Preparation and Nuclear Magnetic Resonance Spectral Analysis of Some 1,3,2-Dithiaphospholans

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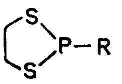
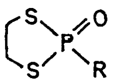
The preparation of 1,3,2-dithiaphospholans and their 2-oxo- and 2-thioxo-derivatives is described. ^{1}H and ^{31}P N.m.r. data are reported and discussed. The ^{1}H n.m.r. spectra of four dithiaphospholans have been fully analysed on the basis of an $[AB]_2X$ system, giving values for the ^{1}H chemical shifts, the (H,H) coupling constants of the $CH_2{\cdot}CH_2$ group and the (H,P) coupling constants involving that group.

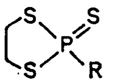
OUR interest in the 1,3,2-dithiaphospholans stems from three main aspects of their chemistry. First, they are potentially useful intermediates in the preparation of pentaco-ordinate phosphorus–sulphur compounds. N.m.r. studies on these[1-4] and related heterocycles[5-7] have revealed unusual structural features. Secondly, we were concerned with the structures of the 1,3,2-dithiaphospholans, several *X*-ray crystal structure studies of which have recently been reported.[8-12] The results of these studies together with some preliminary n.m.r. work prompted us to investigate in detail the third aspect, namely the ^{1}H n.m.r. spectra. Such studies have already been reported for the diaza-,[12a] oxaza-,[12b] and dioxa-phospholans.[13-16] On the basis of the crystal structures and ^{1}H n.m.r. spectra, deductions can be made concerning the structure and stereochemistry of the dithiaphospholan ring.



(I)



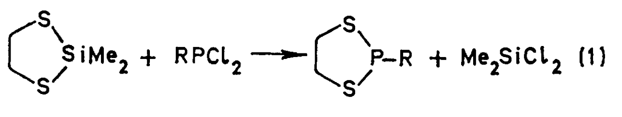
(II)



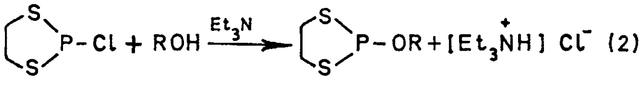
(III)

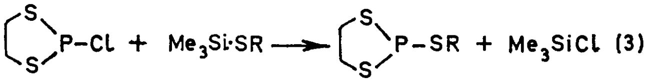
a = Cl
b = Ph
c = Me
d = NEt$_2$
e = OMe
f = SMe
g = C_6F_5

1,3,2-Dithiaphospholans (I) may be synthesised by the following methods: (A) the reaction of phosphorous trichloride or alkylphosphonous dichlorides, $RPCl_2$ (V), with ethane-1,2-dithiol,[17] or (B) the cleavage of 2,2-dimethyl-1,3,2-dithiasilolan (IV)[18] by phosphorous trichloride or the dichloride (V) [equation (1)]. The use of thiasila-compounds as intermediates in reactions with covalent halides is useful and well documented.[18] The phospholans (I) were also prepared, (C), by reaction of 2-chloro-1,3,2-dithiaphospholan (Ia) with alcohols, or alkylthiotrimethylsilanes [*e.g.*, equations (2) and (3)]. In the reaction with alcohols and amines, the hydrogen chloride produced was removed by a tertiary amine.



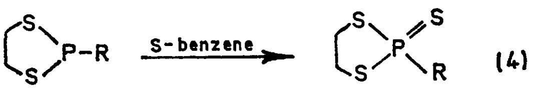
(IV) (V) (I)





(VI)

The four-co-ordinate compounds (II) were synthesised by method (B) with phosphoryl chloride or the alkyl phosphonic dichloride $RPOCl_2$. The sulphur analogues (III) were prepared, (D), by the addition of sulphur to the dithiaphospholan (I) in a suitable solvent (usually benzene) [equation (4)]. The reaction of alkylphosphonothioic dichlorides, $RP(S)Cl_2$, with the dithiasila-compound (IV) also gave compounds (III). Treatment



(I) (III)

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[1] S. C. Peake and R. Schmutzler, *Chem. Comm.*, 1968, 665.

