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Evidence for Rotational Isomers of Methylaminobis(trifluoromethyl)-phosphine and the Infrared Spectra of the Series $RNH{\cdot}P(CF_3)_2$ where R = Me, Et, Bu^t, or Ph

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The infrared spectrum of methylaminobis(trifluoromethyl)phosphine, $MeNH{\cdot}P(CF_3)_2$, has a well resolved doublet in the N–H stretching region and this is shown to result from the presence of two rotational isomers in thermal equilibrium. The methyl proton n.m.r. spectrum over a range of temperature is consistent with this. The infrared spectrum of the corresponding ethyl compound shows the effect much less, and with the t-butyl and phenyl derivatives only one conformer is sterically stable. Assignments are suggested for the detailed infrared spectra.

LITTLE is known of the properties of the primary alkylaminobis(trifluoromethyl)phosphines $RNH{\cdot}P(CF_3)_2$ (R = H, Me, and Ph).[1] This Paper presents the infrared (Table) and n.m.r. spectra of the Me, Et, Bu^t, and Ph derivatives; those for the methyl and possibly the ethyl compounds show the existence of restricted rotation about the P–N bond, caused by the closeness of the CF_3 and alkyl groups. These are the first examples of rotational isomerism in perfluoromethyl or tervalent phosphorus compounds.

Infrared data (in cm.$^{-1}$) for $RNH{\cdot}P(CF_3)_2$ where R = Me, Et, Bu^t, or Ph

Me	Suggested assignments	Et	Bu^t	Ph
3465m	N–H stretching	3460vw	3390br,m	3390br,m
3430ms		3418s		
2980m	C–H stretching	2980m	2970m	3040m
2945m		2940m	2925m	2970m
2920m		2896m	2880m	2900m
2840m		2832m		
2260w	C–F overtones	2280w		
2240w		2250w		
1890w	overtone or combination?			
1476w	CH_3 asym. deform.	1451w	1458w	1600m
1436mw		1400m	1373m	1485m
				1400w
1388m	CH_3 sym. deform.	1348w	1367w	1376w
1279mw	overtone or combination?	1273m	1284m	1278m
1200vs	C–F stretching	1205vs	1210vs	1229s
1165vs		1171vs	1187vs	1192s
1155vs		1164vs	1140vs	1138s
1108vs		1113vs		1100sh,s
1095s	N–C stretching or CH_3 rock	1076s	1089m	1060m
		1030m	990m	952m
		944m	876w	897mw
809m	P–N stretch and CH_3 wag	830m	840m	789w
782mw(sh)		810m		
		778m		745ms
739m,PQR	CF_3 sym. deform.	744s,PQR	728m	
				687ms
563m	CF_3asym. deform.	564m	555m	580m
540mw		546m	534m	
464m	PC_2 asym. stretch	475s	495m	
392m	N–C bend or PC_2 sym. stretch	406m	435m	
345m	CF_3 rocking and wagging PC_2 deform. and CH_3 twist			
315w				
276w				
262vw?				
238m				
195vw?				

Strong bands at *ca.* 3400 cm.$^{-1}$ are readily assigned to N–H stretching vibrations. Harris [1] suggested that the large Trouton constant of the methyl derivative indicated hydrogen bonding. Broadening of the N–H bands compatible with hydrogen bonding was apparent in the spectra of the t-butyl and phenyl compounds (measured as liquid films) but not for the methyl and ethyl derivatives (gas phase).

