π-Interactions in Pentafluorophenylfluorophosphonitriles

By T. CHIVERS and N. L. PADDOCK*

(*Department of Chemistry, University of British Columbia, Vancouver* 8, *B.C., Canada*)

IN connection with studies of the variation in the properties of phosphonitrilic compounds as a function of ring size, we have prepared a series of pentafluorophenylfluorophosphonitriles of the type $N_xP_x(C_6F_5)F_{2x-1}$ (x = 3—8), and have obtained their ^{19}F n.m.r. spectra. The results, given in the Table, can be interpreted by comparison with those of other pentafluorophenyl derivatives.[1,2]

^{19}F N.m.r. parameters for pentafluorophenylfluorophosphonitriles

Compound[a,c]	δ_p[b]	δ_m[b]	$\delta_m - \delta_p$
$N_3P_3(C_6F_5)F_5$	143·8	159·1	15·3
$N_4P_4(C_6F_5)F_7$	144·6	159·3	14·7
$N_5P_5(C_6F_5)F_9$	143·3	159·4	16·1
$N_6P_6(C_6F_5)F_{11}$	144·4	159·4	15·0
$N_7P_7(C_6F_5)F_{13}$	144·4	159·4	15·0
$N_8P_8(C_6F_5)F_{15}$	144·4	159·4	15·0

[a] Measured in 20—40% (v/v) solutions in CCl_3F at 25°. Chemical shifts were found to vary $< 0·1$ p.p.m. over the concentration range 10—50% (v/v).

[b] Chemical shifts of *p*-fluorine (δ_p) and *m*-fluorine (δ_m) in p.p.m. relative to CCl_3F.

[c] J'_{24} (the apparent coupling constant between the *o*- and *p*-fluorine atoms) values in the range 7·3—7·7 c./sec. were observed but could not be determined with great accuracy owing to long-range effects.

The low value of δ_p and large values of $\delta_m - \delta_p$ and J'_{24} indicate strong π-withdrawal from the pentafluorophenyl ring by the phosphonitrilic substituent, in this case a $p\pi$–$d\pi$ effect. The magnitude of the effect is similar to that exerted by a cyano-group, for which the corresponding quantities are[3] $\delta_p = 143·5$ p.p.m., $\delta_m - \delta_p = 15·7$ p.p.m., $J'_{24} = 5·9$ c./sec. Further, the variability of $\delta_m - \delta_p$, while δ_m remains constant, is suggestive of a resonance effect which is dependent on ring size. The rings in both $N_3P_3F_6$ and $N_4P_4F_8$ are planar,[4] and it is likely that $N_5P_5F_{10}$ deviates only slightly from planarity, the bigger rings increasingly so.[5] The primary condition for the application of Hückel theory is therefore satisfied, and we attribute the alternating behaviour of $\delta_m - \delta_p$ up to $N_6P_6F_{12}$ to conjugation of the homomorphic π-system in the pentafluorophenyl group with a homomorphic π-system in the phosphonitrilic ring, already recognized on the grounds of base behaviour and ionisation potentials.[6] Such conjugation could be effected mainly through the d_{z^2} orbital, the use of which is believed[7] to account for the inequality in exocyclic bonds found[8] in the crystal structure of $N_4P_4(NMe_2)_8$, and which, within the ring, interacts symmetrically with sp_y hybrid orbitals on neighbouring nitrogen atoms.

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