[2] S. C. Peake and R. Schmutzler, *Chem. Comm.*, 1968, 1662.

[3] S. C. Peake and R. Schmutzler, *J. Chem. Soc.* (*A*), 1970, 1049.

[4] S. C. Peake, Ph.D. Thesis, Loughborough University of Technology, 1970.

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[9] J. D. Lee and G. W. Goodacre, unpublished results.

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[18] E. W. Abel, D. A. Armitage, and R. P. Bush, *J. Chem. Soc.*, 1965, 7098.

of (IV) with phosphoryl chloride [(B)] gave the chloro-derivative (IIa) in low yields and isolation of the product was not possible. Attempts to prepare (IIa) in higher yields by oxidation of the trivalent chloro-compound (Ia) with nitrogen dioxide yielded an intractable viscous liquid, which was shown by ^{31}P n.m.r. to be a mixture of several phosphorus-containing species. The physical properties and other data of several dithiaphospholans are collated in Table 1.

TABLE 1

1,3,2-Dithiaphospholans

Compound	Method	Yield (%)	B.p. (°C/mmHg)	M.p. (°C)	Analysis (%) Calc.	Analysis (%) Found	Ref.	Lit. b.p. (°C/mmHg) or m.p.
(Ia)	A, B	65	100/10·0		C, 15·2 P, 19·5	C, 15·3 P, 19·4	17 18	B.p. 102/10·0 B.p. 67/1·0
(Ib)	B	90	130/0·7				18	B.p. 136—137/0·2
(Ic)	B	90	66—68/0·7				30	B.p. 90/5·0
(Id)	C	55	88—90/1·0		C, 36·9 H, 7·2 S, 32·8	C, 37·0 H, 7·3 S, 32·7		
(Ie)	C	62	74—75/2·0		C, 23·4 H, 4·3 S, 41·4	C, 23·6 H, 4·5 S, 41·5	17	B.p. 97—98/7·5
(If)	C	76	108—116/2·0		C, 21·2 H, 4·2 S, 56·5	C, 20·6 H, 4·1 S, 55·0		
(Ig)	A, B	72	115—118/0·5		C, 33·1 H, 1·3 P, 22·1	C, 33·1 H, 1·3 P, 22·0		
(IIa)	B	*a*						
(IIb)	B	10	220/0·05		C, 44·4 H, 4·2	C, 43·9 H, 4·4	18	B.p. 180/0·001, M.p. 70
(IIc)	B	45	141/0·7		C, 23·4 H, 4·3 S, 41·4	C, 23·9 H, 4·1 S, 41·6		
(IIe)	B	*a*	*b*					
(IIIa)	D	50		45	C, 12·8 H, 1·1 S, 51·0	C, 12·9 H, 1·3 S, 51·0		
(IIIb)	D	72		68	C, 40·3 H, 3·8 S, 40·4	C, 40·9 H, 3·8 S, 41·3		
(IIIc)	D	61		74	C, 21·2 H, 4·2 S, 56·6	C, 20·8 H, 4·2 S, 56·7	30	B.p. 132—134/2·0 M.p. 74
(IIId)	D	59		35	C, 31·8 H, 6·2 S, 42·2	C, 32·1 H, 5·9 S, 42·2		

[a] Compound not obtained pure owing to separation difficulties. [b] Involatile solid.

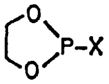
^{31}P *N.m.r. Spectra.*—The ^{31}P n.m.r. data are shown in Table 2. The chemical shifts of the three-co-ordinate derivatives (I) cover a wide range (from −180 to −30 p.p.m.) and depend strongly on the nature of the substituents. Ligands such as Cl, NR_2, or OR cause a larger downfield shift than substituents attached through carbon. Compared with the oxygen analogues (VII) the phosphorus nucleus appears to be less shielded in the sulphur compounds. The reported compounds resemble more the disubstituted acyclic compounds $(RS)_2PX$ [19] in this respect. The phosphorus chemical shifts of the four-co-ordinate derivatives cover a much smaller range, from −113 to −96 p.p.m. There was no significant difference between shifts for the oxygen and sulphur compounds (II) and (III). The substituents Cl, NR_2, and OR give rise to slightly larger shifts compared with those containing a carbon–phosphorus linkage.

