

Alkylaminodithioxodi- λ^5 -phosphanes and Related Complexes.

I. The Structure of 1,2-Dicyclohexyl-1,2-bis(diethylamino)-1,2-dithioxodi- λ^5 -phosphane

BY D. TROY AND J. GALY

Laboratoire de Chimie de Coordination du CNRS associé à l'Université Paul Sabatier, 205 route de Narbonne, 31400 Toulouse, France

AND J. P. LEGROS

Kemiska Institutionen, Box 531, 751 21 Uppsala, Sweden

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Abstract

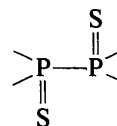
Crystals of the title compound (I), $C_{20}H_{42}N_2P_2S_2$, $S_2P_2^-(C_6H_{11})_2[N(C_2H_5)_2]_2$, $M_r = 436.6$, have been isolated and studied by X-ray single-crystal diffraction methods. The crystals are triclinic, space group $P\bar{1}$, with $a = 7.926$ (3), $b = 8.213$ (3), $c = 10.133$ (3) Å, $\alpha = 98.14$ (3), $\beta = 106.74$ (3), $\gamma = 100.59$ (2)°, $Z = 1$, $V = 607.5$ Å³, $d_m = 1.26 \pm 0.01$, $d_x = 1.19$ Mg m⁻³, $F(000) = 238$, $\mu(Cu K\alpha) = 3.448$ mm⁻¹. The atomic parameters were refined by full-matrix least-squares calculations, giving a final $R = 0.040$. The molecule is in the *meso* form. Short P–N distances (1.665 Å) suggest that the lone pairs of the N atoms are engaged in the P–N bonding; therefore, if (I) is used as a ligand, it should be bonded through the S atoms.

Introduction

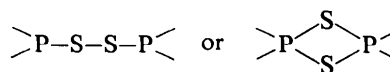
The ability of alkylaminodithioxodi- λ^5 -phosphanes of general formula $S_2P_2(NR_2)_2R'_2$ or $S_2P_2(NR_2)_4$ ($R = C_2H_5$; $R' = C_6H_5$, C_6H_{11}) to form complexes with transition-metal atoms has recently been pointed out (Troy, 1979). On account of the number of potential donor atoms [four in $S_2P_2(NR_2)_2R'_2$ and six in $S_2P_2(NR_2)_4$], special attention should be paid to the coordination mode of the ligand towards the metal atom. On the basis of spectroscopic studies, tremendous change is expected in the geometry of the $S_2P_2(NR_2)_2R'_2$ ligand molecules to allow the two S atoms to be involved in a bidentate coordination process (Troy, 1979), whereas the $S_2P_2(NR_2)_4$ molecule seems to be coordinated through one S and one N atom. In order to check and to improve these results, a crystallographic structural study of the ligand as well as of the complexes has been undertaken.

In this paper, the structural analysis of the ligand 1,2-dicyclohexyl-1,2-bis(diethylamino)-1,2-dithioxodi- λ^5 -phosphane, $S_2P_2(C_6H_{11})_2[N(C_2H_5)_2]_2$ (I), is des-

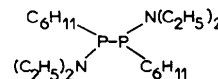
cribed. From previous X-ray studies, dithioxodi- λ^5 -phosphanes are known to contain a



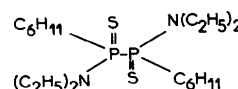
linkage rather than a



skeleton. Since (I) is obtained from reaction of sulphur with



it should be formulated as



and thus, it should contain two asymmetric P atoms. Therefore, the molecule can exist in the (+), (–) and *meso* forms and crystals of the racemate may also exist. Since the coordination process depends upon the relative positions of the donor atoms, it is important to know the exact configuration of the free ligand.

