Nuclear Magnetic Resonance Spectra of Symmetrical Phosphorus Compounds. Part V.[1] ^{1}H Nuclear Magnetic Resonance Spectrum of *P,P′*-Dimethyl-*P,P′*-Di-t-butyldiphosphine *P,P′*-Disulphide, an $[AR_tX_n]_2$ Spin System

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General expressions are given for the X transition frequencies and intensities of the $[AR_tX_n]_2$ spin system with $J_{RR'} = J_{XX'} = J_{RX} = J_{RX'} = 0$. The information is used for the analysis of the ^{1}H n.m.r. spectrum of $[Me(Bu^t)P(S)]_2$. The value of ${}^1J_{PP}$ (118 ± 5 Hz) for this molecule is found to be unusually high for a tetra-alkyldiphosphine disulphide.

NUCLEAR magnetic resonance spectra of the $[AX_n]_2$ type have been analysed[2] for a variety of compounds, and recently[3] spectra of the $[ARX_n]_2$ type have been discussed. The synthesis[4] of $[Me(Bu^t)P(S)]_2$ led us to consider the more general $[AR_tX_n]_2$ spin system, which includes the systems mentioned above as limiting cases. We shall follow the treatment of symmetric spin systems given[2] for $[AX_n]_2$ cases and derive explicit algebraic expressions for transition energies and relative intensities of the X (or R) nuclei subject to the condition that the long-range coupling constants, defined as below, are zero. The system discussed here is in general characterised by 12 n.m.r. parameters: (1), the chemical shifts, ν_A, ν_R, ν_X; (2), the coupling constants, J_{AR}, $J_{AR'}$, J_{AX}, $J_{AX'}$, $J_{AA'}$; (3), the long range coupling constants (which are assumed in what follows to be zero) $J_{RR'}$, J_{RX}, $J_{RX'}$, $J_{XX'}$.

The coupling constants internal to the R_t, R'_t, X_n, and X'_n groups do not affect the spectra, and they will be ignored in the treatment. It proves convenient to use the following linear combinations of coupling constants:

$$N_{AR} = J_{AR} + J_{AR'} \qquad L_{AR} = J_{AR} - J_{AR'}$$
$$N_{AX} = J_{AX} + J_{AX'} \qquad L_{AX} = L_{AX} - J_{AX'}$$

The chemical shift differences $\Delta\nu_{AR}$ and $\Delta\nu_{AX}$ are considered to be much larger than the coupling constants so that the 'X approximation' applies.[5] The magnitude of the shift difference $\Delta\nu_{RX}$ is, however, immaterial since it is assumed that $J_{RX} = J_{RX'} = 0$. The chemical shifts ν_A, ν_R, and ν_X therefore merely control the position of each part of the spectrum, whereas the appearance of all parts depends solely on the parameters, N_{AR}, L_{AR}, N_{AX}, L_{AX}, and $J_{AA'}$.

THEORY

The symbols α and β will be used for the basis spin states of the A and A′ nuclei, while the basis states of the groups R_t, R'_t, X_n, and X'_n will be referred to by the quantum numbers associated with their total spin components in the direction of the static magnetic field (the *z* direction). These quantum numbers will be denoted *q*, *s*, *p*, and *m* respectively. The full basis spin states will be written with the order AA′ $R_tR'_t$ $X_nX'_n$. Because of the assumptions listed above there will be no off-diagonal elements of the nuclear spin Hamiltonian between states differing in $m_A + m_{A'}$, where quantum numbers m_A and $m_{A'}$ refer to the *z* component of spin of the A and A′ nuclei respectively. Therefore we may separate the total matrix representation of the Hamiltonian into three sub-matrices appropriate for: (i) the αα, (ii) the ββ, and (iii) the αβ and βα states of the A and A′ nuclei. Sub-matrices (i) and (ii) may be treated with the usual[5] 'X approximation'; the only R and X transitions arising from these sub-matrices will be at:

$$\nu_R \pm \tfrac{1}{2}N_{AR}$$
$$\nu_X \pm \tfrac{1}{2}N_{AX}$$

Each of these transitions will have one quarter of the total intensity associated with the appropriate type of nucleus.

