Dynamic Nuclear Magnetic Resonance and *X*-Ray Diffraction Studies of Tris(diphenylthiophosphoryl)methane and some Related Compounds

By **Ian J. Colquhoun** and **William McFarlane,*** Department of Chemistry, City of London Polytechnic, Jewry Street, London EC3N 2EY
Jean-Marie Bassett, Department of Chemistry, The City University, Northampton Square, London EC1V 0HB
Samuel O. Grim, Department of Chemistry, University of Maryland, College Park, Maryland 20742, U.S.A.

The ^{31}P n.m.r. spectra of $(Ph_2P)_3CH$ (1), $(Ph_2P)_2[Ph_2P(S)]CH$ (2), $(Ph_2P)[Ph_2P(S)]_2CH$ (3), and $[Ph_2P(S)]_3CH$ (4) in the temperature range −100 to +40 °C show that internal rotation about the P–methine-C bonds is essentially unhindered in (1) and (2) but restricted in (3) and (4) with E_a values of 29 and 49 kJ mol^{-1} respectively. An *X*-ray diffraction study of (4) shows that the preferred conformation has one P=S bond along the methine C–H direction and the other two opposed to it, and this persists in solution, even at higher temperatures. The magnitudes of the ^{31}P–^{31}P and ^{31}P–H couplings in (3) and in $(Ph_2P)[Me_2P(S)][Ph_2P(S)]CH$ are used to propose the preferred conformations of these molecules.

MOLECULES of the type $[R_2P(E)]_3CH$ [R = Me or Ph; E = lone pair, S, or Se] are of interest in connection with their ability to form stable anions by removal of the methine proton, and their potential as multi- and ambidentate ligands for a wide range of transition metals.[1-3] When R = Me there appears to be little hindrance to internal rotation about the P–CH bonds, and an *X*-ray diffraction study of $(Me_2P)_3CH$ has shown that in the solid state it adopts a configuration in which internal steric interactions appear to be small.[3] Molecular models suggest that for R = Ph and E $\neq$ lone pair, rotation about these P–C bonds might be sufficiently restricted to give separate signals from stereochemically different atoms in the low-temperature n.m.r. spectra, and we report here ^{31}P n.m.r. studies over a temperature range of −100 to +40 °C of the set of related compounds $(Ph_2P)_3CH$ (1), $(Ph_2P)_2[Ph_2P(S)]CH$ (2), $(Ph_2P)[Ph_2P(S)]_2CH$ (3), and $[Ph_2P(S)]_3CH$ (4). Neither (1) nor (2) showed any effects over our temperature range at a measuring frequency of 24.2 MHz, but at low temperatures (3) and (4) gave ABX and A_2X spectra respectively, which is indicative of freezing out of particular rotamers having P=S bonds with different orientations. In the case of (4) this interpretation was confirmed by a single-crystal *X*-ray diffraction study which showed that in the solid state the configuration adopted by this molecule has one P=S bond aligned approximately along the methine C–H direction, and the other two opposed to this. A band-shape analysis of the n.m.r. spectra also yielded values of 29 and 49 kJ mol^{-1} for the activation energies associated with the processes of internal rotation about the P–CH bonds in (3) and (4) respectively, and ^{31}P-$\{^{31}P,^{1}H\}$ and ^{31}P-$\{^{1}H\}$ selective multiple-resonance experiments on $(Ph_2P)[Me_2P(S)][Ph_2P(S)]CH$ (5) gave the signs of the ^{31}P–^{31}P coupling constants in this type of molecule.

EXPERIMENTAL

The compounds were made by previously published methods [1,2,4] and were purified by recrystallisation to constant melting point.

Proton-decoupled ^{31}P n.m.r. spectra were recorded at 24.2 MHz under conditions of complete proton decoupling on a JEOL FX-60 Fourier-transform spectrometer. Solutions of the compounds in CH_2Cl_2 + *ca.* 10% C_6D_6 to provide an internal field-frequency lock were examined in 10-mm o.d. tubes. A pulse angle of 60° and a repetition time of 2.2 s were normally used, and prior to transformation the free induction decay was weighted exponentially to maximise the signal-to-noise ratio without appreciably affecting the linewidths. Temperatures were calibrated to ±1 °C using a pentane thermometer inserted in the probe. The density-matrix spectral simulation program DNMR by Binsch and Kleier [5] from the Daresbury Laboratory n.m.r. program library was used to calculate the spectra of (3) and (4) for a range of exchange rates, T_2* being set at 0.1 s.