TABLE 2

^{31}P N.m.r. data [a]

Compound	δ_P [b]	Compound	δ_P [b]
(Ia)	−179·2	(IIe)	−113·4 [c]
(Id)	−160·8	(IIa)	−109·5 [d]
(Ie)	−150·8	(IIb)	−96·8 [c]
(If)	−117·0	(IIc)	−96·4 [c]
(Ib)	−46·7	(IIId)	−109·6 [c]
(Ic)	−44·5	(IIIa)	−109·2 [c]
(Ig)	−29·6 [c]	(IIIb)	−98·6 [c]
		(IIIc)	−97·6 [c]

[a] All spectra were obtained for neat samples except where stated otherwise. [b] ^{31}P Chemical shift in p.p.m. from the resonance of external 85% H_3PO_4 (positive when the compound signal is at the higher field). [c] Benzene solution. [d] Neat mixture of products (see text).



(VII)

^{1}H *N.m.r. Spectra.*—The general appearance of the ^{1}H n.m.r. spectra for the four- and three-co-ordinate phosphorus species was very different. While both series showed second-order spectra for the $CH_2{\cdot}CH_2$

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[19] V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer in ' Topics in Phosphorus Chemistry,' vol. V, eds. M. Grayson and E. J. Griffith, Interscience, London, New York, and Sydney, 1967, ch. 4, pp. 227—447.

fragments, the spectra due to the three co-ordinate species showed several close bands which appeared as a single broad band in low resolution spectra, while those for the four-co-ordinate species showed a much more widely spread complex symmetrical set of bands. ^1H N.m.r. data for all twelve compounds which were prepared in a pure state are listed in Table 3. For the compounds (Ib) and (IIIb—d) the ^1H n.m.r. spectra of the $CH_2{\cdot}CH_2$ fragments were analysed on the basis of an $[AB]_2X$ spin system[20] (see below).

TABLE 3

^1H N.m.r. data[a]

	δ_H				
Compd.	Ring methylene protons[b]	Protons in R	$\lvert J_{PH}\rvert$	$\lvert J_{HH}\rvert$	Solvent
(Ia)	3·64				(Neat)
(Id)	*c*	1·05[d]		6·6	(Neat)
(Ie)	2·90	3·09	10·8		Benzene
(If)	3·38	2·18	13·2		(Neat)
(Ib)	3·072[f]	*ca.* 7·5[e]			$CDCl_3$
(Ic)	3·33	1·38	10·2		(Neat)
(Ig)	3·42				$CDCl_3$
(IIc)	3·63	2·58	13·5		$CDCl_3$
(IIId)	3·605[f]	1·165[f,g]		7·01[f]	$CDCl_3$
(IIIa)	3·96				$CDCl_3$
(IIIb)	3·726[f]	*ca.* 7·5[e]			$CDCl_3$
(IIIc)	3·656[f]	2·623[f]	12·9		$CDCl_3$

[a] Chemical shifts (δ/p.p.m.) from tetramethylsilane; coupling constants in Hz. [b] The values quoted refer to δ_H measured to the centre of the $[AB]_2X$ pattern; chemical shifts and coupling constants for the $CH_2{\cdot}CH_2$ fragments of compounds (Ib) and (IIIb—d) are listed in Table 4. [c] Not determined; the resonances overlap with those of the ring methylene protons. [d] Shift for Me protons; the methylene group resonances overlap with those of the ring methylene protons. [e] Complex band. [f] Data from 100 MHz spectra. [g] Shift for Me protons; the methylene resonance is at δ_H 3·420 p.p.m., $\lvert J_{PH}\rvert$ 16·0 Hz (100 MHz data).