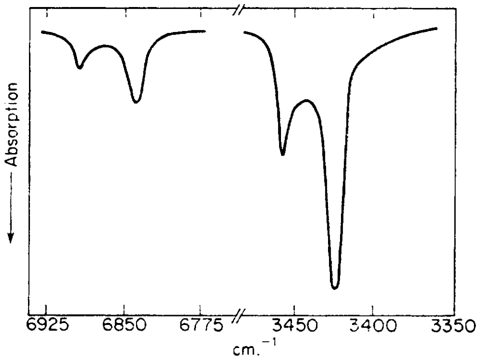

FIGURE 1 Infrared N–H stretching frequencies for gaseous $MeNH{\cdot}P(CF_3)_2$

Significantly the N–H stretching frequency (Figure 1) of the methyl derivative is always split into two bands of unequal intensity at 3465m and 3430ms cm.$^{-1}$ irrespective of the mode of preparation or sample pressure. To confirm that the splitting of the NH fundamental in $MeNH{\cdot}P(CF_3)_2$ was not due to amine or other impurities, some spectra were measured in the presence of $(CF_3)_2PCl$ and $MeNH_2$, but there was no change. Three explanations can be considered: (*a*) the band at 3465 cm.$^{-1}$ may be an overtone or combination tone, its intensity being enhanced by Fermi resonance with the mode at 3430 cm.$^{-1}$; (*b*) hydrogen bonding; (*c*) rotational isomerism. The infrared spectrum (10,000—4000 cm.$^{-1}$) revealed a doublet at 6892 and 6841 cm.$^{-1}$ with the same intensity ratio as the bands at 3465 and 3430 cm.$^{-1}$. These bands can be assigned to the first overtones of the

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[1] G. S. Harris, *J. Chem. Soc.*, 1958, 512.

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N–H stretching vibrations and enable (*a*) to be eliminated. A similar splitting was observed in the Raman spectrum of liquid MeNH·P$(CF_3)_2$ at 3460 and 3429 cm.$^{-1}$. Further, partial deuteration of the N–H proton confirmed that both the bands were due to N–H fundamentals, the position of the infrared doublet in the gas phase being shifted to 2463 and 2419 cm.$^{-1}$. The infrared spectrum of the methyl compound in benzene showed two partially resolved bands at 3440 and 3405 cm.$^{-1}$ (*ca.* 25 cm.$^{-1}$ lower than in the gas phase owing to the effect of solvent) but the doublet structure remains essentially the same in the gas phase, liquid phase, and in benzene, and this is incompatible with (*b*).

We consider, therefore, that the methyl compound exists as unequal amounts of two stable isomers at room temperature; they are present in the gas phase, the liquid phase, and in benzene solutions, and arise from the steric hindrance of the two CF_3 groups on the phosphorus atom with the methyl group and proton on nitrogen. This restricts rotation about the P–N bond. Molecular models based on normal covalent radii show that two forms are possible, one where the proton, and the other where the methyl group, is ' locked ' by the CF_3 groups. Presumably the latter, in which steric congestion is greatest, corresponds to the less abundant isomer. The models indicate that prohibitive lengthening of the P–N, P–C, or C–F bonds would be necessary to overcome the physical barrier. The conformers could be further stabilised if the P–N bond had some π-character.

Rotational isomers should also be revealed by the proton n.m.r. spectrum of MeNH·P$(CF_3)_2$. Figure 2 shows that the methyl resonance is split into two doublets of unequal intensity. By contrast, the spectrum of the t-butyl compound is a simple doublet, consistent with the spin–spin coupling of the methyl protons to a nucleus of spin number $\frac{1}{2}$. Since ^1H resonance attributable to the amino-proton was not found, presumably owing to relaxation by quadrupole interaction or exchange, the doublet structure is probably due to phosphorus–proton rather than proton–proton spin–spin coupling. The coupling constant ($J = ca.$ 10 c./sec.) is of comparable magnitude with J_{P-H} in related dialkylaminofluorophosphines [2] and is larger than usual for J_{H-H} in amines. As observed [3] for $Me_2NP(CF_3)_2$, phosphorus–proton spin–spin coupling is not evident in the ^{31}P n.m.r. spectrum (a septet) but the signals are broad and weak. The appearance of two sets of doublets in the room-temperature ^1H n.m.r. spectrum of MeNH·P$(CF_3)_2$ is therefore consistent with the presence of two conformers in which the methyl protons are in different environments. The relative intensities of the two sets of lines indicate that the isomers are present in differing concentrations and the peak separations show that any interconversion must be slower than 0·05 sec. [$\sqrt{2}/(2\pi\delta)$]. The intensity ratio of the two doublets is similar to that in the infrared and Raman spectra. The coupling constants (J = 10·3 c./sec. at 25°) of the two isomers are identical; this supports phosphorus–proton rather than proton–proton spin–spin coupling as the shielding of the amino-proton will differ in the two conformations.

