

## Alkylaminodithioxodi- $\lambda^5$ -phosphanes and Related Complexes. Part(II)\*. Molecular Structure of Tetrakis(diethylamino)dithioxodi- $\lambda^5$ -phosphane and Vibrational Spectra of Analogous Ligands

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Received June 8, 1981

The tetrasubstituted dithioxodi- $\lambda^5$ -phosphanes  $R(Et_2N)P(S)(P(S)(NEt_2)R$ ,  $R = Et_2N(L_I)$ ,  $C_6H_{11}(L_{II})$ ,  $C_6H_5(L_{III})$ , have been investigated. The crystal structure of  $L_I$  was solved at room temperature. It crystallizes in the monoclinic system, space group  $P2_1/n$ . The cell parameters are  $a = 9.208(2)$  Å,  $b = 12.859(3)$  Å,  $c = 10.397(4)$  Å and  $\beta = 97.56(2)^\circ$  with  $Z = 2$ . A least squares constraint refinement of the structure led to a conventional weighted  $R_w$  factor of 0.090. The molecule is built of two  $(Et_2N)_2P(S)$  moieties related by a symmetry centre lying in the middle of the P–P bond. Thus the  $L_I$  ligand has a similar 'trans' conformation to that previously found for  $L_{II}$ . The nitrogen atoms are in a planar environment and the molecule is expected to coordinate through the sulphur atoms. The methylene carbon atoms are disordered, causing the overall distribution of the atoms to exhibit a pseudo-symmetry about the SPPS plane. Assignments are proposed for the vibrational spectra of the solid ligands, based on the X-ray data and comparisons with related molecules.

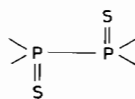
### Introduction

The tetrasubstituted dithioxodi- $\lambda^5$ -phosphanes with general formula  $RR'P(S)–P(S)R''R'''$  constitute a class of potentially bidentate ligands liable to bind to metals through their sulphur atoms. The possibility of rotation about the P–P bond gives them the ability to accommodate a number of geometric requirements when they are chelated. The molecular structures and conformations of the free ligands and their complexes are therefore of particular interest, but the literature on this topic is rather sparse. The molecular structure of 'symmetric' ligands  $R_2P(S)–P(S)R_2$  ( $R = Me, Et,$

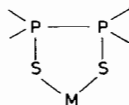
Pr, Bu,  $C_3H_5$ , Ph,  $C_6H_{11}$ ) has been established by spectroscopic methods [1–7] and confirmed by X-ray diffraction for some of them [8–10]. The crystal structures of  $(Me)(Ph)P(S)–P(S)(Me)(Ph)$  [11],  $\square_{P(S)–P(S)} \square$  [12] and  $\diamond_{P(S)–P(S)} \diamond$  [13] have also been determined.

A series of complexes of the ligands  $R_2P(S)–P(S)R_2$  ( $R = Me, Et, Pr, Bu, C_3H_5$ ) with a number of metals has been obtained and studied spectroscopically [2, 6, 14–17]. The only complexes to have been investigated by X-ray diffraction methods are the copper(I) and copper(II) compounds  $[Me_4P_2S_2 \cdot CuCl]_2$  and  $[Me_4P_2S_2 \cdot CuCl_2]_n$  [18, 19].

It is well established that the ligands have the 'trans' conformation

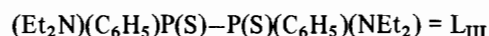
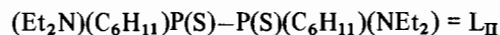
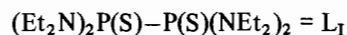


in the solid state (with perhaps a small amount of 'trans-gauche' isomerism in solution for some of them), but the conformation of the chelated ligand



is not so clearly defined.

We are interested here in dithioxodi- $\lambda^5$ -phosphanes containing, in addition to the sulphur atoms, other potential donor atoms such as nitrogen. In this work, the ligands:



\*Part I: reference [20].

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have been synthesized and complexes prepared with a number of metals.

The crystal structure of the  $L_{II}$  ligand has been published previously [20]. In this paper we complete the structural characterization of the free ligands with the crystal structure of the  $L_I$  ligand in order to establish precisely the coordination sites among the six potential donor atoms. An assignment of the IR and Raman spectra is then proposed as a basis for further study of the metal complexes.

### Synthesis

The ligands  $R_2R'_2P_2S_2$  were obtained from the reaction of corresponding diphosphanes  $R_2R'_2P_2$  with sulphur in benzene solution, under nitrogen, as described earlier for  $L_{II}$  and  $L_{III}$  [21]. Stereoisomers of the meso-form and the racemate were isolated in the case of  $L_{II}$  and  $L_{III}$  which contain two asymmetric P atoms. Analytical data, melting points and  $^{31}P$  chemical shifts of  $L_I$ ,  $L_{II}$  and  $L_{III}$  are listed in Table I.

$^{31}P$  NMR spectra were recorded with Perkin-Elmer R 10 and Bruker WH 90 spectrometers. All shifts refer to external  $H_3PO_4$  (85%) and are in ppm with a positive sign indicating a low-field shift.

### X-ray Structure Determination of $L_I$

#### Data Collection

Crystal data are reported in Table II.