Spectral Analysis.—In the analysis of the $CH_2{\cdot}CH_2$ signals in the ^1H n.m.r. spectra of compounds (Ib) and (IIIb—d), the protons in the Ph, Me, and NEt_2 substituents have been neglected, since coupling to the protons of the five-membered ring is negligible. The AB region for an $[AB]_2X$ spin system may be considered as a superposition of two $[ab]_2$ subspectra, corresponding to the two possible spin states of the X nucleus.[21] These subspectra are characterised by the coupling constants of the full system, but by effective chemical shifts:

$$\nu_a = \nu_A + \tfrac{1}{2}J_{AX} \text{ with } \nu_b = \nu_B + \tfrac{1}{2}J_{BX}$$

and

$$\nu_a = \nu_A - \tfrac{1}{2}J_{AX} \text{ with } \nu_b = \nu_B - \tfrac{1}{2}J_{BX}$$

Thus subspectral analysis should provide two compatible sets of (A,A), (B,B), and (A,B) coupling constants, plus effective chemical shifts which give ν_A, ν_B, J_{AX}, and J_{BX}. The relative signs of J_{AX} and J_{BX} are obtained, but not the signs with respect to those of the remaining coupling constants (unless heteronuclear double resonance is used).

The analysis of the $[AB]_2$ spin system is well known.[22] The spectrum is characterised by four coupling constants, J_{AA}, J_{BB}, J_{AB}, and J_{AB}', but these are most conveniently used in the form of linear combinations K, L, M, and N. The spectrum is symmetrical about its mid-point. This provides a simple method of assigning lines to individual subspectra in the full $[AB]_2X$ cases considered here. The only difficulties are those caused by the overlapping of lines or by experimental error in their measurement. There is an initial uncertainty when $J_{AX} \approx J_{BX}$, but this may be readily resolved by a trial computation. However, the symmetry of the $[ab]_2$ subspectra implies that ν_a and ν_b cannot be distinguished. This fact results in an ambiguity in the complete analysis since it is not known how to pair the two subspectra. There will be two solutions, differing only in J_{AX}, J_{BX}, and $\nu_A - \nu_B$. Fortunately the ambiguity is readily resolved by recording the spectra at a different radiofrequency (in our case 60 MHz) and computing the two new cases by altering $\nu_A - \nu_B$ appropriately.[13] Only one case will fit the new observed spectrum.

Explicit equations may be given for certain lines in $[AB]_2$ spectra.[22] Four of these lines depend on $\lvert N\rvert$ and $\lvert\nu_A - \nu_B\rvert$ alone, and eight depend on $\lvert M\rvert$, $\lvert L\rvert$, and $\lvert\nu_A - \nu_B\rvert$. Recognition of these lines can give these parameters directly, and also check the constancy of $\lvert\nu_A - \nu_B\rvert$. We approached the problem using a mixture of computation and direct assignment. In the first place we estimated values of the coupling constants from the literature, and assumed $M = J_{AA} - J_{BB} = 0$ (this reduces the number of explicit lines to eight, with degeneracies). This enabled the lines depending on $\lvert N\rvert$ and $\lvert\nu_a - \nu_b\rvert$ to be picked out, thus providing more accurate data. A fresh computation then allowed the remaining explicit lines to be assigned, giving $\lvert L\rvert$. Computation with variation of K then enabled a complete assignment to be made, and computer iteration gave a complete set of parameters for each subspectrum. The combined information enabled the two possible solutions (see before) to be deduced. Iterative computations for the most likely solution were then carried out for the full five-spin system in each case.

This approach worked well for compounds (IIIb—d) since the assumption $M = 0$ is good to within the line width of the degenerate (or nearly degenerate) pairs of lines: we estimated $\lvert M\rvert < 0{\cdot}2$ Hz on this basis. Compound (Ib) gave a more complex spectrum, since $M \neq 0$, but a full analysis was still feasible. The detailed 60 MHz spectra, obtained for (Ib) and (IIIc), distinguished between the two possible sets of parameters in these cases.