More detailed consideration of sub-matrix (iii) is necessary. However, the assumption that all 'long-range' coupling constants are zero makes it unnecessary to take the symmetry explicitly into account; indeed it is easier not to do so. The basis wave functions are mixed in groups of two

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[1] (*a*) Part I, R. K. Harris and R. G. Hayter, *Canad. J. Chem.*, 1964, **42**, 2282; (*b*) Part II, E. G. Finer, R. K. Harris, M. R. Bond, R. Keat, and R. A. Shaw, *J. Mol. Spectroscopy*, 1970, **33**, 72; (*c*) Part III, R. K. Harris, J. R. Woplin, and R. Schmutzler, *Ber. Bunsengesellschaft Phys. Chem.*, 1971, **75**, 134; (*d*) Part IV, R. K. Harris, J. R. Woplin, M. Murray, and R. Schmutzler, *J.C.S. Perkin II*, 1972, 380.

[2] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

[3] B. E. Mann, *J. Chem. Soc.* (*A*), 1970, 3050.

[4] G. Hägele, unpublished results.

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

only, with matrix elements as follows (chemical shift terms have been omitted for convenience):

$$\begin{array}{lcc} & \alpha\beta qspm & \beta\alpha qspm \\ \alpha\beta qspm & \frac{1}{2}\{(q-s)L_{\mathrm{AR}} + (p-m)L_{\mathrm{AX}}\} & \frac{1}{2}J_{\mathrm{AA'}} \\ \beta\alpha qspm & \frac{1}{2}J_{\mathrm{AA'}} & -\frac{1}{2}\{(q-s)L_{\mathrm{AR}} + (p-m)L_{\mathrm{AX}}\} \end{array}$$

Diagonalisation of these sub-sub-matrices yields the eigenvalues:

$$\varepsilon(q,s,p,m) = \pm\tfrac{1}{2}[\{(p-m)L_{\mathrm{AX}} + (q-s)L_{\mathrm{AR}}\}^2 + J_{\mathrm{AA'}}{}^2]^{\frac{1}{2}} \quad (1)$$

where $(p - m)$ and $(q - s)$ may take any integral value from $-n$ to $+n$ and from $-t$ to $+t$ respectively. It is convenient to introduce the parameters:

$$(p - m) = \chi \qquad (q - s) = \Omega$$

and to consider the X transitions of the general type:

$$(\chi,\Omega) \longrightarrow (\chi - 1,\Omega)$$

where χ can be $-n + 1$ to n, and Ω can be $-t$ to $+t$. There result two pairs of lines symmetrically placed around ν_{X} for each value of χ and Ω. These have separations:

$$S_{\mathrm{i}}^{\mathrm{X}}(\chi,\Omega) = |[\{\chi L_{\mathrm{AX}} + \Omega L_{\mathrm{AR}}\}^2 + J_{\mathrm{AA'}}{}^2]^{\frac{1}{2}} - [\{(\chi-1)L_{\mathrm{AX}} + \Omega L_{\mathrm{AR}}\}^2 + J_{\mathrm{AA'}}{}^2]^{\frac{1}{2}}| \quad (2)$$

$$S_{\mathrm{o}}^{\mathrm{X}}(\chi,\Omega) = |[\{(\chi L_{\mathrm{AX}} + \Omega L_{\mathrm{AR}}\}^2 + J_{\mathrm{AA'}}{}^2]^{\frac{1}{2}} + [\{(\chi-1)L_{\mathrm{AX}} + \Omega L_{\mathrm{AR}}\}^2 + J_{\mathrm{AA'}}{}^2]^{\frac{1}{2}}| \quad (3)$$

The pair with the separation containing the minus sign between the square root terms will be referred to as inner lines; the other pair will be named outer lines. However, it may be seen that all the lines described by (2) and (3) are doubly degenerate (those with χ, Ω have the same separations as those with $-\chi + 1$, $-\Omega$); it is therefore only necessary to consider values of χ from 1 to n. Thus there are $4n(2t + 1)$ possible transition energies for the X nuclei arising from sub-matrix (iii), many of which will be very weak (see below). Analogous expressions may be obtained for the R transitions. It should be noted that the X and R regions of the spectrum are in general different.