Single crystals of  $L_I$  were obtained by evaporation to dryness of a diethylether solution. A thick plate ( $0.8 \times 0.6 \times 0.25$ ) mm was sealed in a Lindeman glass capillary. The space group was determined from precession photographs. The systematic absences ( $0k0$ ,  $k = 2n + 1$ ;  $h01$ ,  $h + 1 = 2n + 1$ ) led to the space group  $P2_1/n$ , a non standard setting of  $P2_1/c$  with general position coordinates  $\pm(x, y, z; 1/2 + x, 1/2 - y, 1/2 + z)$ .

The crystal was mounted on a CAD4 Enraf-Nonius automatic diffractometer. The orientation matrix and the cell parameters were obtained by least squares refinement of the setting angles of 25 reflections. The data collection was run in the  $\omega-2\theta$  scanning mode up to a Bragg angle  $\theta = 20^\circ$ . Other relevant details of the data collection are listed in Table II. The intensity of three standard reflections was monitored throughout the data collection; no significant fluctuation was noticed.

The net intensities were assigned standard deviations according to the formula

$$\sigma^2(I) = \sigma_c^2(I) + (0.03I)^2$$

where  $\sigma_c^2(I)$  was based on counting statistics.

TABLE I. Analytical Data.

Compounds	%C		%H		%N		%P		%S		Melting point (°C)	$\delta^{31}P^a$ (ppm)
	Found	Calc	Found	Calc	Found	Calc	Found	Calc	Found	Calc		
$L_I$	46.1	46.3	9.5	9.7	13.1	13.5	14.4	14.9	15.9	15.5	99-100	66.0
$L_{II}$	55.1	55.0	9.3	9.7	6.3	6.4	14.1	14.2	14.9	14.7	191	73.0
	55.1		9.6		6.4		14.1		14.9		160	77.0
$L_{III}$	57.0	56.6	7.2	7.1	6.8	6.6	14.4	14.6	15.1	15.1	125	58.5
	56.6		7.0		6.4		14.2		15.3		101	59.5

<sup>a</sup> In benzene solutions.

TABLE II. Crystallographic and Physical Data for  $((C_2H_5)_2N)_2P(S)-P(S)(N(C_2H_5)_2)_2$ .

Physical and crystallographic data			
Formula: $C_{16}H_{40}N_4P_2S_2$	Molecular weight: 414.3		
Crystal system: Monoclinic	Space group: $P2_1/n$		
$a = 9.208(2) \text{ \AA}$	$V = 1220.3 \text{ \AA}^3$		
$b = 12.859(3) \text{ \AA}$	$Z = 2$		
$c = 10.397(4) \text{ \AA}$	$F(000) = 452$		
$\beta = 97.56(2)^\circ$			
$\rho_{\text{exp}} = 1.06(4) \text{ g/cm}^3$ ; $\rho_x = 1.13 \text{ g/cm}^3$			
Absorption factor: $\mu_{(\lambda Mo K\alpha)} = 3.45 \text{ cm}^{-1}$			
Data collection			
Temperature : 20 °C			
Radiation: Mo(K $\alpha$ )	$\lambda K\bar{\alpha} = 0.71069$		
Monochromatisation: graphite monochromator			
Crystal detector distance: 207 mm			
Detector window: height* = 4 mm, width* = 4 mm			
Take-off angle: 4°			
Scan mode: $\omega-2\theta$			
Maximum Bragg angle: 20°			
Scan angle: $(1.2 + 0.35 \text{tg}\theta)^\circ$ for omega angle			
Values determining the scan speed:			
SIGPRE* = 0.5	SIGMA* = 0.015	VPRE* = 10°/mn	TMAX* = 50
Controls: -intensity		-orientation	
Reflections: 080, 170, $\bar{1}03$		00 $\bar{6}$ , 015, $\bar{1}03$	
Periodicity: 7200 s		after 200 reflections	
Conditions for constraint refinement			
Reflections for the refinement of the cell dimensions: 25			
Recorded reflections: 2146 (excluding standards)			
Independent reflections: 2052			
Utilized reflections: 1090 ( $I > 3\sigma(I)$ )			
Refined parameters: 183			
Reliability factors: $R = \Sigma k F_o  -  F_c  / \Sigma k F_o  = 0.096$			
$R_w = \{ \Sigma w(k F_o  -  F_c )^2 / \Sigma w k^2 F_o^2 \}^{1/2} = 0.090$			

\*As defined by A. Mosset, J. J. Bonnet and J. Galy, *Acta Cryst.*, B33, 2639 (1977).

The usual Lorentz polarization correction was applied to the net intensities. The standard deviations of the resulting structure factors were calculated as

$$\sigma(F_o) = \frac{\sigma(I)}{2F_o * LP}$$

where LP is the Lorentz polarization factor.

Absorption corrections were calculated by the Gaussian integration method [22] using a 216 points grid; transmission factors ranged between 0.829 and 0.936.

The overall Debye Waller temperature factor deduced from a Wilson plot was very high ( $4.7 \text{ \AA}^2$ ) but all attempts to record low-temperature data resulted in the crystal being cracked. So, in spite of the thermal smearing, the room temperature data were used for structure determination.

### Structure Solution

The structure was solved by direct methods and refined by full matrix least squares procedures [23]. The function minimized was  $\Sigma[w(k|F_o| - |F_c|)^2]$  where  $k$  is the scale factor and  $w$  is the weight of each reflection; this weight was first taken as  $w = 1/\sigma^2(F_o)$  but in the final stages of the refinement all reflections were given a unit weight. Scattering factors were taken from ref. [24] and an anomalous dispersion correction was applied to the S, P and N atoms.

