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The Structure and Photoelectron Spectra of Hexa(methylimido)tetraphosphorus. Evidence for Three-dimensional $p\pi$–$d\pi$ Delocalization

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Compounds with N(III)–P(III) bonds have long interested chemists because of the possibility of bond strength enhancement from $Np\pi \rightarrow Pd\pi$ interaction. Despite a vast literature on the subject, the extent, importance and detailed nature of such interactions remain controversial questions and doubtless the situation is different in different classes of compounds. We have considered these questions in the case of compounds $P_4(NR)_6$, which are expected to have adamantane-like (or hexamethylenetetramine-like) structures, as well as their derivatives in which S or BR_3 groups are coordinated to one or more of the P atoms. Our initial results, concerning the structure and photoelectron (PE) spectrum of $P_4(NMe)_6$ are reported here.

$P_4N_6(CH_3)_6$ crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters a = 14.629(4) Å, b = 24.241(7) Å, c = 8.217(1) Å, β = 94.82(2)°, V = 2904(1) Å^3 and Z = 8. With two molecules in the asymmetric unit all of the molecular dimensions which would be expected to form equivalent sets within a molecule of T_d symmetry are measured 12 or 24 times independently.

The mean dimensions obtained by averaging on the assumption that each molecule should have T_d symmetry are: N–C, 1.48_5 ± 0.02 Å; P–N, 1.69_5 ± 0.013 Å; P· · · P, 2.996 ± 0.008 Å; N–P–N, 101.1 ± 0.7°; P–N–P, 124.3 ± 0.6°; P–N–C, 115.8 ± 1.9°. The average of the sums of the three angles about each nitrogen atom is 356 °, thus indicating that the nitrogen atoms have essentially planar configurations. The refinement of the structure converged only slowly to discrepancy indices of R_1 = 0.084 and R_2 = 0.113; only a few of the hydrogen atoms could be located in difference Fourier maps and since relatively unhindered rotation should occur about each of the 12 independent N–C bonds we suspect that there may be considerable rotational disordering of the methyl groups which accounts for the relatively poor refinement, the relatively high esd's (*ca.* 0.01 for all N–P and N–C bonds) and a surprisingly large spread in the individual values within sets of parameters (*e.g.*, the 24 N–P distances range from 1.65 Å to 1.74 Å).

Nevertheless, the molecular structure is qualitatively as expected. The quantitative detail which was the principal objective of this work is the P–N distance, 1.69_5 Å, from which some indication of the importance of π bonding may be derived. Only a qualitative conclusion is possible due to the uncertainty in selecting an unambiguous distance for a P–N single bond and for some P–N bond of higher order. The sum of Pauling single bond radii[1] for P and N is 1.80 Å, while a value of 1.77 Å, as found[2] in $H_2NP(OH)O_2^-$, has often been proposed. For various phosphonitrilic rings, where a bond order of 1.5 may perhaps be assumed, bond lengths of about 1.59 Å are found.[3] On this basis a π bond order of *ca.* 0.2 ± 0.1 might be assigned. It is important to note that even a small degree of stabilization of each bond by π interaction can be highly important to the molecular energy since there are 12 P–N bonds.

The gas-phase PE spectrum[4] is shown in Figure 1. The series of broad peaks at energies in excess of 11 eV are due to excitations from various σ bonding MO's; a specific assignment is neither possible not necessary at this time. The doublet centred near 10.2 eV seems likely to be due to the phosphorus lone pairs.[5] The four orbitals provide a basis for the A_1 and T_2 representations and the appearance of two close peaks ($\Delta \approx 0.3$ eV) in an intensity ratio of about 3:1 is consistent with the assignment. The relative narrowness of the peaks is also consistent with their involving nonbonding electrons. Any Jahn–Teller effect due to the T_2 excitations is presumably small due to the essentially localized character of these electrons.

The broad absorption from about 7.7 to 9.7 eV is assigned to the nitrogen $p\pi$ electrons. This set of six orbitals forms a basis for the T_1 and T_2 representations. To the extent that there is $Np\pi \rightarrow Pd\pi$ bonding

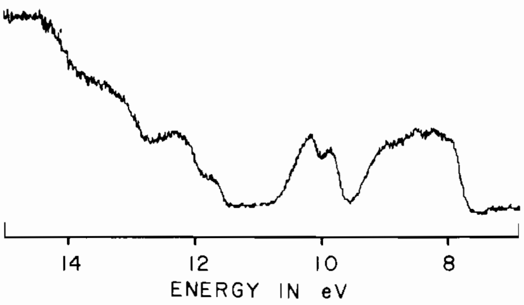

Fig. 1. Gas-phase PE spectrum.

one would expect (a) separation of the T_1 and T_2 components, (b) Jahn–Teller splittings in both excited states, and (c) vibrational broadening which would not be well resolved since skeletal frequencies in the range of 600 - 1200 cm^{-1} and overlapping among the T_1 and T_2 excitations would be involved. The broad and complex shape of this absorption is thus in full accord with the assumption that the N*pπ* electrons occupy bonding orbitals. If they did not, it is difficult to see how the band shape could otherwise be explained.

The mean energy of the "N*pπ*" absorption also suggests that these electrons are stabilized by a bonding interaction. It has been clearly shown[6] that the energy of nitrogen lone-pair electrons is a sensitive function of the *p* character of the orbital they occupy. This is, of course, to be expected, since it can be estimated from atomic spectra[7] that the 2*s* and 2*p* orbitals differ by *ca.* 10 eV in energy. From the data for amines, where the lone pairs occupy orbitals with considerable *s* character, and give PES peaks at 8 - 10 eV, it can be estimated that for a pure 2*pπ* lone pair on the nitrogen atom an energy of well under 7 eV would be expected. Thus the location of the band between 8 and 9 eV indicates appreciable stabilization and this should be due at least in part to *pπ–dπ* interaction.

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