Experimental

Compound (I) was prepared as described earlier (Seidel & Issleib, 1963). Crystals (m.p. 463 K) were isolated and recrystallized from ethyl alcohol solution. A single crystal in the form of a small block was selected for space-group determination and intensity-data collection. It was sealed in a thin-walled Lindemann-glass

Table 1. *Data-collection and refinement details*

(I) Data-collection parameters

Temperature: 295 K
 Wavelength: $\lambda(\text{Cu } K\alpha_1) = 1.54051$, $\lambda(\text{Cu } K\alpha_2) = 1.54433$,
 $\lambda(\text{Cu } K\bar{\alpha}) = 1.54178 \text{ \AA}$
 Detector-crystal distance: 207 mm
 Slit: height = 4 mm; width = 4 mm
 Take-off angle: 4.75°
 Scan mode: $\omega/2\theta$
 Maximum Bragg angle: 78°
 Scan width in ω : $(1.10 + 0.14 \text{ tg } \theta)^\circ$
 Parameters for scan-speed determination: * $\sigma_{\text{pre}} = 0.33$, $\sigma = 0.01$,
 $V_{\text{pre}} = 10^\circ \text{ min}^{-1}$, $T_{\text{max}} = 90\text{s}$

(II) Refinement

Number of reflections for cell-parameter determination: 25
 Number of recorded data: 2751
 Number of independent data: 2581
 Number of observed reflections: 2220
 Number of refined parameters: 119
 Secondary-extinction parameter: $G = 0.1984 \times 10^{-5}$
 Agreement factors: $R = \sum |kF_o - |F_c|| / \sum kF_o = 0.040$
 $R_w = [\sum w^2(kF_o - |F_c|)^2 / \sum w^2 k^2 F_o^2]^{1/2} = 0.066$

* As defined by Mosset, Bonnet & Galy (1977).

tube. Data were collected on a CAD-4 Enraf-Nonius κ -geometry diffractometer, using monochromatized Cu $K\alpha$ radiation.

From precession photographs, the crystal lattice was shown to be triclinic. The cell parameters were determined through a least-squares fit of the 2θ values of 25 reflections measured on the diffractometer. The density, measured by flotation in an acetonitrile-carbon tetrachloride mixture, is in agreement with the value calculated for one molecule per unit cell. Crystal data are listed in the *Abstract*.

Intensity data for independent reflections were collected up to $\theta = 78^\circ$ using an $\omega-2\theta$ scan mode. Relevant parameters of the data collection are summarized in Table 1. A set of four standard reflections was monitored throughout the data collection and no significant change in the intensities was observed.

Structure analysis

The unit cell contains only one molecule; E statistics, Wilson's (1949) ratio, and the $N(z)$ test (Howells, Phillips & Rogers, 1950) indicate a centrosymmetric structure (Fig. 1). Thus the racemate is quite unlikely and the molecule must be in the *meso* form. The structure was therefore solved in the centrosymmetric space group $P\bar{1}$.

Lorentz and polarization corrections were applied to the integrated intensities, but no corrections were made for absorption because the crystal had a nearly isotropic shape with $\mu\bar{R} = 0.5$. The resulting structure factors were assigned standard deviations σ according

to the expression $\sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (0.02F_o^2)^2$, where $\sigma_c(F_o^2)$ is based on counting statistics.

Atoms P, S, N and C(1) were located on a three-dimensional Patterson map. From their positional parameters a set of phases was calculated and a Fourier synthesis was computed which showed the remaining non-hydrogen atoms. The structure was then refined by a full-matrix least-squares procedure with anisotropic temperature factors. The function minimized was $\sum |w(kF_o - |F_c|)|$, where k is the scale factor and w the weight of the reflections calculated as $w = 1/\sigma(F_o)$. The scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1974); anomalous-dispersion correction was introduced for P and S atoms according to Cromer & Liberman (1970).

At this stage the conventional R factors, defined in Table 1, were $R = 0.086$, $R_w = 0.069$. Most of the H atoms were then located on a difference Fourier map, the others being placed in chemically significant positions. Each H atom was assigned an isotropic temperature factor equal to 1.2 times the equivalent isotropic temperature factor of the atom to which it is bonded. Refinement with fixed positional and thermal parameters for H atoms reduced the reliability indices to the final values $R = 0.040$ and $R_w = 0.066$. Isotropic correction for secondary extinction was included by refinement of the coefficient G given in Table 1. In the last cycle, every parameter shift was less than 0.2 standard deviations.

Final positional parameters and equivalent isotropic temperature factors are listed in Table 2.* Tables 3 and 4 list the main interatomic distances and bond angles.