The spectrum of (IIId) in $CDCl_3$ did not display a sufficient number of well resolved lines for this procedure to be feasible, so a benzene solution was used for the detailed analysis. The coupling constants thus obtained were then held constant in several computations with varying $\nu_A - \nu_B$ until approximate agreement with the

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[20] C. W. Haigh, *J. Chem. Soc.* (*A*), 1970, 1682.

[21] P. Diehl, R. K. Harris, and R. G. Jones, *Progr. N.M.R. Spectroscopy*, 1967, **3**, 1.

[22] J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High-Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959.

spectrum of the $CDCl_3$ solution was obtained. It then proved possible to identify the explicit lines which depended on $|N|$ and $|\nu_a - \nu_b|$ in each subspectrum and thus to obtain $\nu_A - \nu_B$ directly.

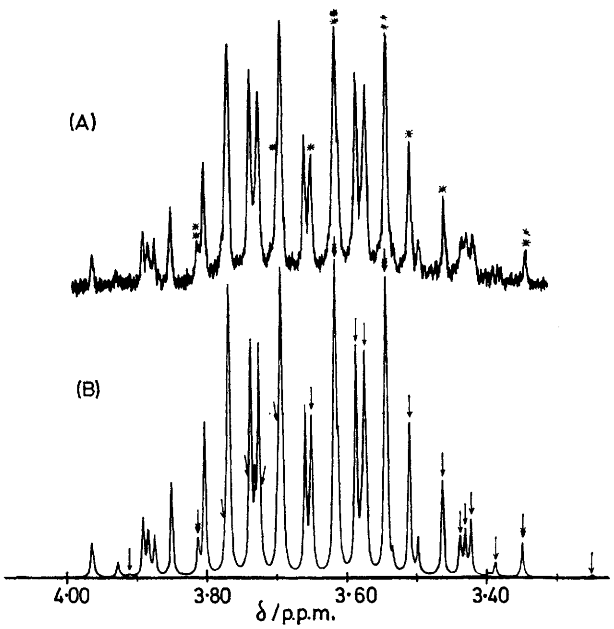
In all cases there remained a residual uncertainty as to the assignment of nuclei A and B (*cis* or *trans* to a substituent at the phosphorus atom). The results of the spectral analyses are given in Table 4. The observed and computed spectra for (IIIb) are illustrated in the Figure.

TABLE 4

^{1}H N.m.r. parameters for the 1,3,2-dithiaphospholans (Ib) and (IIIb—d) [a]

	δ_A [b]	δ_B [b]	$^2J_{AB}$	$^3J_{AB}$	$^3J_{AA}$	$^3J_{BB}$	$^3J_{AX}$ [g]	$^3J_{BX}$ [g]	R.m.s.
(Ib)	3·186	2·958	−11·36	6·70	6·16 [f]	5·40 [f]	±1·87	∓1·09	0·049
(IIIb)	3·804	3·648	−12·03	7·42	3·88 [c]	3·88 [c]	14·84	15·23	0·054
(IIIc)	3·747	3·564	−12·15	7·43	3·77 [c]	3·77 [c]	15·20	14·87	0·071
(IIId)	3·639 [d]	3·571 [d]	−12·00	7·64	3·77 [c]	3·77 [c]	14·94	17·96	*h*

[a] $CDCl_3$ solutions; chemical shifts are $\delta \pm 0{\cdot}001$ p.p.m. [except for (IIId)]; coupling constants $J \pm 0{\cdot}05$ Hz (but see footnote *c*). [b] Nuclei of type A are defined to have a higher Larmor frequency than those of type B. [c] The difference between $^3J_{AA}$ and $^3J_{BB}$ is not well defined for (IIIb—d) but probably has a magnitude of less than 0·2 Hz. [d] Accuracy only ±0·003 p.p.m. For a benzene solution δ_A 3·038 ± 0·001, and δ_B 2·860 ± 0·001 p.p.m., with r.m.s.[e] 0·084. [e] Root-mean-square error of the five-spin iteration by computer. [f] These values may be interchanged. [g] The signs of the (P,H) coupling constants are not known relative to those of the (H,H) coupling constants. [h] No iterative solution was attempted for the $CDCl_3$ solution.



