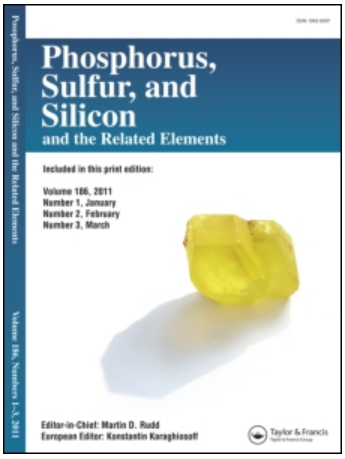

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QUANTUM CHEMICAL SIMULATION OF HYPERVALENT BONDING IN PHOSPHATRANES

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The MNDO approximation was used to study energy, structural and electronic effects of the donor-acceptor P←N bonding in $XPF_3 \cdot NH_3$ complexes simulating phosphatranes. The effects of substituents at the phosphorus on the P←N bonding can be rationalized by changes in the acceptor properties of the low-lying unoccupied MO localized at the phosphorus. Addition of a proton to the substituent X in the XPF_3 molecules (X = lone pair, O) leads to distortion energy reduction due to increasing FPF bond angles in the P←N bonding in the model complexes.

Key words: Quantum chemical simulations; hypervalent bonding; phosphatranes; MNDO approximation; acid-base properties.

Tricyclic silatranes $XSi(OCH_2CH_2)_3N$ are well known,[1] in which the silicon atom forms an intramolecular donor-acceptor bond to the nitrogen. Depending on X, the Si←N bond length varies between 2.02 and 2.34 A.[2,3] The correlation between Si—X and Si←N bond lengths in silatranes [2] can be rationalized with the hypervalent X—Si←N bond order constancy.[3]

The phosphorus analogues of silatranes, $XP(OCH_2CH_2)_3N$ have been studied less thoroughly. Verkade *et al.*[4,5] have applied an NMR technique to reveal an interesting dependence governing the formation and breakage of the P←N bond in phosphatranes with respect to the nature of X. In phosphatranes I–VI (Scheme1) this bond is present and in compounds VII–X it is absent. Geometric parameters of I have been obtained by X-ray diffraction.[6] Addition of positively charged groups to the three-valent phosphorus (I and II) or to the phosphoryl group (V and VI) yields the P←N bond. Addition of neutral acceptors such as BH_3, O and S to the phosphatrane VII phosphorus does not give hypervalent bonds (VIII–X) whereas the P←N bond appears in the BF_3 or $OP(OH)_3$ and phosphatrane complexes (III and IV).

Using an MNDO approximation[7,8] the effect of the structural and electronic factors on the formation of the donor-acceptor P←N bond in phosphatranes is studied choosing the model complexes $XPF_3 \cdot NH_3$, where X is the lone electron pair n_p, O, H^+ and OH^+.

METHOD OF CALCULATION

The torsion angles of the complexes, calculated in a "super-molecule" approximation, were fixed for a symmetrically staggered conformation, and the

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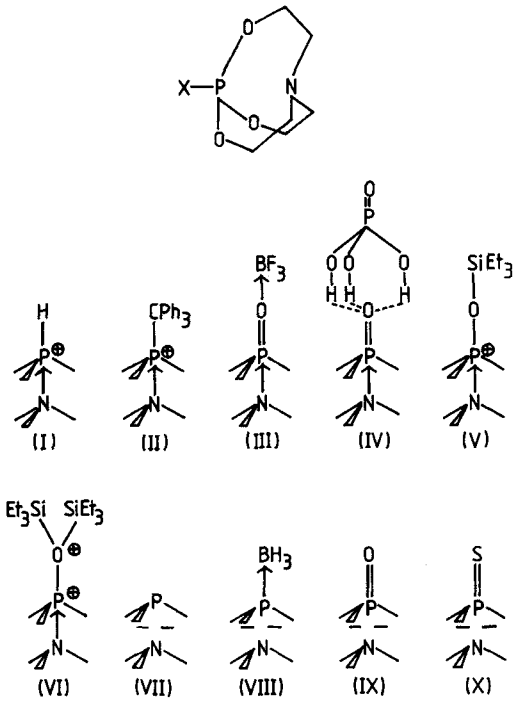
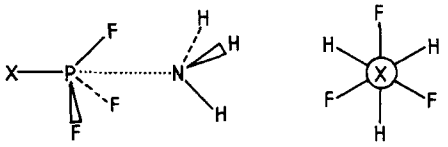