Molecular Structure Determination.—Compound (4) was recrystallised from dichloromethane–hexane (1 : 1) to give colourless transparent prisms elongated along the *b* axis. One such crystal, chosen for its optical clarity and well formed faces, and measuring approximately 0.7 × 0.3 × 0.3 mm, was mounted on a glass fibre with quick-setting epoxy-resin adhesive. The orthorhombic unit cell was determined from Weissenberg and precession *X*-ray photographs using Cu-K_α radiation, while the observed systematic absences ($h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$) defined the non-centrosymmetric space group $P2_12_12_1$.

The crystal was transferred to an Enraf-Nonius CAD4 automatic diffractometer. After optical centring, a search through reciprocal space provided 25 high-angle reflections (Cu-K_α radiation) with which the previously determined unit cell was found and refined.

Data were collected ($3 \leqslant \theta \leqslant 65°$) using nickel-filtered Cu-K_α *X*-radiation, two check reflections ($21\bar{5}$, $4\bar{1}3$) being remeasured every 100 reflections. However, subsequent analysis of the check reflection intensities revealed no significant variation as a function of time over the 49 h of *X*-ray exposure. Data were corrected for Lorentz polarisation effects; of 3 179 unique measured intensities, 2 798 [$F > 2.0\sigma(F)$] were used to solve and refine the structure.

While a substantial portion of the molecule was found using MULTAN,[6] an electron density difference-Fourier map, phased on the three phosphorus and three sulphur atoms only, led to the location of all carbon atoms. Three cycles of least-squares refinement using isotropic thermal parameters for all atoms and a rigid group refinement for the phenyl groups gave a reliability index $R = 0.08$, a difference synthesis revealing the position of the methine

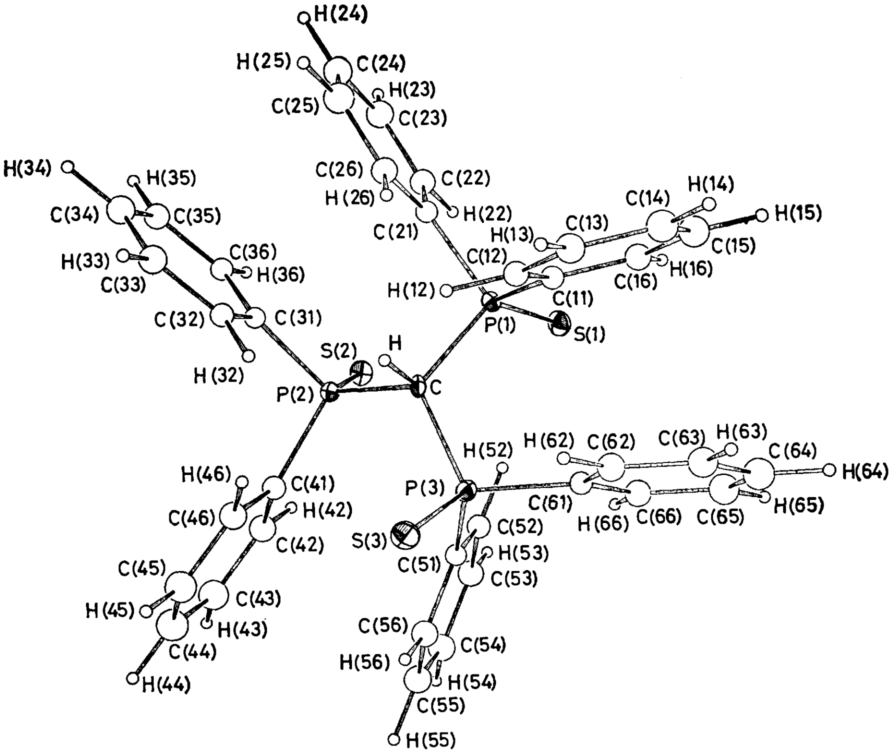

FIGURE 1 Perspective view of a molecule of (4). The thermal ellipsoids enclose volumes of 50% electron probability; hydrogen atoms are given an artificial radius of 0.1 Å