Relative Intensities.—There will be three factors affecting relative intensities of X transitions arising from sub-matrix (iii): (a) The statistical probability of the χ state occurring and undergoing a transition to the $(\chi - 1)$ state, given by ${}^{(2n-1)}C_{(n-\chi)}$ as for the simpler $[AX_n]_2$ system.[2]

(b) The statistical probability of the Ω state, given by: ${}^{2t}C_{(t-\Omega)}$.

(c) A weighting factor which takes into account mixing between the $\alpha\beta$ and $\beta\alpha$ states. This factor is, for the inner lines $(\cos\theta_\chi\cos\theta_{\chi-1} + \sin\theta_\chi\sin\theta_{\chi-1})^2 = \cos^2(\theta_\chi - \theta_{\chi-1}) = \frac{1}{2}(1 + g)$, say, and for the outer lines $(-\sin\theta_\chi\cos\theta_{\chi-1} + \cos\theta_\chi\sin\theta_{\chi-1})^2 = \sin^2(\theta_\chi - \theta_{\chi-1}) = \frac{1}{2}(1 - g)$, where the angles are given by $\tan 2\theta_\chi = J_{\mathrm{AA'}}/\{\chi L_{\mathrm{AX}} + \Omega L_{\mathrm{AR}}\}$.

Thus the full expressions for the X intensities are:

Each inner line:

$$Z_{\mathrm{i}}(\chi,\Omega) = \tfrac{1}{2}(1 + g)^{(2n-1)}C_{(n-\chi)}\,{}^{2t}C_{(t-\Omega)} \quad (5)$$

Each outer line:

$$Z_{\mathrm{o}}(\chi,\Omega) = \tfrac{1}{2}(1 - g)^{(2n-1)}C_{(n-\chi)}\,{}^{2t}C_{(t-\Omega)} \quad (6)$$

where: $g = \cos 2(\theta_\chi - \theta_{\chi-1})$

$$= \frac{\{\chi L_{\mathrm{AX}} + \Omega L_{\mathrm{AR}}\}\{(\chi-1)L_{\mathrm{AX}} + \Omega L_{\mathrm{AR}}\} + J^2{}_{\mathrm{AA'}}}{\{[\{\chi L_{\mathrm{AX}} + \Omega L_{\mathrm{AR}}\}^2 + J^2{}_{\mathrm{AA'}}][\{(\chi-1)L_{\mathrm{AX}} + \Omega L_{\mathrm{AR}}\}^2 + J^2{}_{\mathrm{AA'}}]\}^{\frac{1}{2}}} \quad (7)$$

These intensities are normalised such that the total intensity in the $\chi = n$, $\Omega = t$ sub-spectrum is 2. Multiplication by $4n$ gives intensities such that the total X intensity is given by the usual expression $n2^{2(n+t+1)}$.

It may be noted that the $[AR_tX_n]_2$ spectra in the present situation (zero long-range coupling constants) contain lines (when $\Omega = 0$) at all the frequencies expected for the $[AX_n]_2$ system, and with the appropriate relative intensities, *i.e.* there is an $[ax_n]_2$ sub-spectrum. Recognition of the appropriate lines leads to immediate evaluation of L_{AX} and $J_{\mathrm{AA'}}$.

It should be noted from equations (2) and (3) that the conditions for a deceptively simple triplet [2,5] in the X region differ for the $[AR_tX_n]_2$ and $[AX_n]_2$ spin systems. In the former case the situation is complicated but the condition $L^2{}_{\mathrm{AX}} < 2|J_{\mathrm{AA}}|\Delta\nu_{\frac{1}{2}}$, where $\Delta\nu_{\frac{1}{2}}$ is the resolution, is not sufficient, but rather $|J_{\mathrm{AA}}|$ must be much greater than a function of both L_{AX} and L_{AR}. For the $\chi = 1$ lines an approximate condition is $|L_{\mathrm{AX}}(L_{\mathrm{AX}} + 2\Omega L_{\mathrm{AR}})| < 2|J_{\mathrm{AA}}|\Delta\nu_{\frac{1}{2}}$. This fact implies that conditions of deceptive simplicity for $[AX_n]_2$ systems may sometimes be removed by the presence of a third type of nucleus, *i.e.* in a related system of the type $[AR_tX_n]_2$.