After the S, P and N atoms had been localized and refined with isotropic temperature factors, examination of the Fourier difference map showed each methylene carbon atom to be distributed over two different positions. The occupancy factor of each was given the value 0.5 and was not refined. The temperature factors of all non hydrogen atoms were first refined isotropically and then anisotropically. The

reliability factors dropped to  $R = 0.109$  and  $R_w = 0.110$ .

The hydrogen atoms were not refined. Their contribution was calculated using idealized atomic positions deduced either from difference Fourier synthesis or from geometric considerations; an isotropic temperature factor  $B = 5 \text{ \AA}^2$  was assumed. The final reliability factors were  $R = 0.092$  and  $R_w = 0.086$ .

#### *Pseudo-Symmetry, Disorder and Constraint Refinement*

The model obtained at this stage of refinement displayed the following features:

i) The monomeric  $(\text{Et}_2\text{N})_4\text{P}_2\text{S}_2$  molecule is built of two  $(\text{Et}_2\text{N})_2\text{PS}$  asymmetric units related by a symmetry centre lying in the middle of the P–P bond (Fig. 1).

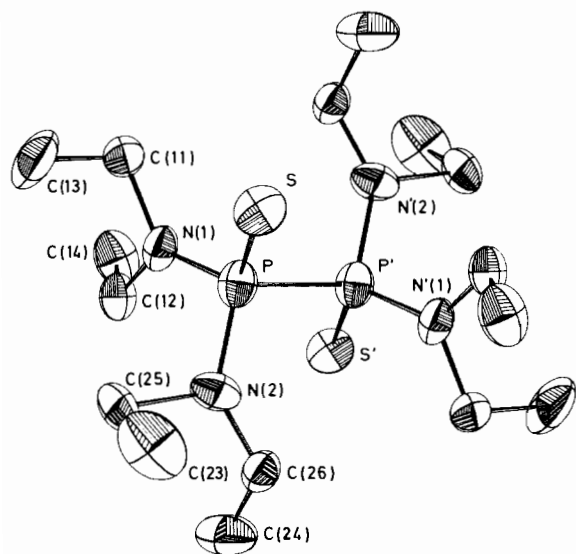


Fig. 1. ORTEP drawing of the  $(\text{Et}_2\text{N})_2\text{P}(\text{S})\text{-P}(\text{S})(\text{NEt}_2)_2$  molecule displaying the numbering scheme. For clarity, the carbon atoms C(15), C(16), C(21), C(22) which are disordered positions of C(11), C(12), C(25), C(26) respectively have not been drawn. The ellipsoids are scaled to enclose 25% probability.

ii) Although the SPPS plane (which is virtually identical to the  $bc$  plane) is not a crystallographic symmetry plane, the overall distribution of the atoms is nearly symmetric about this plane. This is shown by the projection down the P–P bond represented on Fig. 2. To emphasize this 'pseudo-symmetry', the numbering scheme of the carbon atoms is as follows: each carbon atom is given a two digits number C(ij); two atoms having the same j's are 'pseudo-symmetrically related'. Note that because of the disorder C(i5) and C(i6) are alternative positions of C(i1) and C(i2) respectively.

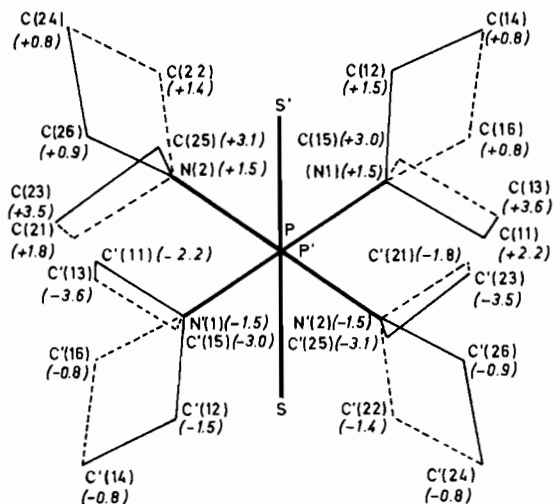


Fig. 2. Projection of the molecule down the P–P bond showing the pseudo-symmetry about the SPPS plane. The projection plane passes through the symmetry centre in the middle of the P–P bond. The heights of the N and C atoms above the projection plane are indicated in Å. The thin full and dotted lines indicate the two alternative positions of the N–C–C chains.

iii) The individual N–C and C–C bond lengths showed some inconsistencies, probably as a result of the disorder and pseudo-symmetry.

To deal with these difficulties a constraint refinement was carried out using the SHELX system [25]. The constraints applied were as follows: all the N–C bonds were forced to be equal and their common length was refined; the starting value was taken as equal to the mean value derived from the conventional refinement. The C–C bonds were treated in the same way. This refinement led to the reliability indexes  $R = 0.118$  and  $R_w = 0.119$ , all temperature factors being anisotropic. The hydrogen contribution was then calculated, each hydrogen atom being placed in a calculated idealized position with fixed isotropic temperature factor  $B = 5 \text{ \AA}^2$ . The C–H bond length was given the value  $0.97 \text{ \AA}$ . The  $-\text{CH}_2-$  and  $-\text{CH}_3$  groups were then refined as independent rigid bodies. Final reliability factors were  $R = 0.096$  and  $R_w = 0.090$ . In the final cycle all parameter shifts were less than 0.2 times their standard deviation.