hydrogen atom. This latter was allowed to contribute to the structure factor calculation, but not permitted to refine. The rigid group constraint was lifted and phenyl hydrogen atoms were inserted in calculated positions with isotropic temperature factors fixed at *ca.* 120% of those of the attached carbon atoms. Further refinement of the model with anisotropic thermal parameters for phosphorus, sulphur, and the methine carbon atom reduced R to 0.072. At this stage, correctness of the absolute configuration was tested by inversion of the atom co-ordinates followed by a structure factor calculation. A lower R (0.066) signified that the inverted configuration was the correct enantiomorph and a further four cycles of full-matrix least-squares refinement using weighted F_0 moduli, such that $w = 1.000\,7/[\sigma^2(F) + 0.002\,83\ F^2]$, led to convergence at $R = 0.065$ ($R' = 0.071$). A final difference Fourier map was featureless apart from some noise (maximum *ca.* 0.5 e Å^{-3}).

The scattering factors used were from ref. 7 (P, C, and S) and ref. 8 (H). Derived atomic co-ordinates are listed in Table 1, while H-atom calculated positions are in Appendix A. Appendices B and C contain listings of thermal parameters and structure factors respectively. Structure solution and refinement were accomplished using MULTAN 80 [6] and SHELX 76,[9] both implemented on the CDC 7600 computer at the University of London Computer Centre. Molecular illustrations were obtained using ORTEP-II.[10] The appendices have been deposited as Supplementary Publication No. SUP 23017 (17 pp.).*

Crystal data. $C_{37}H_{31}P_3S_3$, $M = 664.8$, Orthorhombic, space group $P2_12_12_1$, $a = 11.935\,4(8)$, $b = 13.857\,6(9)$, $c = 20.085\,3(24)$ Å, $U = 3\,322.03$ Å^3, $Z = 4$, $D_c = 1.33$ g cm^{-3}, $F(000) = 1\,384$, $\lambda = 1.541\,78$ Å, $\mu(\text{Cu-}K_\alpha) = 34.53$ cm^{-1}.

RESULTS AND DISCUSSION

Figure 1 shows the molecular conformation adopted in the solid state by (4) which has S(3) in a position *trans* to S(1) and S(2). Figure 2 shows the packing of the unit cell in which the closest intermolecular contacts are not significantly less than the sums of the appropriate van der Waals radii; hence this configuration is the one which minimises the intramolecular repulsive forces, and is therefore probably also the one adopted in solution. In fact, the observed conformation in the solid may well be determined by interactions between the phenyl groups, each of which is oriented approximately parallel to its nearest neighbour on the adjacent phosphorus atom with an interannular spacing rather less than the interlayer spacing of 3.35 Å in graphite. For example, C(11)–C(61) = 3.26, C(21)–C(31) = 3.33, and C(41)–C(51) = 3.19 Å. However, in agreement with the n.m.r. results, the sulphur atoms must also be significant since S(1)–S(2) = 3.64 Å, which probably accounts for the values of 116.7 and 113.7° for the interbond angles C–P(1)–S(1) and C–P(2)–S(2) respectively (*cf.* 113° in PPh_3S [11]). By contrast C–P(3)–S(3) = 107.3°, presumably because the unique S(3) is subject to fewer steric constraints. The P–C–P interbond angles at the methine carbon of 112.7, 117.2, and 115.9° suggest similar constraints.