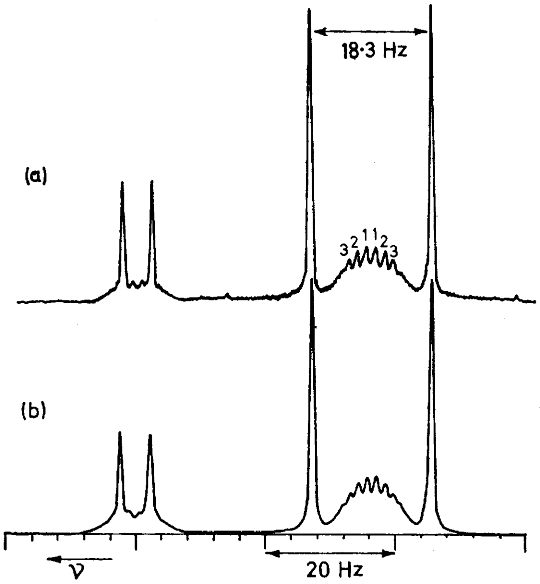

FIGURE 1 The 100 MHz ^{1}H n.m.r. spectrum of $[Me(Bu^t)P(S)]_2$; (a), observed spectrum for a saturated solution in benzene; (b), spectrum simulated by the computer program DOKI using the spin parameters reported in Table 2 and linewidths 0·6 Hz for the *N*-doublets and 1·2 Hz for the χ-lines

In conditions just short of deceptive simplicity, *i.e.* with $|J_{\mathrm{AA}}| \gg |L_{\mathrm{AR}}|$, $|L_{\mathrm{AX}}|$, a square root approximation may be applied to equation (2), yielding, for the inner lines:

$$S_{\mathrm{i}}^{\mathrm{X}}(\chi,\Omega) = |[2(\chi L_{\mathrm{AX}} + \Omega L_{\mathrm{AR}}) - L_{\mathrm{AX}}]L_{\mathrm{AX}}/2J_{\mathrm{AA}}| \quad (8)$$

The X and R regions are still, however, different.

Computer programmes [4,6] have been written, based on equations (2)—(7), which calculate the complete set of R and X transitions, thus allowing simulation of the R_t and X_n parts of $[AR_tX_n]_2$ spectra.

The ^{1}H *n.m.r. spectrum of* $[Me(Bu^t)P(S)]_2$. In Figure 1 (a) the 100 MHz spectrum of a saturated solution of $[Me(Bu^t)$-

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[6] J. Nichols, M.Sc. Thesis, University of East Anglia, Norwich, 1971.

$P(S)]_2$ in benzene is illustrated. The ' N-doublets ' for the Me and Bu^t groups are easily discernible, yielding the values:

$$N_{\mathrm{Me}} = 4{\cdot}55\ \mathrm{Hz} \text{ and } N_{\text{t-Bu}} = 18{\cdot}30\ \mathrm{Hz}$$

Since the long range (P,H) coupling constant $^{4}J_{\mathrm{PH}}$ is likely to be very small, we assume $L_{\mathrm{Bu^t}}$ is 18·3 Hz (this is confirmed by calculations). To determine L_{Me} and J_{PP} we make use of the t-butyl region of the spectrum alone, since in the methyl region the N doublet obscures the remaining structure.