100 MHz ^{1}H n.m.r. spectrum of compound (IIIb) (CH_2 region); (A), observed spectrum for a solution in $CDCl_3$, (B), computer-simulated spectrum (using the parameters given in Table 4). The arrows in (B) indicate lines due to the low-frequency $[ab]_2$ subspectrum (the number of arrow-heads indicates degeneracy or near-degeneracy). The asterisks in (A) indicate 'explicit' lines in the low-frequency sub-spectrum (see text); the double asterisks denote the two-fold near-degeneracy arising because $M \approx 0$

DISCUSSION

The detailed spectral analyses were carried out successfully on the basis of an $[AB]_2X$ spin system. This implies that the five-membered ring is planar or, more likely, that intramolecular processes interconvert a range of non-planar forms at rates that are large on the n.m.r. time scale at room temperature but that inversion at phosphorus is slow on this time scale. This result is expected, and is consistent with the known situation for the corresponding dioxaphospholans.[13-16] There must also be rapid internal rotation about the P–Ph bonds in (Ib) and (IIIb), the P–Me bond in (IIIc), and the P–N bond in (IIId).

The signs of the (H,H) coupling constants are based on the assumption that $^2J_{HH}$ is negative; it follows that all the values of $^3J_{HH}$ are positive, as expected. The spectral analysis determines the relative signs of J_{AX} and J_{BX}, but not those of the (P,H) coupling constants relative to J_{HH}. However, it may be confidently assumed that all values of $^3J_{PH}$ involving pentavalent phosphorus [*i.e.* in (IIIb and d)] are positive.[23] However, the two values of $^3J_{PH}$ for (Ib) are small in magnitude and opposite in sign. It is therefore not possible on the basis of our present data to determine which value is absolutely positive.

The magnitudes of all the coupling constants J_{HH} are in the expected ranges. The results for (IIIb—d) are remarkably similar: corresponding values differ by 0·22 Hz or by 3·5% at the most. It may be confidently concluded that the molecular conformations are very similar. The values of the *trans* coupling constants are considerably greater than the *cis* coupling constants. The difference between $^3J_{HH,trans}$ and $^3J_{HH,cis}$ is smaller for compound (Ib). However in this case also $^3J_{HH,trans} > {}^3J_{HH,cis}$; the reverse is true for dioxaphospholans.[13,15,16] In the case of compounds of the type (VII) it has been suggested [15] that the stable dihedral angle for the $CH_2{\cdot}CH_2$ fragment is *ca.* 30°, implying that J_{trans} is for an angle of 150°. Our results suggest that for (Ib) the dihedral angle is substantially increased, and that there is a larger increase for (IIIb—d). Presumably in these compounds the $CH_2{\cdot}CH_2$ fragment is nearly staggered in conformation, with a dihedral angle approaching 60°. This is consistent with the greater degree of flexibility conferred by the presence of sulphur rather than oxygen atoms in the ring.

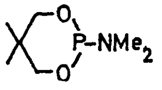
The inequality of $^3J_{AA}$ and $^3J_{BB}$ for (Ib) is of interest, since it does not appear to have been detected in related compounds by other workers,[13-16] nor is it apparent for (IIIb—d). Presumably it implies either a long-range effect of the lone pair of the phosphorus on J_{HH} (analogous to the effects observed on $^2J_{HH}$ of a lone pair over

[23] E. Duval and E. A. C. Lucken, *Mol. Phys.*, 1966, **10**, 499.

fewer intervening bonds [24]), or an imbalance in populations or geometries of envelope conformations with phosphorus ' up ' and ' down '. Unfortunately it is not possible at present to be certain whether nuclei A are *cis* to the phenyl substituent or whether the *cis* positions are occupied by nuclei B. In the dioxaphospholan series (VII) Haake, McNeal, and Goldsmith [15] have suggested the high frequency resonances (A) are due to protons *cis* to the substituent at phosphorus, but there is no certainty in this conclusion.