* Lists of structure factors, anisotropic thermal parameters and unrefined hydrogen coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34853 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

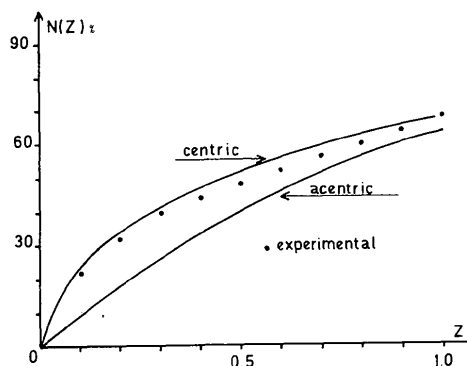


Fig. 1. Intensity-distribution curve and Wilson's ratio for hkl data. Experimental: $R = 0.653$; theoretical centric: $R = 0.637$; theoretical acentric: $R = 0.785$.

Table 2. Positional parameters ($\times 10^4$) and equivalent isotropic thermal parameters

Here and in following tables e.s.d.'s are in parentheses.

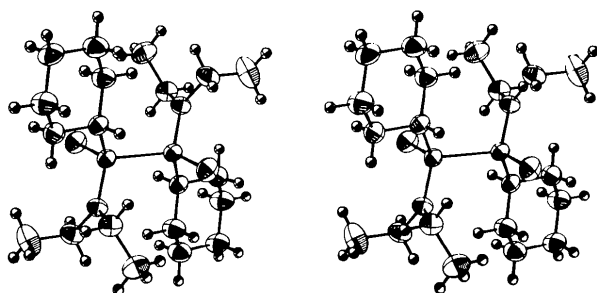
	x	y	z	B_{eq} (\AA^2)
P	948 (1)	-517 (1)	804 (1)	3.0
S	1919 (1)	-2164 (1)	-161 (1)	4.3
N	2553 (2)	1099 (2)	1908 (2)	3.3
C(1)	-439 (3)	-1419 (3)	1826 (2)	3.3
C(2)	-1922 (4)	-2997 (4)	951 (3)	4.5
C(3)	-3021 (4)	-3747 (4)	1837 (3)	5.0
C(4)	-1815 (4)	-4168 (4)	3132 (3)	4.8
C(5)	-340 (4)	-2613 (4)	3997 (3)	5.0
C(6)	789 (3)	-1863 (3)	3129 (3)	4.1
C(7)	2187 (3)	2271 (3)	2985 (2)	3.9
C(8)	2774 (5)	4119 (4)	2980 (3)	5.3
C(9)	4456 (3)	1315 (3)	1990 (3)	4.2
C(10)	5597 (5)	800 (6)	3265 (4)	7.2

Table 3. Interatomic distances (\AA)

P-P	2.254 (1)	C(1)-C(6)	1.533 (3)
P-S	1.954 (1)	C(2)-C(3)	1.535 (4)
P-N	1.665 (2)	C(3)-C(4)	1.510 (4)
P-C(1)	1.845 (2)	C(4)-C(5)	1.520 (4)
N-C(7)	1.480 (3)	C(5)-C(6)	1.535 (4)
N-C(9)	1.462 (3)	C(7)-C(8)	1.504 (4)
C(1)-C(2)	1.537 (3)	C(9)-C(10)	1.513 (4)

Table 4. Main bond angles ($^\circ$)

P-P-N	108.4 (1)	C(7)-N-C(9)	115.7 (2)
P-P-S	109.4 (1)	P-C(1)-C(2)	112.3 (2)
P-P-C(1)	104.9 (1)	P-C(1)-C(6)	109.6 (2)
N-P-S	113.0 (1)	C(2)-C(1)-C(6)	109.7 (2)
N-P-C(1)	106.7 (1)	C(1)-C(2)-C(3)	111.2 (2)
S-P-C(1)	114.0 (1)	C(2)-C(3)-C(4)	111.5 (2)
P-N-C(7)	122.1 (2)	C(3)-C(4)-C(5)	110.4 (2)
P-N-C(9)	121.7 (2)	C(4)-C(5)-C(6)	111.9 (2)
N-C(7)-C(8)	114.9 (2)	C(5)-C(6)-C(1)	110.4 (2)
N-C(9)-C(10)	113.3 (2)		

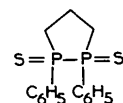
Fig. 2. Stereoscopic drawing of the $S_2P_2(C_6H_{11})_2[N(C_2H_5)_2]_2$ molecule. Ellipsoids are scaled to enclose 50% probability. H atoms are given an arbitrary isotropic thermal parameter.