TABLE 1

The assignment for the t-butyl region of the $[Me(Bu^t)P(S)]_2$ spectrum

Lines [a]	S_i(obs)/ Hz	(χ,Ω) [b]	S_i(calc.)/ Hz [c]	Intensity (calc) [c,d]	S_i(plot) [e]
1	1·41	4,3	0·94	0·001	1·44
		3,2	1·09	0·018	
		2,1	1·25	0·069	
		1,0	1·41	0·115	
		1,1	1·57	0·086	
		2,2	1·72	0·028	
		3,3	1·88	0·003	
2	4·28	5,3	3·69	0·001	4·16
		4,2	3·84	0·009	
		3,1	3·99	0·044	
		2,0	4·13	0·092	
		1,−1	4·28	0·086	
		1,2	4·43	0·035	
		2,3	4·57	0·005	
3	6·71	6,3	6·20	0·000	6·60
		5,2	6·34	0·003	
		4,1	6·47	0·022	
		3,0	6·60	0·059	
		2,−1	6·73	0·069	
		1,−2	6·85	0·035	
		1,3	6·98	0·006	

[a] See Figure 1a. [b] Assignment (see text) assuming L_{AR} and L_{AX} are opposite in sign. [c] Calculated on the basis of the parameters given in Table 2. [d] This gives the intensity of each line relative to the intensity of one of the N doublet lines as unity. [e] Separations of maxima in the plotted spectrum, using χ linewidths of 1·2 Hz. The plotting routine only calculates intensities at 0·02 Hz intervals.

The principal problem in the spectral analysis lies in obtaining the correct assignment of the most intense pairs of lines, labelled 1, 2, and 3 in Figure 1. Their intensity indicates that they must correspond to low values of χ and $|\Omega|$. We proceeded by assigning each pair in turn as due to the ($\chi = 1$, $\Omega = 0$) subspectrum (this allows $|J_{\mathrm{PP}}|$ to be obtained and all the other $\Omega = 0$ lines calculated), then assigning one of the other strong pairs to the ($\chi = 1$, $\Omega = 1$) or ($\chi = 1$, $\Omega = -1$) subspectrum (this allows L_{AR} to be obtained). Full calculation then showed whether or not this was a feasible solution. The only solution which fitted the intensities as well as the frequencies of the transitions was that given in Table 1. The spin parameters obtained are listed in Table 2.

TABLE 2

N.m.r. data for diphosphine disulphides [a,b,c]

	δ_{P}	$\lvert J_{\mathrm{PP}}\rvert$	N_{M}	L_{M}	$^{2}J_{\mathrm{PM}}$ [d]	$^{3}J_{\mathrm{PM}}$ [d]	δ_{M}	Ref.
$[Me_2P(S)]_2$	33·4	18·7	5·48	20·0	−12·74 *	+7·26 *	1·96	1*a*
$[Me(Bu^t)P(S)]_2$ [e]	48·05 ± 0·4	118 ± 5	4·55 ± 0·05	19·3 ± 1·5	−11·9 †	+7·4 †	1·667 ± 0·001	This work
$Me_2P(S)P(S)Ph_2$	40·1 [f]	22·5			13·0 [g]	7·8 [g]	1·92	9

[a] M methyl protons, B t-butyl protons. [b] The chemical shifts are given in p.p.m. and are with respect to tetramethylsilane and 85% H_3PO_4 for δ_{H} and δ_{P} respectively (positive signs mean that the sample resonance is to high frequency of the reference resonance). [c] Coupling constants are measured in Hz. For the signs see the text. [d] The spectral analysis does not distinguish between the coupling constants marked * or between those marked † (see the text). [e] The data for $[Me(Bu^t)P(S)]_2$ may represent averages for the two stereoisomers (see the text). Other parameters for this compound are $N_{\mathrm{B}} = 18{\cdot}30 \pm 0{\cdot}05$ Hz, $L_{\mathrm{B}} = 18{\cdot}3 \pm 0{\cdot}5$ Hz (leading to $^{3}J_{\mathrm{PH}} = 18{\cdot}3 \pm 0{\cdot}3$ Hz, $^{4}J_{\mathrm{PH}} = 0{\cdot}0 \pm 0{\cdot}3$ Hz), and $\delta_{\mathrm{B}} = 1{\cdot}317 \pm 0{\cdot}001$. [f] Of the MeP group. [g] Signs not determined.

