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ON THE ELECTRON DIFFRACTION STUDY AND CONFORMATION OF THE 2-CHLORO-1,3-DITHIA-2-PHOSPHOLANE

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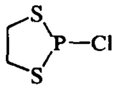
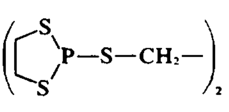
Abstract—An electron diffraction study of the 2-chloro-1,3-dithia-2-phospholane has been performed. A phosphorus edge envelope conformation with axial chlorine fits the best the experimental data. This result, compared with other structural information obtained using NMR (liquid state) and X-ray diffraction techniques suggests some conformational changes of the dithiaphospholane ring depending upon its physical state. However this conclusion, due the difficulty of the electron diffraction study must be supported by additional conformational studies.

Résumé—Une étude structurale du chloro-2-dithiaphospholane-1,3,2 a été effectuée par diffraction électronique. Une conformation du type enveloppe à pointe carbone et chlore axial donne le meilleur accord avec les résultats expérimentaux. Ce résultat, comparé avec ceux obtenus par résonance magnétique nucléaire (phase liquide) et diffraction aux rayons X (phase solide), suggère un changement conformationnel du cycle dithiaphospholane entre les trois états considérés. Ce résultat demande cependant à être confirmé de par l'indétermination existant dans l'étude par diffraction électronique.

In contrast to the many stereochemical studies on 5-membered rings containing first row elements (C, N, O, . . .) comparatively less attention has been paid to the corresponding 5-membered rings containing second row elements (P, S, . . .).[1] We wish to report here the electron diffraction study of the 2-chloro-1,3-dithia-2-phospholane **1** along with a comparison with the stereochemical information obtained by NMR and X-ray diffraction on other 1,3-dithia-2-phospholane molecules.



1 2-chloro-1,3-dithia-2-phospholane.



2 2,2′-(ethylenedithio)bis-1,3-dithia-2-phospholane.

I. *Electron diffraction*

Experimental. The techniques for obtaining the electron diffraction patterns[3,4] and their density distributions[5] have been essentially the same as used earlier (*cf* e.g. Ref 6). The nozzle temperature was about 130° during the exposures. The wavelength of the electron beam was determined from the diffraction patterns of thallium (I) chloride.[7] The experimental scale error was estimated to be 0·2%.

The ranges of intensity data used were $2{\cdot}25 \leqq s \leqq 11{\cdot}75$ Å^{-1} and $7{\cdot}25 \leqq s \leqq 32{\cdot}0$ Å^{-1} with Δs step of 0·25 Å^{-1}. Here $s = 4\pi\lambda^{-1} \sin \vartheta/2$, λ is the electron wave length and ϑ is the scattering angle. The experimental molecular intensities corresponding to the two camera ranges were obtained in the same way as described.[6] The final versions of the experimental background are shown in Fig 1. The experimental molecular intensities, in the form of $sM^E(s)$ are shown in Fig 2. The numerical values can be obtained by writing to the Budapest authors.

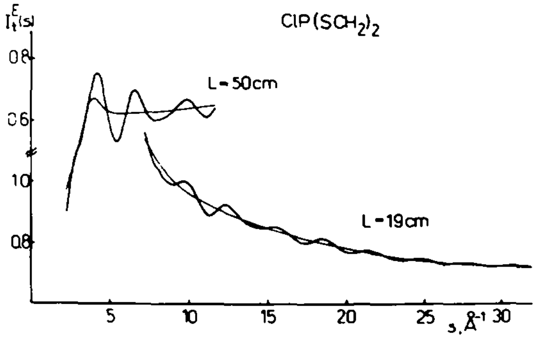


Fig 1. The total experimental intensities and experimental backgrounds drawn in.

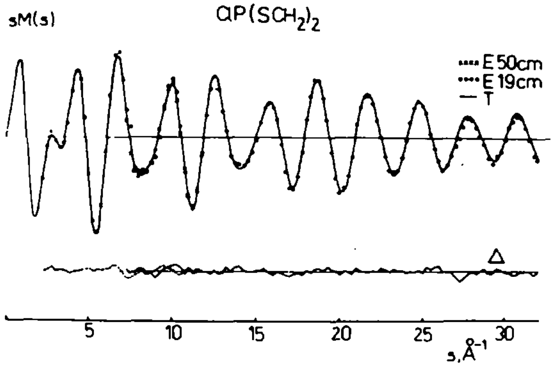


Fig 2. Experimental (crosses and dots for 50 cm and 19 cm camera ranges, respectively) and theoretical (full line) molecular intensities and the difference curves (Δ). The theoretical curve was computed for the model whose parameters are presented in Table 1.