The magnitudes of $^3J_{PH}$ are also in the expected ranges. The values for (Ib) are lower than usual [13–16,23] for compounds of trivalent phosphorus but are not without precedent.[25] However, the variation in sign has not been found for cyclic compounds containing the P–O–C–H fragment; † on the other hand a substantial variation of $^3J_{PH}$ with dihedral angle has been demonstrated,[16,27] together with a pronounced effect from the orientation of the lone pair on phosphorus.[28] It is probable that for compound (Ib), the low (negative) value of $^3J_{PH}$ corresponds to the dihedral angle P–S–C–H nearer to 90°, by analogy with P–O–C–H, but the difference between the two $^3J_{PH}$ values is sufficiently small that it might be dominated by the orientation of the phosphorus lone pair.[28]

The only anomaly in the coupling constants reported for (IIIb—d) in Table 4 is the relatively high value of $^3J_{BX}$ for (IIId). It is possible that this variation is apparent rather than real, *i.e.* that it is due to the limited range of compounds studied. However similarly anomalous (P,H) coupling constants were observed for the dimethylamino-compound (VIII).[28b]



(VIII)

X-Ray crystal structure studies have recently been carried out on compounds (IIIa),[8] (IIIb),[10,11] (IIIc),[9] and (IIId).[9] The phenyl derivative (IIIb) possesses a mirror plane of symmetry which bisects the heterocyclic ring through phosphorus and the carbon–carbon bond, and contains the carbon atoms of the phenyl group and the exocyclic sulphur atom. Such a striking degree of symmetry is not found in the other derivatives. In each case the tetrahedral arrangement of substituents at phosphorus is slightly distorted, and the heterocyclic ring is puckered. Such puckering may lead to the adoption of an ' envelope ' conformation for (IIIb) in the solid state, but for compounds (IIIa), (IIIc), and (IIId) the puckering appears to lead to an unsymmetrical ring formation with pairs of C–C–S and C–S–P angles being unequal. Comparison of these results with the ^{1}H n.m.r. analysis supports the assumption made earlier in the text that, for compounds in solution, the heterocyclic ring undergoes rapid intramolecular conversion between puckered forms at a rate which is fast on the n.m.r. time scale. There is also the possibility that the heterocyclic rings exist in an ' envelope ' conformation in solution with the phosphorus atom at the apex of the ' flap '. Interatomic distances between the substituents and the $CH_2 \cdot CH_2$ protons in the crystalline state have, as yet, not been calculated.

EXPERIMENTAL

The usual precautions in handling air- and moisture-sensitive compounds were observed. Ethane-1,2-dithiol was commercially available. 2,2-Dimethyl-1,3,2-dithiasilolan (IV) was prepared by the method of Abel and his co-workers.[18]

^{1}H and ^{31}P N.m.r. spectra were recorded with a Perkin-Elmer R10 spectrometer at 60 and 24·3 MHz, respectively. Non-spinning tubes were used for the ^{31}P spectra, into which sealed capillaries containing 85% phosphoric acid were inserted as a standard. Tetramethylsilane was used as an internal standard for the ^{1}H spectra, which were recorded in 4·6 mm spinning tubes. Liquid samples were measured neat; solid samples were dissolved in benzene or $CDCl_3$.

For the detailed spectral analyses, the ^{1}H n.m.r. spectra were recorded at 100 MHz with a Varian Associates HA 100 spectrometer in the frequency-sweep mode, for solutions in $CDCl_3$ at ambient probe temperature (*ca.* 35 °C). Tetramethylsilane was used as an internal reference and to provide a signal for the field–frequency locking. In each case the measured peak positions were the average of at least four scans at a scale of 1 Hz cm^{-1} and a 0·02 Hz s^{-1} [0·05 Hz s^{-1} for (IIIb)] scan rate. For compound (IIId) benzene was the solvent with tetramethylsilane as internal standard. For (Ib) and (IIIc) spectra were also recorded at 60 MHz with a Perkin-Elmer R12 spectrometer.

