Apicophilicity of Substituent Groups and the Structures of some Trigonal Bipyramidal Trifluoromethylphosphoranes

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Summary Low temperature n.m.r. spectroscopy is capable of distinguishing axial and equatorial substitution in trigonal bipyramidal trifluoromethylphosphoranes allowing the establishment of a partial 'apicophilicity' series for some substituent groups which appears to be based chiefly on inductive rather than mesomeric or electronegative parameters of the groups.

THE basic trigonal bipyramidal framework is now well established for five-co-ordinate phosphorus compounds but the location of substituent groups within this structure is much less certain in cases where two or more different groups are present. Initial studies[1] suggested that axial positions were preferentially occupied by the most electronegative substituents, perhaps as the result of greater ionic character of bonding in this direction or possibly as a consequence of enhanced π bonding in the equatorial plane. The concept of apicophilicity[2] recognizes that the location of substituent groups is determined by a balance of various factors such as electronegativity, π bonding and possibly also steric effects but does not imply any particular origin.

Various new trifluoromethylphosphoranes, (I), (II), (V—VII), (IX), (X), (XIII), and (XIV) (Table 1) were prepared by complete or partial replacement of halogen atoms in $(CF_3)_3PX_2$ or $(CF_3)_2PMeX_2$ (X = F, Cl) by means of Me_2NH or Me_3SiR (R = NMe_2, OMe, SMe). Compound (XI) was prepared by chlorination of $(CF_3)_2PMe$ and compound (XII) by fluorination of (XI). The bis(amino)-fluorophosphoranes (VIII) and $(CF_3)PF_2(NMe_2)_2$ were prepared by controlled pyrolysis of (I). All compounds listed in the Tables show the presence of equivalent CF_3 groups in their ^{19}F n.m.r. spectra above appropriate temperatures ranging from $-120°$ (XI—XIV) to $+90°$ (X). Even when non-equivalent CF_3 groups are present, n.m.r. equivalence by averaging can occur by means of monomolecular Berry or Turnstile 'pseudorotatory' processes.[2] This equivalence persists in compounds (XI)—(XIV) on cooling to $-120°$ but compounds (I)—(X) show features in their low-temperature spectra which are clearly compatible with axial and equatorial placement of CF_3 groups in these molecules. Further confirmation of the presence of both axial and equatorial groups came from observation in compounds (I)—(X) of the coupling constant between them, $^4J_{FF}$, ranging from 11 to 21·5 Hz.

In the tris(trifluoromethyl)phosphorane series, compounds (I)—(III) show two types of CF_3 resonance with

TABLE 1

		Temperature[a] for non-equivalence of CF_3 groups	Parameters of axial CF_3 groups			Parameters of equatorial CF_3 groups			
Compound		(t/°C)	ϕ_F[b]	$^2J_{FP}$/Hz	No.	ϕ_F[b]	$^2J_{FP}$/Hz	No.	$^4J_{FF}$/Hz
2 Axial, 1 equatorial									
(I)	$(CF_3)_3P[NMe_2]_2$	-40	57·0	50·5	2	55·6	108	1	16·5
(II)	$(CF_3)_3P(OMe)_2$	-80	63·7	88	2	62·2	108	1	13·5
(III)	$(CF_3)_3P[OSiMe_3]_2$	-40	*ca.* 72	*ca.* 103	2	63·7	111·5	1	13·5
(IV)	$(CF_3)_3PH_2$[d]	-90	61·0	71	2	36·7	120	1	11
1 Axial, 2 equatorial									
(V)	$(CF_3)_3PClNMe_2$	-120	57·7	*ca.* 53	1	59·3	130	2	*ca.* 13
(VI)	$(CF_3)_3PFNMe_2$	-40	58·6	*ca.* 40	1	62·3	130	2	16
(VII)	$(CF_3)_3PF(SMe)$	-70	N.i.[e]	33·8	1	N.i.	134	2	13
1 Axial, 1 equatorial									
(VIII)	$(CF_3)_2PF[NMe_2]_2$	-70	R.r.[f]	R.r.	1	61·4	125·5	1	21·5
(IX)	$(CF_3)_2PF(Me)(OMe)$	-60	R.r.	R.r.	1	68·6	125·0	1	11·8
(X)	$(CF_3)_2PF(Me)NMe_2$	-60	*ca.* 64	*ca.* 40	1	64·8	122·5	1	14
2 Equatorial									
(XI)	$(CF_3)_2P(Me)Cl_2$	—	—	—	0	79·7	134	2	—
(XII)	$(CF_3)_2PMeF_2$	—	—	—	0	63·3	156	2	—
(XIII)	$(CF_3)_2P[NMe_2]Cl_2$	—	—	—	0	67·8	157	2	—
2 Axial									
(XIV)	$(CF_3)_2(Me)P(OMe)_2$	—	**61·9**[g]	68·5	2	—	—	0	—