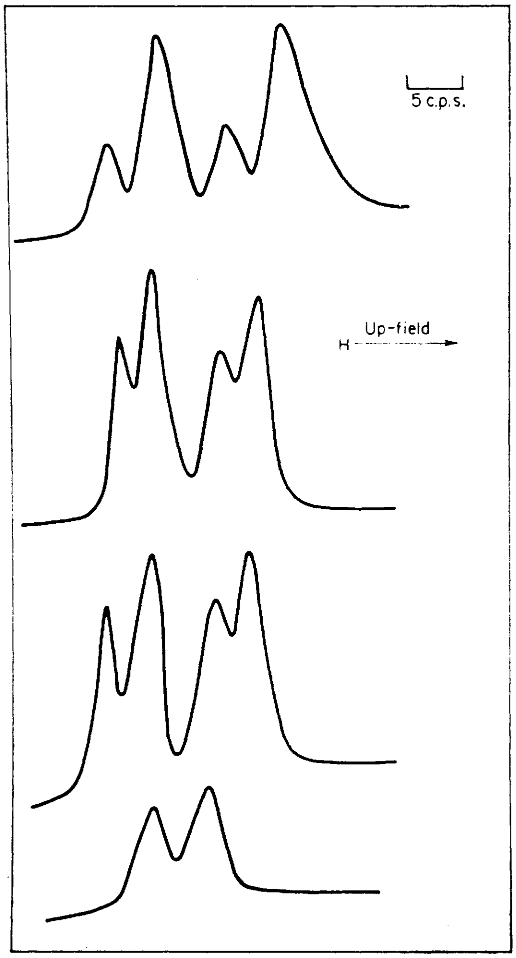

FIGURE 2 Proton nuclear magnetic resonance spectra of MeNH·P$(CF_3)_2$ at temperatures, from top downwards, of −35, +25, +73, and +103°

Further evidence for rotational isomerism comes from the temperature-dependence of the methyl resonance (Figure 2). As expected, the two conformations become more equally populated as the temperature increases. The temperature-dependence is characteristic of molecules in which there is restrictred rotation about a single or double bond.[4] Free rotation occurs above 88°, where the two doublets coalesce.

Rotational isomers are produced primarily by steric repulsion between groups rotating about a single or double bond.[5] The rate of rotation and hence conformer

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[2] R. Schmutzler, *J. Chem. Soc.*, 1965, 5630.

[3] K. J. Packer, *J. Chem. Soc.*, 1963, 960.

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

[5] S. Mizushima, ' Structure of Molecules and Internal Rotation,' Academic Press, New York, 1954.

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population depends on the bulkiness of the substituents and the temperature. Thus, in compounds of the type studied here, more than one member of the series can exhibit isomerism provided the sizes of the corresponding substituents are not too different. Here the ethyl compound showed a slight tendency to exist as two conformers as indicated by a very weak infrared band at 3460 cm.$^{-1}$. We were unable to confirm this by ^{1}H n.m.r. There was no evidence for a second N–H stretching vibration in the compounds $RNH{\cdot}P(CF_3)_2$ ($R = Bu^t$, Ph, or H), presumably because of free rotation in $(CF_3)_2PNH_2$ and because the bulky Bu^t and Ph groups lock the molecules in the more favourable steric conformation only.

The complete infrared spectrum (20—4000 cm.$^{-1}$) has been recorded for the methyl compound and most of the assignments shown in the Table are securely based upon analogies with other perfluoro- and substituted amino-compounds;[6,7] some uncertainties or alternatives are indicated. By the same arguments, analogous assignments can be made for the other derivatives though their spectra were only recorded down to 400 cm.$^{-1}$ owing to experimental difficulties.