The sample tubes for this detailed work were degassed by use of the freeze–thaw technique with a vacuum line, then sealed. Some oxidation of the sample of (Ib) occurred before the tube was prepared; this produced a strong impurity peak, at higher frequency than the $CH_2 \cdot CH_2$ band, which obscured a few of the weaker peaks. All the sample tubes were of 5 mm o.d.; sample spinning was employed.

The computations were carried out using the iterative program LACX [29] with an I.C.T. 1905E computer at the University of East Anglia. Between 27 and 37 lines were fitted in each case, and the errors on non-overlapping lines in the final calculations were less than 0·1 Hz for compounds (Ib), (IIIb), and (IIIc) [compound (IIId) gave marginally worse errors for reasons which are not clear].

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† While this paper was being prepared an article [26] was published which showed values of $^3J_{PH}$ varying in sign for the P–S–C–H fragment in a compound related to (Ib).

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1,3,2-*Dithiaphospholans*.—The following examples are typical preparative procedures.

2-*Diethylamino*-1,3,2-*dithiaphospholan* (Id). [*Method* (*C*)].—Diethylamine (7·3 g, 0·1 mol) was added dropwise with stirring to a solution of triethylamine (10·1 g, 0·1 mol) and 2-chloro-1,3,2-dithiaphospholan (Ia)[17] (15·8 g, 0·1 mol) in dry ether (150 ml) under nitrogen. The mixture was then heated under reflux for 1 h and filtered. The ether was removed *in vacuo* and the residue was distilled to yield 2-diethylamino-1,3,2-dithiaphospholan (10·8 g, 55%) a liquid, b.p. 88—90° at 1·0 mmHg.

2-*Methylthio*-1,3,2-*dithiaphospholan* (If) [*Method* (*C*)].—Trimethyl(methylthio)silane (VI; R = Me) (12·0 g, 0·1 mol) and the chloro-compound (Ia) (15·8 g, 0·1 mol) were heated under reflux under dry nitrogen for 8 h. Chlorotrimethylsilane (8·9 g, 82%) was distilled off. Distillation of the residue *in vacuo* yielded 2-methylthio-1,3,2-dithiaphospholan (13·0 g, 76%), b.p. 108—116° at 2 mmHg.

2-*Methyl*-2-*oxo*-1,3,2-*dithiaphospholan* (IIc) [*Method* (*B*)].—Methylphosphonic dichloride (6·7 g, 0·05 mol) and 2,2-dimethyl-1,3,2-dithiasilolan (7·5 g, 0·05 mol) were heated under reflux for 3 h in an atmosphere of dry nitrogen. Dichlorodimethylsilane (5·2 g, 81%) was distilled off. The residue was distilled *in vacuo* and yielded 2-methyl-2-oxo-1,3,2-dithiaphospholan (4·5 g, 45%), b.p. 141° at 0·7 mmHg, a liquid which slowly solidified.

2-*Chloro*-2-*thioxo*-1,3,2-*dithiaphospholan* (IIIa) [*Method* (*D*)].—A suspension of powdered sulphur (3·4 g, 0·106 mol) in a solution of 2-chloro-1,3,2-dithiaphospholan in dry benzene (100 ml) was heated at 200° for 48 h in a sealed, evacuated glass tube. After cooling the tube to room temperature and breaking the glass seal under nitrogen, the benzene was removed *in vacuo* and the remaining viscous oil was triturated several times with light petroleum (b.p. 40—60°). On cooling to the temperature of solid CO_2 and scratching the walls with a glass rod, the oil solidified to a yellowish white material which was recrystallised (× 4) from ether–light petroleum (b.p. 40—60°) to give white crystals of 2-chloro-2-thioxo-1,3,2-dithiaphospholan (9·5 g, 50%), m.p. 45°.

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