Discussion

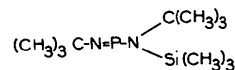
A stereoscopic drawing (Johnson, 1965) of the molecule is shown in Fig. 2. The numbering of the atoms is indicated in Fig. 3.

The distribution of bonds around the P atom is nearly tetrahedral. The small deviations from the ideal tetrahedral angle can easily be explained by the larger size of the S and P atoms as compared with C and N atoms, and by the rather short S-P separation. So, as expected, the P'-P-S angle is equal to the tetrahedral angle, while the S-P-C(1) and S-P-N angles are larger and the others smaller.

Table 5 compares the P-P, P-S and P-C distances in dithioxodi- λ^5 -phosphanes. The large P-P distance observed in (I), very close to those obtained in



(Lee & Bolorizadeh, 1978), could be due to a steric effect on account of the large volume occupied by the groups bonded to the P atoms. It seems that there is no double-bond character in the P-P bond of this compound. The P-S and P-C distances are similar to those obtained previously and close to the sum of the double-bond and single-bond radii, respectively, according to Pauling (1960). In the same type of comparison, the P-N distance is closer to the double bond than to the single bond (sum of the covalent radii: P-N = 1.80, P=N = 1.60 \AA). When compared with the structure of



(Pohl, 1976) it appears to be intermediate between the P-N single bond (1.77 \AA) and the P=N double bond

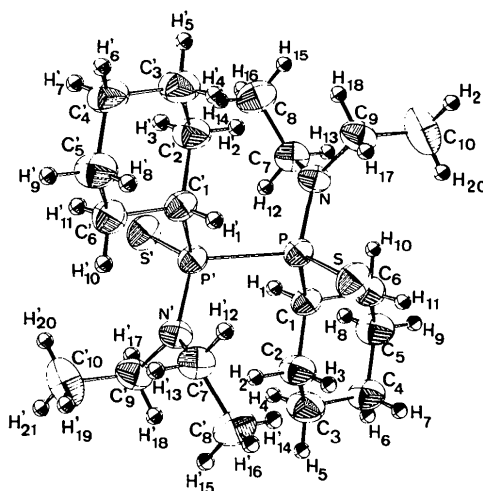
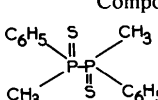
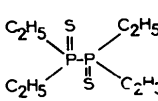
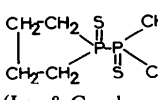
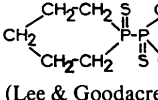
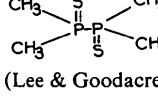
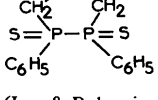
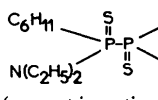
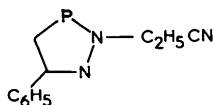


Fig. 3. Numbering of the atoms in the molecule.

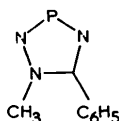
Table 5. P-P, P=S and P-C distances (Å) in some dithioxodi- λ^3 -phosphanes (X-ray diffraction methods)

Compound	P-P	P=S	P-C
 (Wheatley, 1960)	2.21	1.98	1.82 1.88
 (Dutta & Woolfson, 1961)	2.22 (1)	1.94 (1)	1.830 (15)
 (Lee & Goodacre, 1969)	2.210 (4)	1.950 (4)	1.820 (7) 1.820 (7)
 (Lee & Goodacre, 1970)	2.210 (4)	1.950 (4)	1.810 (7) 1.810 (11)
 (Lee & Goodacre, 1971)	2.245 (6) 2.161 (4)	1.951 (3) 1.970 (4) 1.965 (4)	1.800 (8) 1.820 (8) 1.820 (8)
 (Lee & Bolorizadeh, 1978)	2.253 (2)	1.943 (2) 1.944 (2)	1.802 (6) 1.817 (6) 1.832 (6) 1.838 (6)
 (present investigation)	2.254 (1)	1.954 (1)	1.845 (2)
Sum of the covalent radii corrected for the difference of electronegativity (Pauling, 1960)	2.20	1.92 (double bond)	1.84

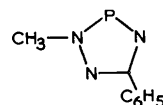
(1.54 Å), but this latter value, rather short, suggests partial triple-bond character. This P-N separation of 1.665 Å is in the vicinity of the P-N distances in the following compounds:



