Huckel-type Interactions in Phosphonitrilic Derivatives

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THERMOCHEMICAL measurements[1] have confirmed the theoretical expectation[2] that $p\pi$–$d\pi$ bonds in $(NPCl_2)_n$ involve chiefly the d_{xz}-orbital, the properties of the resulting system varying smoothly with ring size, to a first approximation. Nevertheless, pentameric phosphonitrilic chloride $(NPCl_2)_5$ differs from the tetramer and hexamer in being a weaker base in sulphuric acid,[3] and in requiring a greater activation energy for nucleophilic attack at phosphorus.[4]

Both these results suggest that the (weaker) π'-system, formed partly by delocalisation of lone-pairs on the nitrogen atoms[5] may be predominantly of the Hückel type, leading to an alternation of properties; further, of the two orbitals concerned, ($d_{x^2-y^2}$ and d_{xy}) the former, which interacts symmetrically with the *s*–*p*-hybrids on neighbouring nitrogen atoms,[5] overlaps them the more strongly.[6] We have therefore determined mass-spectrometrically the ionisation potentials of several phosphonitrilic derivatives $(NPX_2)_n$, and find that the highest occupied orbital of the trimer lies deeper than that of the tetramer [see Table for $X{=}Cl$; *cf.* ionisation potentials[7] of benzene (9·24 *e*v) and cyclo-octatetraene (7·99 *e*v)]. The variation in the fluoride series is more marked than in the chloride series, the values for the trimer (11·64 *e*v) and the tetramer (10·86 *e*v) being significantly above and below the series limit (11·1 *e*v) which is reached at about $(NPF_2)_{5\text{ or }6}$. Similar but smaller decreases from trimer to tetramer are found if the substituents are of lower electronegativity; in all cases, a proper allowance for the contraction of the *d*-orbitals by the positive charge on the ion (which stabilises especially the smallest rings) would increase the difference between trimer and tetramer. We have also compared the electron densities at nitrogen by measuring the solubility of HCl in solutions of $(NPCl_2)_n$, (n = 3—8). The basicities alternate, (Table), being greater for $n = 4,6,8$, than for $n = 5,7$; the trimer is a special case, since delocalisation of the lone pairs is restricted geometrically.

All the results are consistent with the modulation of the main π-system by weaker Hückel interactions in the π'(in-plane) system. The lowest unoccupied Hückel orbitals lie lower in the even- than in the odd-numbered members, and consequently, in appropriate circumstances, the former molecules should be the better acceptors, as well as better donors.

TABLE

n in $(NPCl_2)_n$	3	4	5	6	7	8
ΔpK[a]	0	0·10	0·28	0·08	0·18	0·14
Ionisation potential (*e*v)[b]	10·26	9·80	9·83	9·81	9·80	—

[a] $\Delta pK = \log_{10}(K_3/K_n)$, where K_n is the equilibrium constant for the reaction $(NPCl_2)_n + HCl \rightarrow (NPCl_2)_n,HCl$ in carbon tetrachloride; reproducibility ± 0·03.

[b] Determined mass-spectrometrically; reproducibility ± 0·05 ev.

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