Final atomic parameters from the constraint refinement are given in Table III, interatomic distances and bond angles are reported in Table IV. The observed and calculated structure factors can be obtained upon request from the authors.

All the carbon atoms have very high thermal parameters, but the strongly elongated ellipsoids of the methyl carbon atoms may well indicate that these atoms are disordered too; however, this disorder could not be solved. These indications together with

TABLE III. Atomic Coordinates and Thermal Factors of All Non-hydrogen Atoms.<sup>a</sup>

Atom	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
S	0.0015(4)	0.3594(2)	0.1747(3)	0.117(2)	0.093(2)	0.086(2)	-0.0004(2)	0.016(2)	0.036(2)
P	0.0287(3)	0.4994(2)	0.1083(2)	0.089(2)	0.091(2)	0.063(1)	-0.010(2)	0.005(1)	0.011(2)
N(1)	0.1976(9)	0.5435(7)	0.1355(8)	0.059(5)	0.119(8)	0.066(5)	-0.008(5)	0.004(4)	-0.003(5)
N(2)	-0.076(1)	0.5912(8)	0.1623(9)	0.091(7)	0.105(7)	0.089(7)	0.013(6)	0.041(6)	-0.009(6)
C(11)	0.316(2)	0.472(2)	0.180(2)	0.08(2)	0.13(2)	0.12(2)	-0.01(2)	0.03(1)	-0.04(2)
C(12)	0.242(2)	0.652(1)	0.130(2)	0.07(1)	0.12(2)	0.06(1)	-0.03(1)	-0.01(1)	0.01(1)
C(13)	0.373(2)	0.483(2)	0.322(1)	0.11(1)	0.28(2)	0.12(1)	0.02(1)	-0.04(1)	0.01(1)
C(14)	0.361(1)	0.674(1)	0.048(1)	0.13(1)	0.13(1)	0.11(1)	-0.04(1)	0.023(8)	-0.014(9)
C(15)	0.253(3)	0.559(2)	0.271(1)	0.10(2)	0.29(4)	0.09(2)	-0.06(2)	0.01(2)	0.01(3)
C(16)	0.304(2)	0.565(1)	0.048(2)	0.12(2)	0.12(2)	0.10(2)	0.02(2)	-0.05(2)	-0.01(2)
C(21)	-0.205(2)	0.555(2)	0.216(2)	0.11(2)	0.11(2)	0.19(3)	-0.03(2)	0.05(2)	-0.04(2)
C(22)	-0.056(2)	0.701(1)	0.140(2)	0.15(3)	0.12(2)	0.10(2)	-0.01(2)	0.05(2)	0.00(2)
C(23)	-0.177(2)	0.569(1)	0.361(1)	0.31(3)	0.17(2)	0.15(2)	-0.03(2)	0.15(2)	-0.01(1)
C(24)	-0.187(2)	0.769(1)	0.098(1)	0.17(1)	0.13(1)	0.13(1)	0.03(1)	0.04(1)	0.01(1)
C(25)	-0.051(2)	0.613(2)	0.301(1)	0.14(2)	0.09(2)	0.13(2)	0.00(2)	0.07(2)	-0.03(2)
C(26)	-0.200(2)	0.652(1)	0.105(2)	0.08(2)	0.12(2)	0.07(1)	-0.02(2)	0.03(1)	-0.01(1)

<sup>a</sup>Estimated standard deviations on the least significant figure are given in parentheses in this and subsequent tables. The form of the anisotropic thermal factor is  $\exp[-2\pi^2(U_{11}a^2h^2 + \dots + 2U_{12}ab*hk + \dots)]$ .

TABLE IV. Selected Bond Lengths and Bond Angles.

P-P'	2.244(5)	S-P-P'	109.6(2)
P-S	1.956(4)	S-P-N(1)	114.7(4)
P-N(1)	1.644(8)	S-P-N(2)	115.2(4)
P-N(2)	1.667(9)	P'-P-N(1)	105.3(4)
N-C*	1.451(6)	P'-P-N(2)	105.2(4)
C-C*	1.503(9)	N(1)-P-N(2)	105.9(5)
		P-N(1)-C(11)	119(1)
		P-N(1)-C(12)	126(1)
		P-N(1)-C(15)	115(1)
		P-N(1)-C(16)	131(1)
		P-N(2)-C(21)	116(1)
		P-N(2)-C(22)	123(1)
		P-N(2)-C(25)	117(1)
		P-N(2)-C(26)	135(1)
		C(11)-N(1)-C(12)	114(1)
		C(15)-N(1)-C(16)	114(1)
		C(21)-N(2)-C(22)	120(2)
		C(25)-N(2)-C(26)	108(1)

\*Common bond length.

the high value of the final reliability indices suggest strongly that the proposed disorder scheme is incomplete, but the essential features of the structure have been correctly defined.

#### Discussion

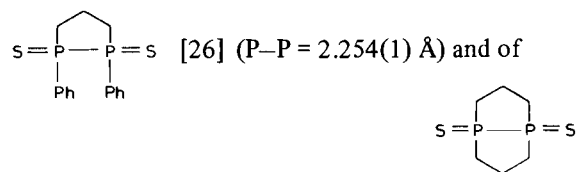
The  $L_I$  molecules lie across the symmetry centre and thus adopt the 'trans' conformation, the SPSS skeleton being strictly planar. This feature was previously observed in the structure of  $L_{II}$  [20]. Available X-ray structures of alkyl or aryl-substituted dithioxodi- $\lambda^5$ -phosphanes display the same feature [8-13].