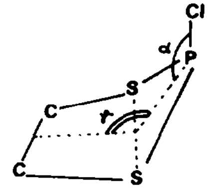


Fig 4.

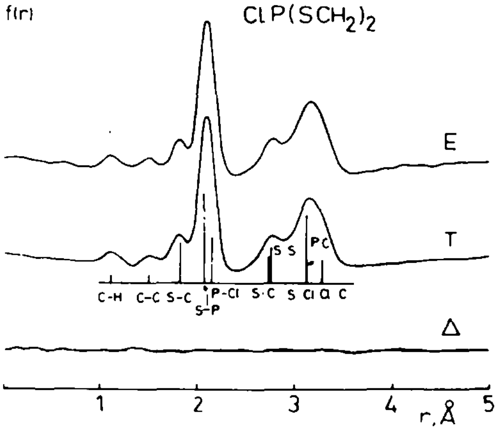


Fig 5. Experimental (E) and theoretical (T) radial distributions and the difference curve (Δ). The artificial damping constant $a = 0{\cdot}002$ Å². Curve T was computed for the model whose parameters are presented in Table 1. Individual interatomic distances and their relative weights are also indicated. The number of dots specifies the number of bond angles separating the atoms.

Structure analysis. Two conformations *viz.* envelope with the P atom in the edge (C_s symmetry, *cf* Fig 3a) and half-chair (*cf* Fig 3b) have been considered in detail. Of these, satisfactory agreement with the experimental data could be achieved for the envelope model with the chlorine atom in axial position, only. In addition to the five bond lengths, the following five angles have been chosen to describe the geometry of the envelope model, C–C–S, C–C–H, H–C–H, and α (*cf* Fig 4).

Experimental radial distributions have been obtained in the usual way.[6] One of them is shown in Fig 5 together with a theoretical curve calculated for the best parameter set of the envelope model. The assignment of the maxima of the radial distributions to the internuclear distances of the envelope model is also shown. In labelling the non-bond distances, the number of dots specifies the number of bond angles separating the two atoms. The height of the vertical bars is roughly proportional to the relative weight of each individual distance. It is seen that the lengths of S–P and P–Cl bonds are very close to each other and the maxima of non-bond distances overlap particularly badly. Non-bond distances involving H atoms are distributed all over the region between 1·8 and 4 Å.

For structure refinement the least squares method was applied to the molecular intensities in the same manner as for 1,4-thioxane.[6] The only difference was that the data corresponding to two camera ranges have been treated separately in this case and the sum

$$\sum_{s=2\cdot25}^{11\cdot75} W_s[\mathrm{M^E}(s) - k_1\mathrm{M^T}(s)]^2 + \sum_{s=7\cdot25}^{32\cdot0} W_s[\mathrm{M^E}(s) - k_2\mathrm{M^T}(s)]^2$$

was minimized where W_s are the weights and k_1 and k_2 the respective scale factors and $\mathrm{M^T}(s)$ the calculated theoretical molecular intensities. Because of strong correlations among the parameters, the approach of block refinements[8] has been extensively

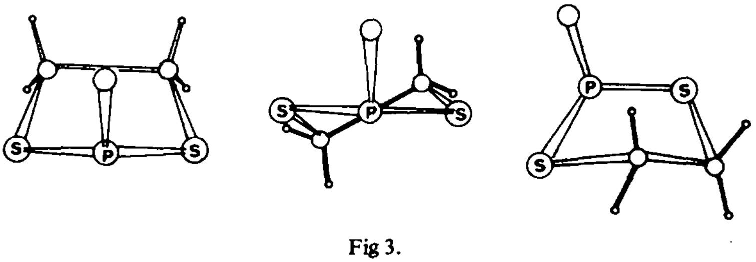


Fig 3.

used. Often amplitudes of vibration for nearly equal distances were grouped together and the differences between them constrained to be constant. There was, however, an additional unrestricted refinement for all the parameters involved in any of the block refinements for a more realistic determination of the standard deviations. The results of the least squares refinement for the envelope model are compiled in Table 1.