The low temperature (<200 K) ^{31}P n.m.r. spectrum of

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

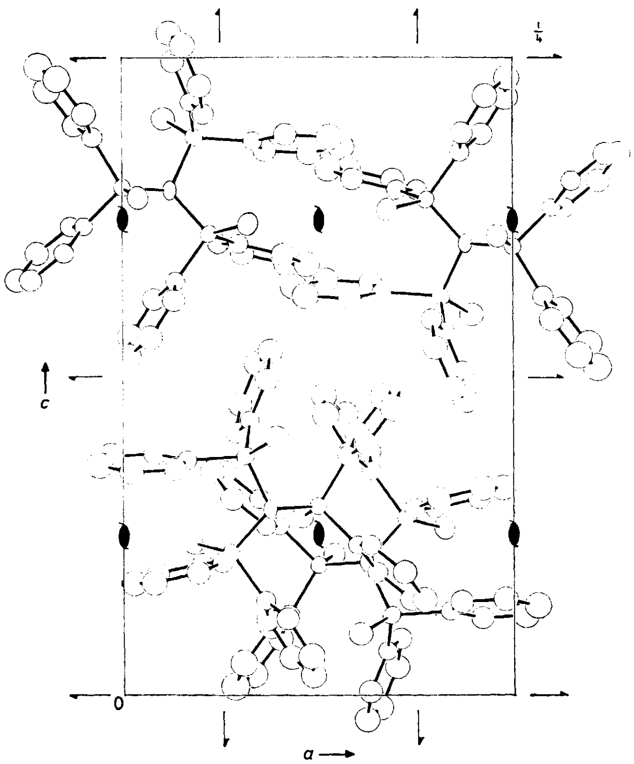


FIGURE 2 Contents of the unit cell of (4) viewed from the origin down the *b* axis

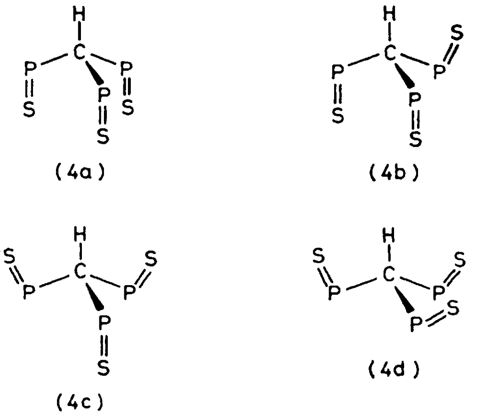
TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) of derived atoms of compound (4), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
P(1)	2 778(1)	4 066(1)	2 231(1)
P(2)	4 995(1)	4 614(1)	2 962(1)
P(3)	3 142(2)	3 381(1)	3 746(1)
S(1)	1 778(2)	5 150(1)	2 388(1)
S(2)	4 598(2)	5 946(1)	2 798(1)
S(3)	3 936(2)	2 223(2)	4 038(1)
C	3 773(5)	3 758(5)	2 919(3)
H *	4 210	3 220	2 710
C(11)	2 023(6)	2 939(5)	2 074(4)
C(12)	2 520(6)	2 030(5)	2 076(4)
C(13)	1 925(8)	1 199(6)	1 919(4)
C(14)	797(9)	1 294(7)	1 759(5)
C(15)	289(9)	2 185(7)	1 757(5)
C(16)	882(7)	3 012(6)	1 914(4)
C(21)	3 640(6)	4 212(5)	1 484(4)
C(22)	3 696(7)	5 123(6)	1 186(4)
C(23)	4 302(8)	5 249(7)	591(5)
C(24)	4 830(8)	4 452(7)	316(5)
C(25)	4 825(9)	3 556(7)	621(5)
C(26)	4 212(7)	3 436(6)	1 193(4)
C(31)	6 006(6)	4 140(5)	2 355(3)
C(32)	6 338(6)	3 188(5)	2 345(4)
C(33)	7 189(8)	2 909(6)	1 927(4)
C(34)	7 696(8)	3 549(6)	1 505(5)
C(35)	7 365(7)	4503(6)	1 512(4)
C(36)	6 483(6)	4 808(5)	1 925(4)
C(41)	5 755(6)	4 469(5)	3 740(4)
C(42)	5 977(8)	5 298(6)	4 119(4)
C(43)	6 679(9)	5 215(8)	4 675(5)
C(44)	7 146(10)	4 369(8)	4 841(5)
C(45)	6 908(9)	3 548(7)	4 507(5)
C(46)	6 245(8)	3 579(6)	3 940(4)
C(51)	3 259(6)	4 402(5)	4 300(3)
C(52)	2 915(7)	5 328(6)	4 119(4)
C(53)	3 005(8)	6 098(6)	4 562(4)
C(54)	3 424(8)	5 931(7)	5 188(5)
C(55)	3 790(8)	5 031(6)	5 376(5)
C(56)	3 682(8)	4 261(6)	4 944(4)
C(61)	1 646(6)	3 139(5)	3 677(3)
C(62)	1 324(7)	2 169(6)	3 540(4)
C(63)	213(8)	1 938(7)	3 494(5)
C(64)	−598(9)	2 621(7)	3 591(5)
C(65)	−312(9)	3 557(7)	3 744(5)
C(66)	812(7)	3 830(6)	3 787(4)

* Positional parameters not refined.