The overall 'pseudo-symmetry' about the SPSS plane does not mean that the  $L_I$  molecule must be 'symmetric' about this plane. Indeed, when the steric possibilities are taken into account, it can be seen that the  $(Et_2N)_2PS$  asymmetric unit can only adopt the two alternative geometries described by the following sequence: C(13)-C(11)-N(1)-C(12)-C(14), C(23)-C(25)-N(2)-C(26)-C(24) (full lines on Fig. 2) or C(13)-C(15)-N(1)-C(16)-C(14), C(23)-C(21)-N(2)-C(22)-C(24) (dotted lines on Fig. 2).

Other configurations are impossible for steric reasons.

The spacial arrangement of the bonds around the P atom in  $L_I$  is nearly tetrahedral with the expected deformations due to the larger size of S and P atoms with respect to the N atoms. The P-P bond length (2.244(5) Å) is of the same magnitude as in the  $L_{II}$  molecule (2.254(1) Å). Such a 'long' P-P bond (as compared with the mean value 2.21 Å observed in the alkyl analogs) is not uncommon since  $Ph_2P(S)-P(S)Ph_2$  exhibits a 2.263(4) Å P-P separation [10]. The steric crowding of the groups bonded to the P

atoms could be responsible for the lengthening of the P-P bond. Further comparisons are afforded by the structures of



[27, 28] (two polymorphic forms with P-P = 2.204(3) and 2.197(5) Å). However in the structure of  $Me_2P(S)-P(S)Me_2$  [8] there are two independent molecules with P-P separations of 2.161(4) and 2.245(6) Å. These results disagree with the common idea of a fairly constant P-P bond length. It seems from the above discussion that the length of the P-P bond can vary slightly (perhaps under steric strains).

The P-S distance in  $L_I$  is quite similar to that in  $L_{II}$  and in other dithioxodi- $\lambda^5$ -phosphanes.

The two P-N bond lengths (1.644(8) and 1.667(9) Å) compare fairly well with those observed in other compounds where the P-N bonds are believed to be intermediate between a single and a double bond (some comparisons are given in ref. [20]). The increase of the P-N bond multiplicity is commonly attributed to a  $p\pi \rightarrow d\pi$  interaction between the 'lone pair' of the N atom and the empty d orbitals of the P atom. This is supported by the planar distribution of the bonds around nitrogen. Thus the N atoms are not expected to possess significant donor properties.

#### Vibrational Spectra

Infra-red spectra were recorded in the 4000-250  $cm^{-1}$  region with Perkin-Elmer 335 and 225 spectrophotometers. Raman spectra were obtained at the University of Aberdeen using a Cary 83 Raman spectrophotometer with 488.0 nm laser excitation, calibrated against appropriate neon lines.

Details of the vibrational spectra of the solid compounds  $L_I$ ,  $L_{II}$  and  $L_{III}$  are collected in Table V, with proposed assignments as far as possible. In the cyclohexyl and phenyl-substituted compounds  $L_{II}$  and  $L_{III}$  there are obviously possibilities for confusion between vibrations of the cyclohexyl or phenyl groups and those of the diethylamino groups, but in general the correlations between the three sets of spectra are good. Assignments for  $L_I$  and for the skeletal and diethylamino vibrations in  $L_{II}$  and  $L_{III}$  are given in the left-hand column of the Table; additional or possible alternative assignments for cyclohexyl or phenyl modes are indicated in the right-hand column. No Raman data are available for  $L_I$ .

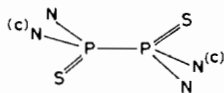
The skeletal PS and PP stretching vibrations are readily identified in the light of the X-ray data for

TABLE V. Vibrational Spectra ( $\text{cm}^{-1}$ ).