[a] Between these two temperatures (see Table 2) there occurs an intermediate phase where the spectra are transitional and not fully resolved. [b] P.p.m. to high field of $CFCl_3$ unless otherwise stated. [c] R. G. Cavell, R. D. Leary, and A. J. Tomlinson, *Inorg. Chem.*, 1972, **11**, 2758. [d] Ref. 4. [e] N.i. = not investigated. [f] R.r. indicates that restricted rotational motion which affects the axial CF_3 groups occurs at temperatures above those required to resolve those same axial CF_3 groups and prevents the evaluation of these data. [g] P.p.m. to high field of CF_2Cl_2.

intensity ratios of 2:1. The former, to higher field of the latter in these cases, are characterized by low values of the coupling constant ${}^{2}J_{\mathrm{FP}}$ ($\leqslant 103$ Hz) and are assigned to axial CF_3 groups while the latter, having higher values of ${}^{2}J_{\mathrm{PF}}$ ($\geqslant 108$ Hz) are due to equatorial CF_3 groups. The relationship between coupling constants and '*s*' electron density[3] suggests that equatorial groups with greater '*s*' character in bonding should have higher values of ${}^{2}J_{\mathrm{FP}}$. Similar features have been reported by Cowley *et al.*[4] for $(CF_3)_3PH_2$.

The compounds (V)—(VII) all have spectra indicative of the presence of 2 equatorial CF_3 groups (large ${}^{2}J_{\mathrm{FP}}$, higher-field resonance) and one axial CF_3 group (low ${}^{2}J_{\mathrm{FP}}$, low-field resonance). On the other hand the phosphoranes $(CF_3)_3PX_2$ (X = F,[5] Cl[6]) have high ${}^{2}J_{\mathrm{PF}}$ values and unchanged n.m.r. spectra[5b] down to $-120°$ suggesting the presence of equatorial CF_3 groups only. The distinguishability of CF_3 groups at ordinary temperatures or moderately low temperatures (to $-50°$) suggests that the barrier to the CF_3 'pseudorotatory' averaging process is relatively large. We should therefore normally expect to resolve axial and equatorial substituted CF_3 groups (if both are present in the molecule) and hence we are led to the conclusion that $(CF_3)_3PX_2$ halogeno-phosphoranes contain equivalent, equatorial CF_3 substituents.

In the bis(trifluoromethyl)phosphorane series, compounds (VIII)—(X) show low-temperature spectra indicative of one axial and one equatorial CF_3 group (Table 1) whereas compounds (XI)—(XIV) and $(CF_3)_2PF_2X$ (X = H,[4] NMe_2[7]) and $(CF_3)_2PX_3$ (X = F[5], Cl[8]) all have unchanged ${}^{19}F$ n.m.r. spectra down to $-120°$. The low magnitude of ${}^{2}J_{\mathrm{PF}}$ in compound (XIV) suggests purely axial CF_3 substitution in this case whereas the larger magnitudes of ${}^{2}J_{\mathrm{PF}}$ in the remaining cases suggest equatorial CF_3 substitution.