(4) is almost first order and consists of a doublet at δ 12.5 p.p.m. and a triplet at δ 20.7 p.p.m. which clearly arise from at A_2X spin system with $J(AX) = 6$ Hz. Either of the conformers (4b) or (4c) below would give this type of spectrum whereas (4a) and (4b) would each give a single line if it is assumed that small torsional variations in the positions of phenyl groups can be ignored. In view of the solid-state structure of (4) it is therefore reasonable to assume that at low temperatures the solution conformation adopted is (4b). At high temperatures (>300 K) the ^{31}P spectrum collapses to a single line at δ 15.8 p.p.m. which is sufficiently close to the weighted mean of the two slow-exchange chemical shift positions (δ 15.3 p.p.m.) to suggest that other conformers such as (4c) are not present to an appreciable extent. The exchange process can thus be represented as (4b) $\rightleftharpoons$ (4b′) $\rightleftharpoons$ (4b″) (see below), and involves concerted rotations about two of the P–methine-C bonds for each step.



The phenyl groups are omitted for clarity

Figure 3 shows the experimental and matching calculated ^{31}P spectra [5] for this system at several different temperatures and exchange rates, and from a plot of ln *K* against $1/T$ a value of 49 ± 2 kJ mol^{-1} was obtained for the activation energy of the process.

At temperatures above 270 K the proton-decoupled ^{31}P spectrum of (3) is an A_2X pattern with δ(PS) 43.5, δ(P) −12.0 p.p.m., and $J(PP) = 49.5$ Hz. Below 180 K this changes to the ABX pattern shown in Figure 4, which was analysed by standard methods [12] to yield the chemical shifts and coupling constants given in Table 3.

TABLE 2

Intramolecular bond distances (Å) and angles (°) with estimated standard deviations in parentheses