P-N = 1.676 Å (Andrianov, Struchkov, Shvetsov-Shilovskii, Ignatova, Bobkova & Mel'nikov, 1973);



P-N = 1.627 and 1.654 Å (Legros, Charbonnel, Barrans & Galy, 1978);



P-N = 1.67 and 1.62 Å (Legros, Charbonnel, Barrans & Galy, unpublished results); where resonance occurs between single and double bonds. Furthermore, the distribution of the bonds around the N atom is planar. These features can be explained by a $p\pi-d\pi$ interaction between the lone pairs of the N atom and the d orbitals of the P atom. In that case, the coordination of the ligand may occur through the S atoms since the 'lone pairs' of the N atoms are already engaged. This assumption will be checked by solving the structures of related complexes.

The shortest intermolecular S...H separation being 3.14 Å, no intermolecular hydrogen bonding is assumed, since the sum of the van der Waals radii for S and H is 3.05 Å according to Pauling (1960), or 2.92 Å according to several other workers (van der Helm, Lessor & Merritt, 1960; Fava Gasparri, Nardelli & Villa, 1967; Lee & Bryant, 1969*a,b*).

Other distances and angles are normal and no further discussion is needed. Nevertheless, it should be pointed out that the C_6H_{11} groups are stabilized in the chair conformation and no disorder due to a 'flip-flop' phenomenon is observed.

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The Structure and Absolute Configuration of PR Toxin

BY F. BAERT,* M. FOULON AND G. ODOU

Laboratoire de Physique des Solides, Equipe de Dynamique des Cristaux Moléculaires associée au CNRS (n° 465), Université des Sciences et Techniques de Lille I, 59650 Villeneuve d'Ascq, France

AND S. MOREAU

INSERM (U42), 369 rue Jules Guesde, 59650 Villeneuve d'Ascq, France and Laboratoire de Chimie Organique Physique, Université des Sciences et Techniques de Lille I, 59650 Villeneuve d'Ascq, France

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Abstract

$C_{17}H_{20}O_6$ is orthorhombic, space group $P2_12_12_1$, with $a = 13.980$ (11), $b = 12.341$ (12), $c = 9.609$ (9) Å, $Z = 4$. The structure was determined from 2622 independent intensities and refined to $R = 0.043$. The absolute configuration was solved by the Bijvoet method and corresponds to that predicted on chemical bases. The crystal structure is stabilized by van der Waals forces only.

Introduction

PR toxin has been isolated from cultures of *Penicillium Roqueforti* (Wei, Schnoes, Hart & Strong, 1975). The biological properties result particularly in the inhibition of protein and RNA synthesis (Moule, Jemmali & Rousseau, 1976). A study of the relationships between the chemical structure and the biological properties suggested the important role of an aldehyde group in position 12 associated with an epoxide group and an α,β -unsaturated ketone (Moule, Moreau & Bousquet, 1977). In order to discover the action mechanism, it was important to determine the absolute configuration,

since the octant rule of circular dichroism cannot be used on such a complicated ketone. The impossibility of obtaining a well crystallized Br derivative led us to attempt the determination of the absolute configuration from the anomalous dispersion of the O atoms.

Experimental

A well shaped crystal $0.30 \times 0.24 \times 0.21$ mm was chosen. The crystallographic data are reported in Table 1. Intensities for 2622 reflections were measured by the ω - 2θ scan on a four-circle Philips diffractometer. The scan width was 1.2° . The data were corrected for Lorentz and polarization factors, but not for absorption or extinction. 1284 reflections with $I \geq 3\sigma(I)$ were considered in the determination of the structure.

Table 1. *Crystal data*

$C_{17}H_{20}O_6$, orthorhombic, $P2_12_12_1$	
$M_r = 320.27$	$\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$
$a = 13.980$ (11) Å	$\mu(\text{Mo } K\alpha) = 0.103 \text{ mm}^{-1}$
$b = 12.341$ (12)	$\lambda(\text{Cu } K\alpha) = 1.5418 \text{ \AA}$
$c = 9.609$ (9)	$\mu(\text{Cu } K\alpha) = 0.812 \text{ mm}^{-1}$
$V = 1657.8 \text{ \AA}^3$, $Z = 4$	$F(000) = 680$
$D_x = 1.28 \text{ Mg m}^{-3}$	Room temperature 294 (2) K

* To whom correspondence should be addressed.