# $^{19}F$ Nuclear Magnetic Resonance of the Hexafluoroacetone Adducts of Phosphetans. The Relative Apicophilicities of Groups

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*Summary* The variable-temperature $^{19}F$ n.m.r. spectra of the hexafluoroacetone adducts of a series of 1-substituted phosphetans give data on the relative apicophilicities of different groups which are interpreted in terms of electronegativity and back-bonding factors.

WE recently showed[1] by means of variable-temperature $^{19}F$ n.m.r. spectroscopy that in the 1:2-adduct of the phosphetan (**1**; $R^1$ = H, $R^2$ = Ph) with hexafluoroacetone (HFA) the pseudorotation, (**2**) ⇌ (**3**), which places the four-membered ring diequatorial and leads to equivalence of the four trifluoromethyl groups has a free energy of activation ($\Delta G^*$) at the coalescence temperature of *ca.* 20 kcal mol$^{-1}$. A study of the variation† of $\Delta G^*$ with $R^2$ will give data on the relative apicophilicities‡ of various groups, which are essential to an understanding of the course of substitution at phosphorus, and we now report on such a study with the phosphetans (**1**; $R^1$ = Me).

† Comparison of $\Delta G^*$ values obtained at different coalescence temperatures is valid only if the entropies of activation are small. This would be expected for intramolecular pseudorotations and appears to be the case.[10]

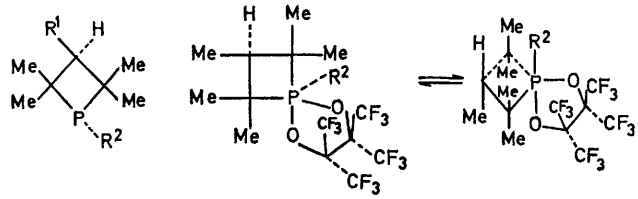
‡ This term was introduced by Ugi and Ramirez.[5] Its use avoids preconceived ideas on the origin of the effect.

*N.m.r. data on the adducts* (**2**; $R^1$ = Me)

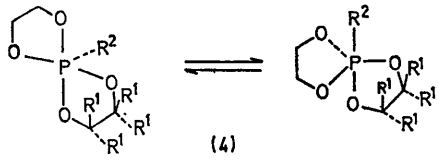
| $R^2$ [a] | Ph *cis* | Ph | CH : $CMe_2$ | $Pr^i$ | Me | $NMe_2$ [b] | OPh [b,c] | $OCH(CF_3)_2$ | Hc,m |
|---|---|---|---|---|---|---|---|---|---|
| $^{31}P$ [d] | −7·3 | −3·4 | −7 [e] | −18·5 | −5·8 | −20 [e] | −24 [e] | −23 [e] | |
| $^{19}F$ $T^c$ | 140 [f] | >180 [f] | 135 [g] | 93 [g] | 85 [g] | 63 [h] | −77 [i] | j, k | j, l |
| | | | | | | | −85 | | |
| Δν Hz | 153 | 133 | 219 | 83 | 166 | 86 | *ca.* 220 | | |
| $\Delta G^*$/(kcal $mol^{-1}$) | 19·6 | >22 | 19·1 | 17·8 | 16·9 | 16·2 | *ca.* 9 | | |
| Electronegativity [d] | | 2·49 | 2·37 | 2·28 | 2·27 | 2·40 | 2·68 | 3·74 [o] | 2·2 |

[a] *trans* to the 3-Me except as shown. [b] Prepared from chlorophosphetan. [c] Mixture of *cis* and *trans*. [d] P.p.m. relative to 85% $H_3PO_4$. [e] From heteronuclear decoupling of $^1H$ n.m.r. spectrum. [f] 1-Bromonaphthalene. [g] *o*-Dichlorobenzene. [h] Toluene. [i] $CFCl_3$. [k] Sharp singlet at −80°; broad at −125°. [l] Sharp singlet at −115°. [m] Decomposed above 20° to give [**1**; R = $OCH(CF_3)_2$]. [n] Ref. 2. [o] For $OCF_3$.

The results given in the Table relate to the n.m.r. spectra of the HFA-adducts of the phosphetans (**1**; $R^1$ = Me) and to the pseudorotations (**2**) ⇌ (**3**).§ They differ in several respects from those expected on the basis of the preference rule,[3] *i.e.*, that the most electronegative groups will prefer to occupy the apical positions. The apicophilicities of the carbon substituents are clearly in the inverse order of their electronegativities while on the basis of electronegativity



(1) (2) (3)



(4)

alone the dimethylamino-group would be expected to be much more apicophilic relative to the similarly sized isopropyl. The difference (>13 kcal $mol^{-1}$) in the activation energies for placing phenyl and phenoxy in apical positions, which presumably underestimates the relative apicophilicities of these two groups, is also larger than would be expected on the basis of previous data[4] relating phenyl and ethoxy.

The recent calculations of Ugi and his co-workers, which show that back-bonding into phosphorus *d*-orbitals is more effective from equatorial than from apical positions, offer an explanation of these apparent anomalies. The apicophilicity of a given group becomes a balance between electronegativity, increase in which favours occupation of the apical position, and ability to back-bond into phosphorus *d*-orbitals, increase in which favours occupation of the equatorial positions, with steric factors playing an unknown role. As both the effective electronegativity[2] of and the back-bonding possibilities for a given group will vary with the nature of the other substituents attached to the phosphorus, the overall apicophilicity of that group will vary in an individual way with changes in the environment of the phosphorus to which it is attached. The application of these ideas to the interpretation of the above data implies a large degree of back-bonding from both equatorial amino and phenyl groups. The former may be related to the barriers to rotation round the PN bonds to equatorial amino groups observed in a variety of aminophosphoranes[6] and the consequences of the latter are being explored.

The high apicophilicity of hydrogen is in agreement with data reported for the phosphoranes (**4**; $R^1$ = Me, $R^2$ = H) ($T^c$ = 37°)[7] and (**4**; $R^1$ = H, $R^2$ = OMe) ($T^c$ = 172°)[8] and with calculations on $PH_2F_3$.[5] The phosphetan (**1**; $R^1$ = Me, $R^2$ = SPh) unfortunately did not give an adduct with HFA while the phosphetans (**1**; $R^1$ = Me, $R^2$ = $CH_2Ph$ and $CH_2CH:CH_2$) gave oxaphosphetans presumably by rearrangement of the initial adducts.[9] The adduct from (**1**; $R^1$ = Me, $R^2$ = $Bu^t$) decomposed above 60°.

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§ All the adducts, except that with $R^2$ = H, are unaffected by water; the observed n.m.r. phenomena are therefore probably not due to irregular processes involving opening of the five-membered rings.[5]


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