C–P(1)	1.871(6)	P(1)–C–P(2)	112.5(3)
C–P(2)	1.881(6)	P(1)–C–P(3)	117.2(3)
C–P(3)	1.896(7)	P(2)–C–P(3)	116.2(3)
C–H	1.00 *	H–C–P(1)	101 *
P(1)–S(1)	1.945(2)	H–C–P(2)	95 *
P(2)–S(2)	1.934(2)	H–C–P(3)	111 *
P(3)–S(3)	1.954(3)	S(1)–P(1)–C	116.5(2)
		S(2)–P(2)–C	113.8(2)
P(1)–C(11)	1.830(8)	S(3)–P(3)–C	107.3(2)
P(1)–C(21)	1.831(8)		
P(2)–C(31)	1.837(8)	C–P(1)–C(11)	104.2(3)
P(2)–C(41)	1.818(8)	C–P(1)–C(21)	105.9(3)
P(3)–C(51)	1.808(7)	C–P(2)–C(31)	104.7(3)
P(3)–C(61)	1.822(8)	C–P(2)–C(41)	110.9(3)
C(11)–C(12)	1.395(10)	C–P(3)–C(51)	107.1(3)
C(12)–C(13)	1.387(12)	C–P(3)–C(61)	112.0(3)
C(13)–C(14)	1.390(14)	C(11)–P(1)–C(21)	103.3(3)
C(14)–C(15)	1.376(12)	S(1)–P(1)–C(11)	112.6(2)
C(15)–C(16)	1.386(12)	S(1)–P(1)–C(21)	113.1(2)
C(16)–C(11)	1.403(11)	C(31)–P(2)–C(41)	101.7(3)
C(21)–C(22)	1.398(10)	S(2)–P(2)–C(31)	112.9(2)
C(22)–C(23)	1.408(12)	S(2)–P(2)–C(41)	112.0(3)
C(23)–C(24)	1.386(12)	C(51)–P(3)–C(61)	105.5(3)
C(24)–C(25)	1.395(12)	S(3)–P(3)–C(51)	114.9(2)
C(25)–C(26)	1.374(13)	S(3)–P(3)–C(61)	110.3(2)
C(26)–C(21)	1.401(10)	C(11)–C(12)–C(13)	122.1(7)
C(31)–C(32)	1.378(9)	C(12)–C(13)–C(14)	118.0(8)
C(32)–C(33)	1.373(11)	C(13)–C(14)–C(15)	120.8(10)
C(33)–C(34)	1.369(12)	C(14)–C(15)–C(16)	121.2(9)
C(34)–C(35)	1.380(11)	C(15)–C(16)–C(11)	119.3(8)
C(35)–C(36)	1.405(11)	C(16)–C(11)–C(12)	118.6(7)
C(36)–C(31)	1.388(9)	C(21)–C(22)–C(23)	120.0(8)
C(41)–C(42)	1.403(11)	C(22)–C(23)–C(24)	118.2(9)
C(42)–C(43)	1.402(13)	C(23)–C(24)–C(25)	122.4(9)
C(43)–C(44)	1.341(14)	C(24)–C(25)–C(26)	118.7(9)
C(44)–C(45)	1.350(13)	C(25)–C(26)–C(21)	121.0(8)
C(45)–C(46)	1.387(13)	C(26)–C(21)–C(22)	119.4(7)
C(46)–C(41)	1.423(11)	C(31)–C(32)–C(33)	119.5(7)
C(51)–C(52)	1.395(10)	C(32)–C(33)–C(34)	121.6(8)
C(52)–C(53)	1.394(11)	C(33)–C(34)–C(35)	119.3(9)
C(53)–C(54)	1.372(12)	C(34)–C(35)–C(36)	120.6(8)
C(54)–C(55)	1.374(12)	C(35)–C(36)–C(31)	118.3(7)
C(55)–C(56)	1.382(12)	C(36)–C(31)–C(32)	120.8(7)
C(56)–C(51)	1.402(11)	C(41)–C(42)–C(43)	118.6(9)
C(61)–C(62)	1.424(10)	C(42)–C(43)–C(44)	120.9(6)
C(62)–C(63)	1.368(12)	C(43)–C(44)–C(45)	121.8(11)
C(63)–C(64)	1.367(13)	C(44)–C(45)–C(46)	120.1(10)
C(64)–C(65)	1.377(13)	C(45)–C(46)–C(41)	119.5(8)
C(65)–C(66)	1.396(13)	C(46)–C(41)–C(42)	118.6(8)
C(66)–C(61)	1.399(10)	C(51)–C(52)–C(53)	120.9(7)
P(1)–C(11)–C(12)	124.2(6)	C(52)–C(53)–C(54)	119.0(9)
P(1)–C(21)–C(22)	118.5(6)	C(53)–C(54)–C(55)	121.3(10)
P(2)–C(31)–C(32)	122.7(5)	C(54)–C(55)–C(56)	119.9(9)
P(2)–C(41)–C(42)	118.0(6)	C(55)–C(56)–C(51)	120.3(8)
P(3)–C(51)–C(52)	122.4(5)	C(56)–C(51)–C(52)	118.4(7)
P(3)–C(61)–C(62)	116.9(6)	C(61)–C(62)–C(63)	119.7(9)
		C(62)–C(63)–C(64)	121.0(10)
		C(63)–C(64)–C(65)	120.5(11)
		C(64)–C(65)–C(66)	120.5(11)
		C(65)–C(66)–C(61)	119.2(8)
		C(66)–C(61)–C(62)	119.0(7)

* Hydrogen-atom positional parameters not refined.