The procedure for estimation of total errors σ_t shown in Table 1 was the same as described[6] with the only difference that factor $\sqrt{2}$ was used to take account of possible correlation among the observations. The parameters determined show no extraordinary features. Some of the mean amplitudes of vibration for bonds seem to be too small and some σ_t values are so large that they suggest no determination at all. This is in agreement with the fact that numerous correlation coefficient between parameters have been observed to be very large.

Concerning the possibility of other conformations present in the vapors, the planar and the envelope forms with one of the C atoms in the edge seem very unlikely due to the fact that the experimental radial distribution curve does not contain appreciable contributions at distance values larger than 3·5 Å. However, because of the complexity of the radial distribution curve corresponding to closely packed interatomic distances, it is safer to state the following. The electron diffraction data are in excellent agreement with an envelope model with phosphorus atom in the edge and chlorine in axial position while the presence of other forms may be undetected.

Table 1. Results of the least squares refinement of molecular parameters for the envelope model with phosphorus in edge and axial chlorine of 2 - chloro - 1,3 - dithia - 2 - phospholane 1

	Bond lengths	σ_t	Amplitudes	σ_t
P–Cl Å	2·153	0·029	0·036	0·053
P–S	2·077	0·015	0·031	0·028
S–C	1·828	0·008	0·077	0·008
C–C	1·513	0·008	0·032	0·014
C–H	1·124	1·010	0·052	0·012

	Angles[a]	σ_t
$<\vartheta$, deg	136·2	7·5
< C–C–S	109·9	0·9
$<\alpha$	97·0	1·1
< Cl–P–S[a]	95·3	3·1
< S–P–S[a]	83·3	2·1
< P–S–C[a]	106·2	2·5

Non-bond distances[a,b]	σ_t	Amplitudes	σ_t	
Cl.S, Å	3·125	0·073	0·130	0·041
Cl. .C	3·286	0·037	0·064	0·020
S.S	2·764	0·052	0·107	0·016
P.C	3·127	0·045	0·061	0·018
S.C	2·743	0·015	0·181	0·113

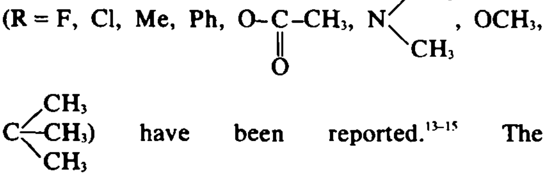
[a] Only those not involving hydrogen atoms.
[b] Dependent parameters.

DISCUSSION

The structural data here obtained on the 2 - chloro - 1,3 dithia - 2 - phospholane 1 can be compared with the results obtained on other three coordinated phosphorus molecules. A significant lengthening of the P–Cl bond, in comparison with phosphorus trichloride (2·042 by electron diffraction),[9] is observed in compound 1. Such a trend has already been observed in three coordinated phosphorus molecules which contain an O or an N atom directly bonded to the P atom.[10] The P–S bond length is close to the mean value found in other ^{III}P molecules,[11] the same goes for the S–C bond length as compared with values obtained on other 5-membered rings.[12] Bond angles around the P atoms are rather small, but due to the lack of structural data concerning the ^{III}P derivatives there are not many values they may be compared with.

It is interesting to compare the ring conformation obtained on the 2 - chloro - 1,3 - dithia - 2 - phospholane 1 in the gas phase using the electron diffraction technique, along with the results obtained by other technique: nuclear magnetic resonance (liquid phase) and X-ray diffraction (solid state) on various 1,3 - dithia - 2 - phospholanes.