The complete ^{1}H n.m.r. spectrum was then simulated using the computer programme[4] DOKI, and is shown in Figure 1(b). It was not possible to fit the bandshape of Figure 1(a) with a general linewidth for both the N-doublets and the χ-lines. The χ-lines proved to be much broader; the best fit was achieved with halfwidths of 0·6 Hz for the N-doublets and 1·2 Hz for the χ-lines, as in Figure 1(b). Similar effects of differing line widths have been found previously for other symmetric spin systems containing phosphorus.[1b] It is, indeed, normal for the N-doublets to be sharper than the χ-lines. Although several possible explanations have been advanced, the origin of the effect is not well understood.

The methyl and t-butyl regions of our spectrum are rather similar (except for the N-doublets). This arises because L_{AR} and L_{AX} are close in magnitude.

DISCUSSION

The chemical shift values for the methyl and t-butyl groups are consistent with the results obtained[7] for a variety of compounds of the type $Me(Bu^t)P(S)X$, as are the coupling constants $^{2}J_{\mathrm{PCH}}$ and $^{3}J_{\mathrm{PCCH}}$. We assume, by comparison with related compounds,[8] that $^{2}J_{\mathrm{PCH}}$ is negative. However it should be noted that the spectral analysis does not distinguish between $^{2}J_{\mathrm{PCH}}$ and $^{3}J_{\mathrm{PPCH}}$ (the analogous difficulty for the t-butyl group does not present a real problem since $^{4}J_{\mathrm{PH}} \simeq 0$ is far more reasonable than $^{3}J_{\mathrm{PH}} \simeq 0$). A similar assignment problem exists for $[Me_2P(S)]_2$ (see ref. 1*a*). When corresponding assignments are made for the two molecules $[MeRP(S)]_2$, R = Me and Bu^t, it may be seen that there is close agreement of the magnitudes of both $^{2}J_{\mathrm{PCH}}$ and $^{3}J_{\mathrm{PPCH}}$; moreover the relative signs of the two coupling constants are opposite in both cases. Our assignment of $^{2}J_{\mathrm{PCH}}$ and $^{3}J_{\mathrm{PPCH}}$ (see Table 1) is based on two pieces of evidence: (i) for a variety of compounds of the type $Me(Bu^t)P(S)X$ the value of $|^{2}J_{\mathrm{PCH}}|$ lies[8] between 11·5 and

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[7] G. Hägele, Dissertation, Technische Hochschule, Aachen, 1969.

[8] G. Mavel, *Progr. N.M.R. Spectroscopy*, 1966, **1**, 251.

12·3 Hz, and (ii) for the compound $(CH_3)_2P(S)P(S)Ph_2$ it has been shown conclusively[9] that $|^2J_{PCH}| = 13{\cdot}0$ Hz and $|^3J_{PPCH}| = 7{\cdot}8$ Hz.

In contrast, the magnitudes of $^1J_{PP}$ are very different in the two cases. The value for $Et_2P(S)P(S)$(cyclohexyl)$_2$ is 69 Hz.[10] This variability of $^1J_{PP}$ is evident for a variety of molecular types;[11] the reasons for this situation are not well understood. The series of tetra-alkyldiphosphine disulphides appears to be suitable for study since substituent electronegativity changes may be relatively small. The two factors most likely to influence $^1J_{PP}$ in such cases are (i) changes in P–P bond *s*-character[12] due to substituent bulk, and (ii) changes in conformation, also arising from substituent bulk effects. Recently[13] it has been shown that $^1J_{PP}$ differs substantially for the two stereoisomers of $[MePhP]_2$, and this has been attributed to internal rotation effects. However, such variations were not found[13] for MePhPP(S)PhMe. We have been unable to resolve spectra due to the two stereoisomers (if present in our solution) of $[Me(Bu^t)P(S)]_2$. Our value of $^1J_{PP}$ must be regarded as a weighted average if both isomers are present (this average would arise not from chemical exchange but from lack of spectral resolution). Alternatively it may be that only a single stereoisomer is present, as was concluded for $[Me(Bu^t)P]_2$ from ^1H and ^{31}P magnetic resonance evidence by Scherer and Glick.[14] However, we do not believe that our ^1H n.m.r. evidence warrants any definite conclusion regarding the number of stereoisomers present in our solution; on the other hand, if both isomers are present the chemical shift difference between their Me(or Bu^t) protons must be less than 0·003 p.p.m. In the case of $[MeFP(S)]_2S$ it has been shown[1d,15] that the chemical shift difference between the methyl protons is 0·003 p.p.m. for $CDCl_3$ solution and 0·014 p.p.m. for a C_6D_6 solution.