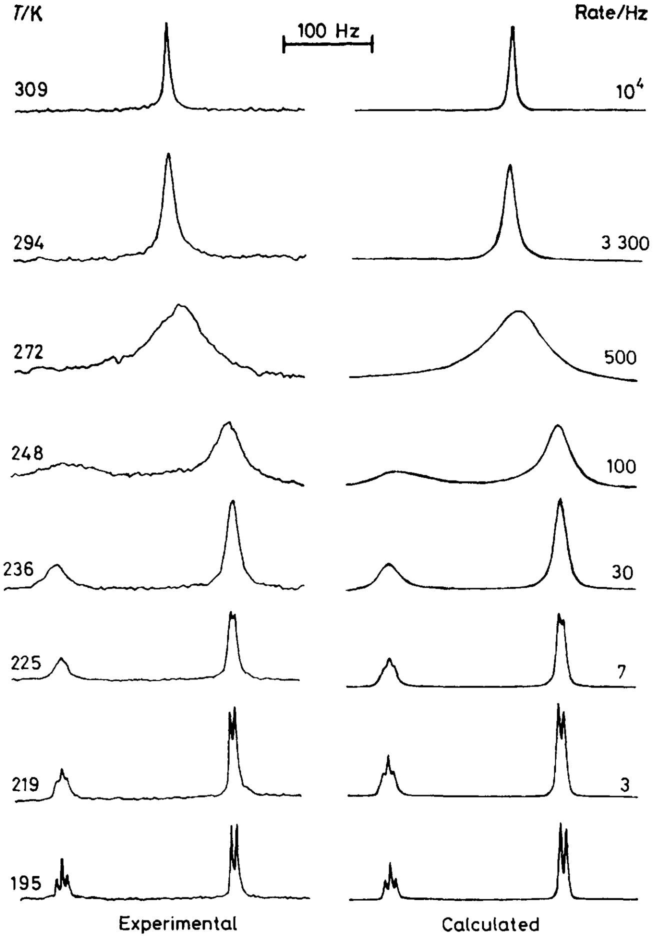
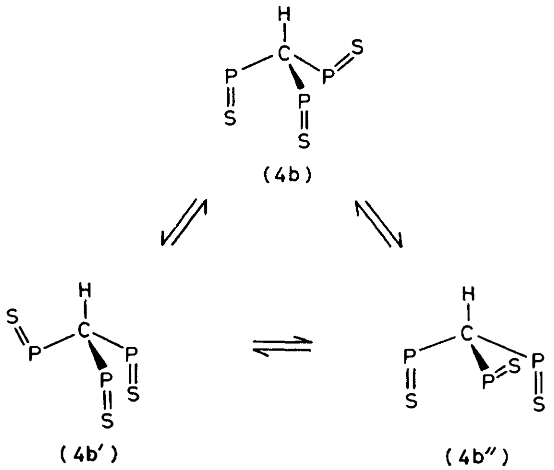
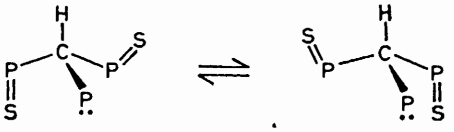


FIGURE 3 Experimental and calculated ^{31}P-$\{^1H\}$ n.m.r. spectra of (4) recorded at 24.2 MHz for a range of temperatures and exchange rates

The value of J(PP) in the fast-exchange spectrum is very close to the mean (49.1 Hz) of J(AX) and J(BX) in the slow-exchange limit. This is fully consistent with the exchange process in (3) being analogous to that occurring in (4), and involving either of the molecular configurations (3a) or (3b), but not both, with a concerted pair of rotations about the P(S)–C bonds. Band-shape analysis [5] yielded 29 ± 2 kJ mol^{-1} for the activation energy of this process. This is significantly lower than the activation energy for the corresponding process in (4), and is consistent with the idea that in these species the presence of sulphur atoms on phosphorus leads to greater



steric interactions than do lone pairs. The two P(S)–P coupling constants [*viz.* J(AX) and J(BX)] are very different and this is to be expected in view of the different stereochemical relationships between the two P(S) nuclei and the third phosphorus, although insufficient information is available on two-bond P^{III}–P^{V} coupling for us to state unequivocally which relationship leads to the larger coupling. However, the closeness of the mean value of ${}^2J(P^{V}P^{III})$ to the value observed under conditions of fast exchange strongly suggests that only one of (3a) and (3b) is involved to any appreciable extent, even at higher temperatures, since this coupling should vary significantly according to the orientation of the phosphorus lone pair.[13] The methine proton resonance of (3) at higher temperatures is a triplet of doublets, with ${}^2J(P^{V}\text{–H}) = 17$ Hz and ${}^2J(P^{III}\text{–H}) = 2.3$ Hz. The small value of the latter coupling strongly suggests that the lone pair on phosphorus is oriented away from the C–H bond,[14] so that the actual conformer present is (3a), and the exchange process is represented by (3a) $\rightleftharpoons$ (3a′) as shown below.