An interesting region is 750—1050 cm.$^{-1}$, since P–N stretching vibrations in organophosphorus–nitrogen compounds may occur[8] at 870—1050 cm.$^{-1}$. Electronegative groups such as CF_3 will lower these limits but the extent is difficult to estimate. Only two bands occur between 750 and 1050 cm.$^{-1}$ in $MeNH{\cdot}P(CF_3)_2$ (782 and 809 cm.$^{-1}$) and one may be associated with the P–N bond. The other band is likely to be an internal wagging mode of the alkyl group and the two vibrations will couple strongly if they belong to the same symmetry class. Similarly the bands at 810 and 830 cm.$^{-1}$ in $EtNH{\cdot}P(CF_3)_2$ can be assigned to the P–N stretching mode coupling with an ethyl rocking mode. Assignments for the t-butyl and phenyl compounds are less certain.

In the absence of detailed force-constant calculations, conclusions about the strength of the P–N bond must be tentative. It seems unlikely from our results than an uncoupled P–N stretching vibration in $RNH{\cdot}P(CF_3)_2$ molecules occurs above 850 cm.$^{-1}$. The limits suggested[8] for $\nu(P{=}N)$ and $\nu(P{-}N)$ in organophosphorus–nitrogen compounds are 1430—1170 and 1050—870 cm.$^{-1}$, respectively. Thus we infer that there is very little p_π–d_π bonding in these compounds, consistent with their chemical reactivity.[9] The value of 850 cm.$^{-1}$ is slightly lower than the frequencies of the comparable vibrations in $NH[P(CF_3)_2]_2$, $MeN[P(CF_3)_2]_2$, and $N[P(CF_3)_2]_3$[10] (925, 869, and 859 cm.$^{-1}$, respectively); one expects the π-bonding to be enhanced in the latter compounds and indeed they are more resistant to cleavage and have little basic character. Burg and others[10–14] have attributed the stability of a number of P–N compounds to p_π–d_π bonding. Possibly the expected increase in the P–N stretching mode due to π-bonding is offset by a lengthening of the P–N bond. Overlap calculations[15] show that a lengthening of the P–N bond by about 0·2 Å has little effect on the extent of the π bonding, whereas such lengthening could substantially reduce the P–N stretching frequency.

EXPERIMENTAL

All volatile compounds were manipulated in a vacuum system. The primary alkyl- and aryl-aminobis(trifluoromethyl)phosphines were prepared by Harris method[1] and characterised by molecular weight and infrared, n.m.r., and mass spectra.[9] The bis(trifluoromethyl)phosphine compounds tended to distil with excess of the amine and rigorous trap-to-trap fractionation was necessary. Purity was monitored by mass spectrometry.

Infrared spectra were recorded on a Perkin-Elmer model 125 spectrophotometer (10,000—400 cm.$^{-1}$) and an R.I.I.C. Fourier spectrophotometer (F.S. 520) in the range 400—20 cm.$^{-1}$. The latter is essentially an evacuated Michelson interferometer with a ' Melinex ' beam divider. The Fourier transform was obtained on an English Electric KDF9 computer and an effective resolution of *ca.* 5 cm.$^{-1}$ was used throughout. Gas spectra were obtained in 10 cm. cells fitted with NaCl, KBr, CsI, or ' Polythene ' windows. The sample pressures varied from 5 mm. Hg for observing the C–F fundamentals to 500 mm. Hg for far-infrared measurements. Liquid and solution spectra were obtained as usual; cells were loaded in a nitrogen-filled dry-box.

Raman spectra were recorded with a Cary model 81 Raman spectrophotometer with 0·2 ml. sealed liquid cells. The exciting line was Hg 4358 Å and a filter solution of ethyl violet and *o*-nitrotoluene in isopropyl alcohol was used.

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