It has been shown[4] to be likely that rotation about the P–C axis is restricted for compounds of the type $Br(Bu^t)P(S)–C_R$ (C_R = Et and Pr^i); a similar steric hindrance might be expected for rotation about the P–P bond in $[Me(Bu^t)P(S)]_2$. This would imply major contributions to the spectrum from meso-rotamer 2 and racemic-rotamer 5 (see Figure 2); these forms have *trans* Bu^t groups. However an opposing influence might arise from a preference of the sulphur atoms for mutually *trans* positions. At all events the substitution of one Bu^t for Me in $[Me_2P(S)]_2$ would undoubtedly lead to an increase in the population of forms with *gauche* sulphur atoms. The data of Table 2 therefore suggest that forms with *gauche* sulphur atoms have larger magnitudes of $^1J_{PP}$ than forms with *trans* sulphur atoms. Unfortunately the signs of $^1J_{PP}$ are not established for this series of compounds. When $^1J_{PP}$ was first measured[1a] for $[Me_2P(S)]_2$ its value was sufficiently low to raise some doubts as to the presence of a direct P–P bond. Our present results show that the low value must be regarded as fortuitous, due to the nature of the alkyl substituents and their influence on molecular geometry.

The ^{31}P chemical shift of $[Me(Bu^t)P(S)]_2$ is to high frequency of that for $[Me_2P(S)]_2$. This is in agreement with the trend observed[7] for the substitution of Bu^t for Me in compounds containing the P=S grouping.

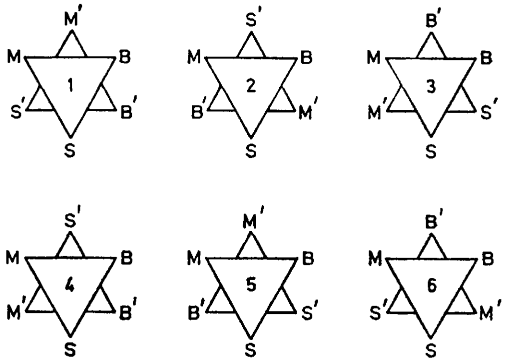

FIGURE 2 Rotameric forms of $[Me(Bu^t)P(S)]_2$; rotamers 1—3 are those of the meso-form, while rotamers 4—6 are those of the racemic form; mirror images have been omitted

EXPERIMENTAL

The synthesis of $[Me(Bu^t)P(S)]_2$ and related compounds is to be published elsewhere.[4] The compound studied here is a colourless solid, m.p. 115·5—116·5 °C (recrystallised from CCl_4). A saturated solution in benzene was used for the n.m.r. work, with a few drops of TMS added to serve as an internal reference. After degassing, the sample was sealed under a vacuum in a standard 5 mm O.D. tube. 100 MHz ^1H N.m.r. spectra were obtained with a scan rate of 0·05 Hz s^{-1} and scale 2 Hz cm^{-1} using a Varian HA 100 spectrometer operating in the frequency-sweep mode.

Frequencies were calibrated using a frequency counter to correct for chart non-linearity; they are regarded as accurate to about $+0{\cdot}05$ Hz. The spectra were obtained at ambient probe temperature (*ca.* 38 °C).

One of us (G. H.) would like to thank the Deutsche Forschungsgemeinschaft, in association with the Royal Society, for a Research Fellowship, and another of us (J. M. N.) is grateful to the S.R.C. (U.K.) for the award of an Advanced Course Studentship.

[2/1164 *Received, 22nd May,* 1972]

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