(3a) (3a′)

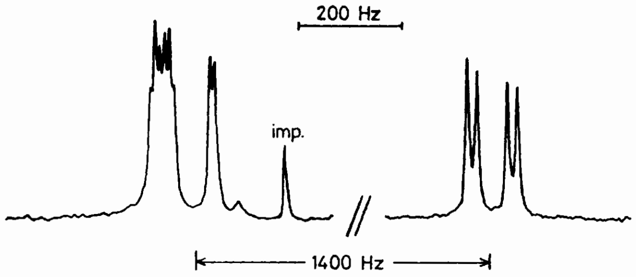
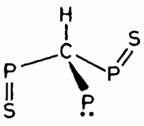
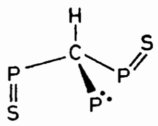


FIGURE 4 24.2-MHz ${}^{31}P\text{-}\{{}^{1}H\}$ n.m.r. spectrum of (3) at 163 K in CH_2Cl_2–$CFCl_3$ (imp. = impurity)



(3a)



(3b)

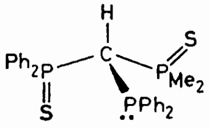
TABLE 3

Phosphorus-31 n.m.r. parameters for compounds (3) and (5)

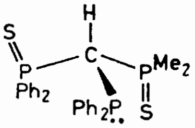
Parameter [a]	(3) (at 175 K)	(5) (at 300 K)
$\delta({}^{31}P^{III})$/p.p.m.[b]	-12.0	-7.9
$\delta({}^{31}P^{V}_{A})$/p.p.m.[b]	46.7	44.0
$\delta({}^{31}P^{V}_{B})$/p.p.m.[b]	44.0	43.2
${}^2J({}^{31}P^{III} \cdots {}^{31}P^{V})$/Hz [c]	(+)18.5	+28.5
${}^2J({}^{31}P^{III} \cdots {}^{31}P^{V}_{B})$/Hz [c]	(+)79.8	+85.2
${}^2J({}^{31}P^{V}_{A} \cdots {}^{31}P^{V}_{B})$/Hz [c]	(−)9.2	-6.0

[a] In (5), P^{V}_{A} carries two methyl groups; the assignment in (3) is uncertain. [b] To high frequency of 85% H_3PO_4, ±0.1 p.p.m. [c] Relative signs in (5) were determined by homonuclear ^{31}P double resonance. The large ${}^2J$(PP) is assumed to be positive (see I. J. Colquhoun, S. O. Grim, W. McFarlane, J. D. Mitchell, and P. H. Smith, *Inorg. Chem.*, in the press).

Table 3 also gives n.m.r. parameters for (5) which even at room temperature gives an ABX spectrum since all three phosphorus atoms bear different substituents. It is especially striking that the ${}^{31}P$–${}^{31}P$ coupling constants in the 'high' temperature spectrum of (5) are very similar to those in the 'low' temperature spectrum of (3). This suggests (i) that only a single conformer of (5) is present even at high temperatures, (ii) that this conformer has one of its P=S bonds aligned approximately along the methine-C–H direction, and the other opposed to it, and (iii) that the trivalent phosphorus atom has the same orientation as in (3), *i.e.* its lone pair is directed away from the methine-C–H bond. The last point is supported by the small (*ca.* 0) value[1] of the ${}^{31}P^{III}$–CH coupling constant, and there are thus two possible conformations to be considered, (5a) and (5b), of which only one is actually present to any appreciable extent. The couplings ${}^2J({}^{31}PH)$ of 17.4 and 12.1 Hz to the $Me_2P(S)$ and $Ph_2P(S)$ groups respectively tend to suggest that the former has the P=S bond aligned along the C–H direction,[14] and we therefore tentatively suggest that the actual conformation adopted is (5a). Inspection of a molecular model shows that there is considerable steric interference between the phenyl groups in (5b) which is substantially avoided in the preferred conformation (5a).



(5a)



(5b)

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