Assignments Skeletal $\text{Et}_2\text{N}$	$L_I$	$L_{II}$		$L_{III}$		Assignments	
	IR <sup>a</sup>	IR <sup>a</sup>	R <sup>b</sup>	IR <sup>a</sup>	R <sup>b</sup>	$\text{C}_6\text{H}_{11}$ <sup>c</sup>	$\text{C}_6\text{H}_5$ <sup>d</sup>
CH <sub>2</sub> wag	{ 1200 s 1170 sh 1160 s	1195 s	1192 m	1195 s	1190 w	{ CH <sub>2</sub> C-C	{ $\beta$ -CH (a, c)
		1175 ms	1180 w	1185 sh			
		1162 s	1160 w	1160 m			
CH <sub>3</sub> rock	{ 1103 m 1075 w	1105 ms	1110 w	1095 s	1100 s	{ skeletal C-C	{ x-sens(q) $\beta$ -CH (d)
		1082 w	1077 mw	1080 mw	1085 m		
CH <sub>2</sub> twist	1055 m	1058 w	1060 m 1048 mw	1060 m			
$\nu\text{C-C}$	1010 vs	1010 vs, br 995 ms	1000 w	1020 vs 1010 vs 1000 ms	1000 vs		$\beta$ -CH(b)
$\nu\text{N-C}$	{ 945 s 932 s 912 m	932 vs	937 w	955 sh	940 w	{ $\gamma$ -CH rCH <sub>2</sub> skeletal C-C	{ ring (p) $\gamma$ CH(h, i) $\gamma$ CH(g)
		912 m	928 mw	925 sh	925 w		
		912 m	915 w	893 vw			
CH <sub>2</sub> rock	{ 790 s 775 sh	790 vs	792 vw	787 s	775 w		
		775 sh	778 vw	770 ms			
$\nu_s\text{P-C}$			756 m	750 s 743 vs	750 w		{ $\gamma$ CH(f)
$\nu_{as}\text{P-C}$		740 vs					
$\nu\text{P-N}$	{ 692 s 675 m	672 s	680 w	730 s	735 vw	{ $\phi$ CC(v) x-sens(r)	
		675 m	640 vs	710 vvs, br 690 vvs, br	720 m 693 m		
$\nu_s\text{P-S}$					660 vs		
$\nu_{as}\text{P-S}$	590 s	600 vs		618 vs 608 vs	615 m		$\alpha$ CCC(s)
$\nu\text{P-P}$			547 m		585 vw 565 vw 535 m		
		501 m	498 s	505 w			
PNC <sub>2</sub> def.	{ 480 m 470 w	471 ms	453 m	483 ms, br	488 m	{ skeletal C-C	{ x-sens (y, t)
		450 m	435 w	455 m	478 vs		
PNC <sub>2</sub> def.	{ 423 ms 420 sh	410 w	425 w, sh	428 ms	439 m		
		380 vs		395 vs			$\phi$ CC(w)
			365 ms 345 sh 300 vs, br 245 m 223 vs 203 vs 183 vs 155 vvs		349 vs 300 m 250 m 223 vs 165 vs 155 vvs		

<sup>a</sup>KBr pellets. <sup>b</sup>Powdered solids. <sup>c</sup>See e.g. Ref. 41. <sup>d</sup>Vibrations labelled in conformity with Refs. 39, 40.  
v, very; s, strong; m, medium; w, weak; br, broad; sh, shoulder.

$L_I$  and  $L_{II}$  and by comparison of the spectra with those of the parent diphosphanes [29] and related molecules [1–7, 30]. The trans



skeletons of  $L_I$  and  $L_{II}$  have  $C_{2h}$  and  $C_i$  symmetry respectively. In both cases, only  $\nu_{as}PS$  as IR-active;  $\nu_sPS$  and  $\nu PP$  are Raman-active and the assignments are straightforward. (The internal vibrations of the diethylamino, cyclohexyl and phenyl groups are not effectively coupled and hence have identical IR and Raman frequencies, or very nearly so). The spectrum of  $L_{III}$  is entirely consistent with that of  $L_{II}$  and the molecule clearly must have a centrosymmetric *trans* structure analogous to that of  $L_{II}$ .

The antisymmetric PS stretching modes appear between  $590\text{--}620\text{ cm}^{-1}$  (IR) with the Raman-active symmetric modes about  $40\text{ cm}^{-1}$  higher, as is usually the case in molecules of this type [1, 3, 4, 7]. The PS frequencies in  $L_{III}$  are about  $20\text{ cm}^{-1}$  higher than the corresponding frequencies in  $L_{II}$ , reflecting the difference in substituent effects between the phenyl and cyclohexyl substituent groups [31]. The frequencies in  $L_I$  and  $L_{II}$  are themselves relatively high, compared with the simple tetraalkyl compounds [1, 3, 4] and presumably are influenced by the electron-withdrawing effect of the diethylamino groups.

The P–P stretching modes in  $L_{II}$  and  $L_{III}$  are assigned at  $547$  and  $535\text{ cm}^{-1}$  respectively, close to the value ( $536\text{ cm}^{-1}$ ) observed for the corresponding vibration in tetraphenyl-1,2-dithioxodi- $\lambda^5$ -phosphane [7], and at the upper end of the frequency range (approximately  $430\text{--}550\text{ cm}^{-1}$ ) usually observed for this vibration. The P–P bonds in  $L_I$ ,  $L_{II}$  (and no doubt also  $L_{III}$ ) and the tetraphenyl compound are all relatively long [10, 20] and there is obviously no simple relationship between the P–P bond length and stretching frequency.

Vibrational assignments for dialkylaminophosphines and various related compounds have been made by Lafitte [32], by Goubeau *et al.* [33–35] and by Davidson and Phillips [36]. Such structural data as are available [*e.g.* for tris(dimethylamino)-phosphine [37]] suggest that the dialkylamino groups in these compounds are generally comparable with those in  $L_I$ ,  $L_{II}$  and  $L_{III}$  and can therefore be used as a basis for the assignment of the diethylamino vibrations in the latter molecules. In particular, PN stretching frequencies are assigned near  $700\text{ cm}^{-1}$  and NC stretches near  $900\text{ cm}^{-1}$ .

