Crystal Structure and Bonding in Octamethylphosphonitrilium Salts

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Summary In the cyclic cations in $[\{NPMe_2\}_4H^+]_2CoCl_4^{2-}$ (I) and in the compound $(NPMe_2)_4H{\cdot}CuCl_3$ (II) the bonds to the protonated nitrogen atom (N^+) are long; the subsequent alternation of the P–N bond lengths, which is independent of the conformation of the ring, is interpreted in terms of the approximate equality of the components of a dual π-system.

IN view of the current interest in the nature of the bonding in phosphonitrilic derivatives, we have determined the structures of compounds (I) and (II), in which the π-systems are perturbed by the addition of acceptor groups to the ring. The effect is somewhat greater than in[1] $N_3P_3Cl(NHPr^i)_4{\cdot}HCl$, and has a different pattern. Crystals of (I) are monoclinic, $a = 10{\cdot}435$, $b = 32{\cdot}837$, $c = 11{\cdot}174$ Å, $\beta = 102{\cdot}29°$, $Z = 4$, space group $P2_1/n$, and of (II) are orthorhombic, $a = 15{\cdot}701$, $b = 17{\cdot}728$, $c = 14{\cdot}526$ Å, $Z = 8$, space group *Pbca*. The structures were determined with Mo-K_α counter data by Patterson, electron-density, and least-squares methods, the final *R* being 0·077 for 1324 reflexions for (I) and 0·097 for 1670 reflexions for (II). The structure of (I) consists of a tetrahedral $CoCl_4^{2-}$ ion and two protonated eight-membered phosphonitrilic rings, one with a tub and one with a saddle conformation. (II) contains an eight-membered ring, in a tub conformation, with a proton and a $CuCl_3$ group covalently bonded to opposite nitrogen atoms. In both rings of (I) and in (II) there are four distinct pairs of N–P bonds (Table). A feature of the interionic and intermolecular contacts is the presence of N–H · · · Cl hydrogen bonds. The conformations of the two cations in (I) deviate strongly, and in opposite directions, from that of the parent octamethylcyclotetraphosphonitrile.[2] The mean displacements of the sets of phosphorus and nitrogen atoms from the mean molecular plane, ΔP and ΔN Å, respectively, are:

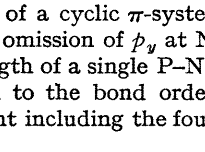
TABLE

Molecule	$[NPMe_2]_4$	(I)	(II)
X	—	H	H
Y	—	—	$CuCl_3$
N(1)–P(1)	1·60	1·70	1·67 Å
N(2)–P(1)	1·60	1·54	1·56
N(2)–P(2)	1·60	1·61	1·60
N(3)–P(2)	1·60	1·58	1·63

	$N_4P_4Me_8H^+$ (tub)	$N_4P_4Me_8$	$N_4P_4Me_8H^+$ (saddle)
ΔP	0·40	0·21	0·02
ΔN	0·59	0·54	0·61

It is clear that large conformational changes may entail only small changes in energy.

The detailed bond lengths and angles, as well as the energy, are also largely independent of conformation. Not only are corresponding pairs of bonds within the same cation equal in length within experimental error (averaged values are shown in the Table), but the mean length of the pair is also the same in both conformations. Within either cation, long and short bonds alternate with increasing distance from the protonated nitrogen atom (N^+), this type of variation being characteristic of a cyclic π-system perturbed at one centre, here by the omission of p_y at N^+. The deviations from 1·77 Å, the length of a single P–N bond,[3] are approximately proportional to the bond orders obtained from a Hückel MO treatment including the four orbitals d_{xz}, $d_{x^2-y^2}$,



p_z and p_y (except at N^+).[4] The mean bond length (1·61 Å) is close to that in the unperturbed molecule (1·60 Å). For a σ-inductive effect, a steady decrease in bond length with increasing distance from N^+ would have been expected. The structures therefore give a clear indication that π-orbital interactions are involved in the ring bonds; the type of variation found does not distinguish between homomorphic and heteromorphic interactions, or any mixture of them.

Protonation ensures that only the p_z-orbital at that particular nitrogen atom takes part in the bonding, and equal interactions between it and the neighbouring phosphorus orbitals (and hence equal immediate bond lengths) are to be expected for the saddle conformation, in which the dihedral angles between the p_z-axis and the normals to the neighbouring N–P–N planes are nearly equal (39°, 43°). In the tub cation, the corresponding dihedral angles are 15° and 60°, the p_z-orbital overlapping principally with π_a and π_s orbitals, respectively.[5] Although the present structure is not accurate enough [σ(P–N) = 0·03 Å] for a proper assessment to be made, the experimental equality of the bonds to N^+ in the tub cation shows that the π_s and π_a contributions (corresponding to interactions within and perpendicular to the local N–P–N plane) cannot be grossly unequal; the competition for control of the conformation between such an inequality and steric interactions involves only weak forces on either side. A similar conclusion has been reached from a study[6] of the structure of $N_6P_6(NMe_2)_{12}$, in which steric interactions play an important part in determining the conformation, without causing inequalities in the bond lengths within the ring. In (II) the ring is protonated at one end and co-ordinated to a $CuCl_3^-$ group at the other. On the basis of the ring bond lengths, the $CuCl_3^-$ group is, as expected, the less good acceptor. Pairs of bonds equidistant from N^+ are equal in length, and, since the molecule has the tub conformation, and since this structure is the more accurate [σ(P-N) = 0·02 Å] the previous conclusion of near-equality of π_a and π_s contributions is reinforced.

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