, $\gamma = 105.52(5)^\circ$, $Z = 2$. 1708 of a possible 1988 independent reflexions in the range $\sin \theta/\lambda \leq 0.59$ were observed and measured diffractometrically. The crystal structure was determined by symbolic addition procedures, and refined by block-diagonal least-squares methods to a final R index of 0.043. The molecule has non-crystallographic $\bar{3}m2$ symmetry. The distance between the phenyl ring planes is 2.809 Å; each ring is chair-shaped, with the atoms lying 0.024 Å above or below the mean plane. The mean length of the bridging double bonds is 1.340(4) Å.

Introduction

The title compound (I) is one of a number of cyclophanes prepared by Professor Boekelheide and his associates. Many of these compounds are highly strained and (I) appears to be more so than most (Boekelheide & Hollins, 1970). The crystal structure analysis was undertaken in order to study the distribution of strain.



Experimental details

Crystal data: F.W. 228.3, $V = 586$ Å³, $D_m = 1.29$ (by flotation), $D_x = 1.29$ g.cm⁻³, $Z = 2$, $\mu = 5.3$ cm⁻¹ (Cu $K\alpha$). The wavelength assumed for Cu $K\alpha_1$ was 1.54050 Å.

The crystal system was deduced from precession and Weissenberg photographs. The space group $P\bar{1}$ is consistent with the structure analysis.

The crystals supplied were well formed and transparent. Most were of tabular habit, but some were approximately equidimensional. The specimen used for unit-cell and intensity measurements was of dimensions 0.3 × 0.2 × 0.2 mm. All measurements were carried out with a four-circle diffractometer and scintillation counter, using nickel-filtered Cu $K\alpha$ radiation with pulse-height discrimination. The intensities were measured in the θ - 2θ scan mode (scans of 2° for $2\theta < 100^\circ$, 3° otherwise), with background counts recorded at the beginning and end of each scan. Reflexions were considered to be unobserved if their net counts were less than 4 (deca-)counts or 0.1 times the corresponding background count. It was observed that on exposure to air and X-rays the transparent crystal became opaque. No accompanying systematic changes were observed in the intensity of a standard reflexion, which was monitored during the measurement of intensity data. However, many months later the specimen was found

* National Research Council of Canada postdoctorate fellow. Present address: Süddeutsche Kalkstickstoffwerke AG, 8223 Trostberg, West Germany.