In the tetrakis(diethylamino) compound  $L_I$  we expect two IR-active PN stretching modes (Au and Bu in terms of the approximate  $C_{2h}$  molecular symmetry,  $a'$  and  $a''$  if the local  $C_s$  symmetry of the diethylamino group only is considered). The cor-

responding vibrations in  $L_{II}$  and  $L_{III}$  should give rise to one IR-active and one Raman-active mode, with a frequency separation depending on the degree of coupling between the  $PNEt_2$  groups. The well-defined IR bands at  $692$  and  $675\text{ cm}^{-1}$  in  $L_I$  are readily assigned to the PN stretching modes, and appropriate IR and Raman bands appear in the corresponding frequency region in the spectra of  $L_{II}$  and  $L_{III}$ . Three NC stretching vibrations (of a possible four) can be assigned between  $900$  and  $950\text{ cm}^{-1}$  in the IR spectrum of  $L_I$ ; there are similar bands in the spectra of  $L_{II}$  and  $L_{III}$  but the assignments here are complicated by possible overlaps with cyclohexyl or phenyl vibrations.

The PC stretching vibrations in  $L_{II}$  are assigned at  $756\text{ cm}^{-1}$  (R, Ag) and  $740\text{ cm}^{-1}$  (IR, Au) by comparison with the spectrum of tetrakis(cyclohexyl)-1,2-dithioxi- $\lambda^5$ -phosphane [1] and other alkylphosphines [38]. Corresponding assignments for  $L_{III}$  are less straightforward as simple PC stretching vibrations cannot usually be identified in the spectra of phenylphosphorus compounds; the PC stretching coordinate is believed to contribute mainly to the x-sensitive 'r' and 't' modes [39–40] near  $700\text{ cm}^{-1}$  and  $500\text{ cm}^{-1}$  respectively. Neither of these can be identified unambiguously in the experimental spectra.

Vibrations between  $400$  and  $500\text{ cm}^{-1}$  in  $L_I$  most probably arise from deformation modes in the diethylamino group. The PNC and  $NC_2$  vibrations are likely to be extensively mixed and no attempt has been made to assign them separately [36]. The disorder in the ethyl groups in  $L_I$  may be expected to affect the internal vibrations of the  $-NEt_2$  groups, but has no detectable influence on the skeletal modes of the molecule.

The Infra-red and Raman spectra of saturated methylene chloride solutions of the ligands are similar to those of the solid compounds and there is no evidence of isomerism arising from rotation of the molecules about the PP bonds.

### Mass Spectra

The mass spectra of  $L_{II}$  and  $L_{III}$  were measured under identical conditions ( $70\text{ e.v.}$ , volatilised at  $200^\circ\text{C}$ ) using an AEI MS30 mass spectrometer. Both compounds yielded rather small molecular-ion peaks ( $L_{II}^+$ ,  $m/e = 436$ ;  $L_{III}^+$ ,  $m/e = 424$ ) with much stronger peaks corresponding to the cleaved species  $(C_6H_{11})(Et_2N)PS^+$  ( $m/e = 218$ ) and  $(C_6H_5)(Et_2N)PS^+$  ( $m/e = 212$ ). In the spectrum of  $L_{II}$ , a strong peak at  $m/e = 353$  corresponds to the fragment  $[(Et_2N)P(S)P(S)(Et_2N)(C_6H_{11})]^+$  resulting from the loss of a cyclohexyl group, and a much weaker peak at  $m/e = 364$  to  $[(C_6H_{11})P(S)P(S)(Et_2N)(C_6H_{11})]^+$ , resulting from the loss of a diethylamino group. There are no other significant fragments above  $m/e = 218$ . In  $L_{III}$ ,



there is a strong peak at  $m/e = 352$ , corresponding to loss of a diethyl-amino group, but no evidence of any fragment at  $m/e = 347$ , which would indicate the loss of a phenyl group. However, the  $L_{III}$  spectrum contains additional peaks at  $m/e = 440$  and  $369$ , which can be attributed to an oxidation product  $[(Et_2N)(C_6H_5)P(S)OP(S)(C_6H_5)(Et_2N)]^+$  and a fragment  $[(Et_2N)(C_6H_5)P(S)OP(S)(C_6H_5)H]^+$  derived from it.

Comparisons with the fragmentation patterns of tetraalkyl- and tetraphenyl-1,2-dithioxodi- $\lambda^5$ -phosphanes are instructive [42]. The ions  $R_3P_2S_2^+$  are readily detected in the spectra of the alkyl compounds, but are missing or very weak in the spectrum of  $Ph_4P_2S_2$ . Moreover, the phenyl compound shows clear evidence of oxidation (forming e.g.  $Ph_2P(S)-O-P(S)Ph_2$ ) but the alkyl compounds, under the same conditions, do not. The differences between  $L_{II}$  and  $L_{III}$  are thus entirely consistent with the differences between their alkyl and aryl substituent groups.

### Acknowledgements

We would like to thank Dr. J. Galy for the facilities placed at our disposal and for fruitful discussions.