In previous papers the full proton NMR spectrum analysis of different 1,3 - dithia - 2 - phospholanes bearing different groups R attached to the P atom (R = F, Cl, Me, Ph, $O{-}\underset{\underset{O}{\|}}{C}{-}CH_3$, $N\begin{matrix}CH_3\\CH_3\end{matrix}$, OCH_3, $C\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}$) have been reported.[13–15] The AA'BB'X NMR spectrum observed for these compounds (Table 1 in Ref 15*b*) show that the corresponding ^{3}J(HH), ^{2}J(HH) and ^{3}J(PH) spin–spin coupling have close values in the different compounds. These parameters are also similar to the one obtained on the dithiaphospholane 2,* a compound giving nice crystals and which have been studied under X-ray diffraction.[16] The small variation observed in the corresponding J values obtained in the studied 1,3 - dithia - 2 - phospholanes, including compound 2, strongly indicate that the 5-membered ring have similar conformations in the liquid state whatever the R group is. In using a Karplus like relationship the torsion angle between the C–H bonds ($\O_{HH}$) (Fig 6) have been shown to be close to 40°,[15b]



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*The NMR coupling constants (in Hz) obtained on 2 are respectively: ^{2}J(HH) = − 11·6; ^{3}J(HHcis) = 4·7 and 5·4; ^{3}J(HHtrans) = 7·1; ^{3}J(PH) = 0 and 0·5.

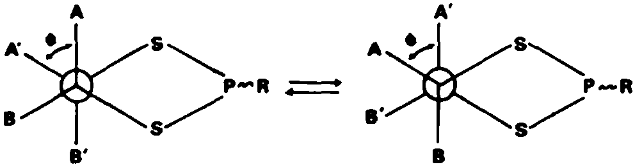
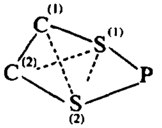


Fig 6. Torsion angle around the CC bond in 1,3-dithia-2-phospholane.

excluding a C_s envelope edge phosphorus conformation (Ø = 0°) as obtained in the gas phase for the conformation fitting the best the electron diffraction data for compound **1**.

Due to the lack of information concerning the stereochemical dependence of the ^3J(PSCH) coupling,[17] it is not possible by use of the NMR data to give more information concerning the ring shape. However the X-ray diffraction results obtained on **2** can be used.



Due to a slight decomposition of the crystal under X-ray irradiation, only the heavy atom positions (C, S, P) have been refined up to now, leading to a conventional R value of 3·9%. The ring which is non planar does not adopt an envelope like conformation. The ring shape may be characterized by two dihedral angles S(1) P S(2); C(1) S(1) S(2) and S(1) P S(2); C(2) S(1) S(2) which are respectively equal to 37°2 and 19°6, the two C atoms being on the same side with respect to the S(1) P S(2) plane. The non-bond distances P C(1) and P C(2) are equal to 2·877 (0·001) Å and 3·028 (0·005) Å.

In using the ring atom coordinates obtained from the X-ray diffraction study of compound **2**, a highly probable position of the H atoms may be obtained in assuming a value of 109° for the HCC bond angle and assuming that the SCC plane is bissecting the HCH angle. Using these hydrogen positions, one found a torsion angle Ø around the CC bond equal to 38° which is very close to the 40° value obtained from the NMR data.[15b] This result suggests that the liquid state conformation of the 1,3-dithia-2-phospholane ring are quite similar to the solid state conformation obtained in **2**.

Thus, the results obtained from three different techniques: electron diffraction (gas phase), NMR (liquid state) and X-ray diffraction (solid state), suggest that the 1,3-dithia-2-phospholane ring conformation have a different conformation in the gas phase and in the solid state. As a consequence for the molecule **1**, 2-chloro-1,3-dithia-2-phospholane, the gas phase conformation (P edge Cs envelope) is different from the liquid state conformation. Such a conclusion may also be obtained on the 2-chloro-1,3-dioxa-2-phospholane, a molecule which has been studied in using gas phase electron diffraction[18] (P edge Cs conformation) and which according to NMR data would prefer to be in a twist-envelope conformation.[19] It should be interesting to check if such a change in conformation in going from the liquid state to the gas phase is a general phenomenon for the 1,3-dithia- and 1,3-dioxaphospholane or holds only for the chloroderivatives. However, we would like to emphasize again in connection with this discussion the indeterminacy of the electron diffraction conclusions concerning the conformation of the 1,3,2-dithiaphospholane ring. Additional information from other techniques, most notably microwave spectroscopy, should help to clarify the matter.

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