Finally the relatively high magnitude of ${}^{2}J_{\mathrm{PF}}$ ($\geqslant 149$ Hz) in all the mono(trifluoromethyl)phosphoranes CF_3PX_4 (X = F,[5a] Cl[8]), CF_3PF_3X (X = H, [4] Me,[7] NMe_2[7]), $CF_3PF_2X_2$ (X = Cl,[9] H,[4] NMe_2[10]) and CF_3PFCl_3[8] suggests exclusive equatorial substitution of CF_3 groups in all cases. Previous structural studies agree with all these conclusions except in the cases of $(CF_3)_2PCl_3$[11] and CF_3PCl_4[12] where vibrational studies suggested axial CF_3 groups. We are in agreement with the equatorial CF_3 substitution in CF_3PF_4 suggested by vibrational spectroscopy[13] and our data do not support the axial CF_3 substitution indicated for this compound by microwave spectroscopy.[14]

All presently available data can be rationalized on the basis of the following apicophilicity series:

$$\mathrm{F, Cl > CF_3 > OSiMe_3, OMe, SMe, NMe_2, H, Me}$$

wherein groups separated by a comma must be regarded as indistinguishable on the basis of present data. Thus axial sites are occupied by two CF_3 groups in (I)—(IV) and (XIV), by one CF_3 and one halogen in (V)—(X) and by two halogens in all other cases. The major inconsistency with other findings occurs in the case of the groups Cl and CF_3 wherein either electronegativity [χ(Cl) = 3·16, $\chi(CF_3)$ = 3·46[15]] or π bonding considerations [$\sigma_R°$, Cl ($-0·20$), CF_3 ($+0·14$)[16]] suggest that CF_3 is more apicophilic than Cl whereas the reverse appears to be true in all known examples. Use of the inductive scale[16] [σ_I F (0·51), Cl (0·47), CF_3 (0·41), OMe (0·26), SMe (0·19), NMe_2 (0·05), H (0·00), Me ($-0·05$)] as a basis for apicophilicity, however, agrees with the crude sequence observed. It is impossible at this time to decide on the relative importance of π-bonding effects beyond concluding that they are much less important than the inductive effect. Similarly steric effects appear to be unimportant here.

Two other features were apparent from the spectra. First, compounds (II) and (III), which contain OMe and $OSiMe_3$ groups whose inductive effect is relatively close to that of CF_3 gave axial ${}^{2}J_{\mathrm{FP}}$ values almost as high as the equatorial ones whereas those compounds containing groups of much smaller inductive effect H, NMe_2, SMe such as (I), and (IV)—(VII) have axial ${}^{2}J_{\mathrm{PF}}$ values much smaller than the equatorial ${}^{2}J_{\mathrm{PF}}$. The value of ${}^{2}J_{\mathrm{PF}}$ (axial) in (VII) is also notable since it is the smallest value reported for this parameter in trifluoromethylphosphorus compounds.

TABLE 2

Parameters appropriate to equivalent CF_3 groups. (See Table 1 for footnotes and compound grouping)

Compound	ϕ_F[b]	${}^{2}J_{\mathrm{FP}}$/Hz	Weighted average† ${}^{2}J_{\mathrm{FP}}$/Hz	Temperature[a] for equivalence (t/°C)
(I)	53·9	71	69·7	75
(II)	63·4	96	94·7	-40
(III)	69·7	108·5	107·2	40
(IV)	N.i.	N.i.	87·3	N.i.
(V)	59·1	105·5	104·3	-50
(VI)	61·0	109	100·0	40
(VII)	60·6	103·7	100·6	0
(VIII)	59·6	86	—	60
(IX)	69·6	82	—	50
(X)	66·5	81·5	81·2	90
(XI)	79·7	134	—	-120
(XII)	63·3	156	—	-120
(XIII)	67·8	157	—	-120
(XIV)	61·9[g]	68·5	—	-120

† Computed from the ${}^{2}J_{\mathrm{PF}}$ values given for inequivalent CF_3 groups and weighted proportionally to their numbers in the molecule.

Finally cooling samples of compounds (I)—(III), (VI)—(X), and (XIV) to very low temperatures (*e.g.* $-140°$) beyond those required to resolve CF_3 inequivalencies led to the onset of extremely complex spectra with a spread of almost 1000 Hz. The equatorial CF_3 regions showed relatively minor changes in fine structure whereas the axial CF_3 regions suffered major changes, each axial group splitting into two extremely complex areas of relative intensity 2:1 apparently coupled to each other (${}^{2}J_{\mathrm{FF}}$ *ca.* 100 Hz). Although the fine details are not yet fully understood, the spectral features appear to be due to cessation of conformational averaging processes of either the CF_3 groups or, more likely, one or more of the other groups in the molecule which destroys the equivalence of the fluorine atoms in the axial CF_3 groups. The very low temperatures required to observe these latter features suggest that they are associated with processes having a low barrier.

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