### References

- 1 A. H. Cowley and W. D. White, *Spectrochim. Acta*, **22**, 1431 (1966).
- 2 M. Arshad, A. Beg and S. H. Khawaja, *Spectrochim. Acta*, **24 A**, 1031 (1968).
- 3 G. P. McQuillan and I. A. Oxton, *Spectrochim. Acta*, **33 A**, 233 (1977).
- 4 G. P. McQuillan and I. A. Oxton, *Spectrochim. Acta*, **34 A**, 33 (1978).
- 5 P. J. D. Park, G. Chambers, E. Wyn-Jones and P. J. Hendra, *J. Chem. Soc. (A)*, 646 (1967).
- 6 A. J. Blake, G. P. McQuillan and I. A. Oxton, *Spectrochim. Acta*, **36 A**, 501 (1980).
- 7 a) A. J. Blake, *Ph.D. Thesis*, Aberdeen University (1979).  
b) A. J. Blake, G. P. McQuillan, I. A. Oxton and D. Troy, *J. Mol. Struct.*, in press.
- 8 J. D. Lee and G. W. Goodacre, *Acta Cryst.*, **B 27**, 302 (1971).
- 9 S. N. Dutta and M. M. Woolfson, *Acta Cryst.*, **14**, 178 (1961).
- 10 A. J. Blake, R. A. Howie and G. P. McQuillan, *Acta Cryst.*, **B 37**, 966 (1981).
- 11 P. J. Wheatley, *J. Chem. Soc.*, 523 (1960).
- 12 J. D. Lee and G. W. Goodacre, *Acta Cryst.*, **B 25**, 2127 (1969).
- 13 J. D. Lee and G. W. Goodacre, *Acta Cryst. B* **26**, 507 (1970).
- 14 W. Levason and F. P. McCullough, *Inorg. Nucl. Chem. Letters*, **12**, 841 (1976).
- 15 G. P. McQuillan and I. A. Oxton, *J. Chem. Soc., Dalton Trans.*, 895 (1979).
- 16 G. P. McQuillan and I. A. Oxton, *J. Mol. Struct.*, **64**, 173 (1980).
- 17 D. W. Meek and P. Nicpon, *J. Amer. Chem. Soc.*, 4951 (1965).
- 18 F. A. Cotton, B. A. Frenz, D. L. Hunter and Z. C. Mester, *Inorg. Chim. Acta*, **11**, 111 (1974).
- 19 F. A. Cotton, B. A. Frenz, D. L. Hunter and Z. C. Mester, *Inorg. Chim. Acta*, **11**, 119 (1974).
- 20 D. Troy, J. Galy and J. P. Legros, *Acta Cryst.*, **B 36**, 398 (1980).
- 21 W. Seidel and K. Issleib, *Z. Anorg. Allg. Chem.*, **325**, 113 (1963).
- 22 P. Coppens, L. Leiserowitz and D. Rabinovich, *Acta Cryst.*, **18**, 1035 (1965).
- 23 Computer programs used in data reduction, solution, refinement and interpretation of the structure are as follows: CAD4 CICT 10, a local program for data reduction by J. Aussoleil and J. P. Legros, MULTAN-78 by Main, Hull, Lessinger, Germain, Declercq and Woolfson, FORDAP, a Fourier synthesis program by Zalkin, the least squares program NUCLS by Doedens and Ibers based on Busing and Levy's ORFLS, AGNOST by Coppens, Leiserowitz and Rabinovich and Tompa for absorption corrections, SADIAN by Baur for calculating atomic distances and angles, ORTEP by Johnson for illustrations, and the function and error program ORFFE by Busing, Martin and Levy.
- 24 'International Tables for X-ray crystallography', Kynoch Press, Birmingham, vol. 4 (1974).
- 25 SHELX-76, a computer program for crystal structure determination, by G. M. Sheldrick.
- 26 J. D. Lee and A. H. Boloorizadeh, *J. Organometal. Chem.*, **152**, 305 (1978).
- 27 J. Kaiser, R. Richter and H. Hartung, *Tetrahedron*, **34**, 1993 (1978).
- 28 H. Hartung, S. Hickel, J. Kaiser and R. Richter, *Z. Anorg. Allg. Chem.*, **458**, 130 (1979).
- 29 D. Troy, *D.Sc. Thesis*, Toulouse University (1981).
- 30 J. Kincaid, K. Nakamoto, J. A. Thiethof and D. W. Meek, *Spectrochim. Acta*, **30 A**, 2091 (1974).
- 31 R. A. Zingaro, *Inorg. Chem.*, **2**, 192 (1963).
- 32 C. Lafitte, *D. Sc. Thesis*, Montpellier University (1965).
- 33 F. Rauchle, W. Pöhl, B. Blaich and J. Goubeau, *Ber. Buns. Ges. Phys. Chem.*, **75**, 66 (1971).
- 34 D. Kottgen, H. Stoll, A. Lentz, R. Pantzer and J. Goubeau, *Z. Anorg. Chem.*, **385**, 56 (1971).
- 35 R. Pantzer, W. D. Bukhardt, E. Walter and J. Goubeau, *Z. Anorg. Chem.*, **416**, 297 (1975).
- 36 G. Davidson and S. Phillips, *Spectrochim. Acta*, **35 A**, 141 (1979).
- 37 A. Vilkov, L. S. Khaikin and V. V. Evdokimov, *J. Struct. Chem. USSR*, **13**, 4 (1972).
- 38 L. C. Thomas, 'Interpretation of the Infra-red spectra of organophosphorus compounds', Heyden, New York (1974).
- 39 D. H. Whiffen, *J. Chem. Soc.*, 1350 (1956).
- 40 G. B. Deacon and J. H. S. Green, *Spectrochim. Acta*, **24 A**, 845 (1968).
- 41 M. Rey-Lafon, C. Rouffi, M. Camiade and M. T. Forel, *J. Chim. Physique*, **67**, 2030 (1970).
- 42 A. J. Blake and G. P. McQuillan, unpublished observations. See also H. Keck and W. Kuchen, *Org. Mass Spectrometry*, **14**, 149 (1979).