SCHEME 1

bond lengths and angles were optimized considering the symmetry of the complex (Scheme 2). Calculations were performed for three types of model complexes. In the first case (model 1) the effect of the bicyclic structure was ignored except for the limitations relating to the symmetry of the model complexes. All the bond lengths and angles were optimized in the calculation for the complexes and isolated molecules. In the second case (model 2) the bicyclic structure was assumed "to define" the length of the donor-acceptor bond. In this case the P←N bond lengths were not optimized, they being taken equal to 2.0 A, a value close to the experimental one for I (1.986 A).[6] The remaining bond lengths and angles in the complexes were optimized. The isolated XPF_3 molecules were calculated using the geometric parameters obtained from their optimization during calculations for the complexes. Such calculations were made to estimate the distortion energy of the acceptor phosphatrane fragment in the bicyclic structure. In the third case (model 3) the effect of the bicyclic structure was



SCHEME 2

considered by the distortion of the angles at the phosphorus. The XPF bond angles were taken to be equal to 90 degrees. Thus the phosphorus atom in the $XPF_3 \cdot NH_3$ complexes are located in the trigonal bipyramid equatorial plane. The remaining bond lengths, as well as the P←N distance and bond angles at the nitrogen, were optimized. As in the previous case, the calculations for the isolated XPF_3 molecules were made by using the geometric parameters that were optimized for the complexes.

The effect of the bicyclic structure on the bond angles at the nitrogen is not given a special treatment as the inversion barriers in the amines are not high both in absolute terms and as compared with those at the phosphorus. The contribution of the distortion energy of the nitrogen bond angles is negligible, producing no effect on the relationship between the energy factors responsible for the donor-acceptor P←N bonding in the phosphatranes.

Such a selection of the model structures is dictated by the following considerations. Due to the fact that the optimized bond angles when using the MNDO method do not exactly correspond to their experimental values, direct calculations for phosphatranes I—X, aimed at estimating the efficiency of the donor-acceptor interaction between the phosphorus and nitrogen, is a problem because of a possible significant error resulting from the angular distortion energy estimation. At the same time, calculations for the above simple model systems seem to permit estimation of the various electronic and structural factors responsible for the P←N bonding in the phosphatranes.

RESULTS AND DISCUSSION

Tables I and II give results of calculations for the structural, energy and electronic characteristics of the XPF_3 molecules and $XPF_3 \cdot NH_3$ complexes. The charges on the phosphorus atoms (q_p) and energies of the lower unoccupied MO (E_{LUMO}) are regarded as characteristics indicating a relative ability of the HPF_3 molecules to undergo electrostatic and orbital controlled interaction, respectively, with the electron donors. The XPF bond angles were taken as parameters describing a change in the geometry of the XPF_3 molecules in the course of the donor-acceptor P←N bonding. The distortion energies (ΔH_d) were calculated by full geometry optimization (model 1) and with geometric parameters obtained in calculations for the complexes (models 2 and 3). The distance between the phosphorus and nitrogen atoms (R_{PN}) corresponds to the position of the minima on the total energy surfaces for the $XPF_3 \cdot NH_3$ complexes, as calculated in the supermolecule approximation; Δq is the electron density transfer from the donor molecule NH_3 to the acceptor molecule XPF_3. The heats of formation of the complexes (ΔH_f) were calculated as differences between the heats of formation (total energies) of the complexes and isolated molecules with the optimized geometric parameters; $\Delta H_f' = \Delta H_f - \Delta H_d$—the heats of formation of the complexes without distortion energies.

In the XPF_3 molecules calculated by full geometry optimization (Table I, model 1) the positive charges on the phosphorus atoms grow in the series $PF_3 < HPF_3^+ < OPF_3 < HOPF_3^+$. The LUMO energy levels in turn decrease in the

TABLE I

Results of the MNDO calculations of XPF_3 (X = LP, O, H^+, HO^+)*

Model	1				2				3			
X	LP	O	H^+	HO^+	LP	O	H^+	HO^+	LP	O	H^+	HO^+
q_P, a.u.	1.203	1.617	1.459	1.717	1.202	1.535	1.418	1.676	1.480	1.400	1.364	1.628
E_{LUMO}, eV	1.620	−2.161	−9.840	−9.592	−1.319	−3.639	−10.180	−10.438	−2.291	−4.986	−10.906	−11.224
∠XPF	118.6	116.2	113.6	111.2	102.0	101.7	98.2	96.7	90.0	90.0	90.0	90.0
ΔH_d, kcal mol^{-1}	0.0	0.0	0.0	0.0	44.63	31.89	29.07	25.28	87.37	94.23	61.80	54.63

* Model 1—bond lengths and bond angles were optimized; model 2—bond lengths and bond angles from the $XPF_3 \cdot NH_3$ (R_{PN} = 2.0 A) complexes; model 3—XPF_3 geometry from $XPF_3 \cdot NH_3$ (XPF = 90°) complexes.

TABLE II

Results of the MNDO calculation of $XPF_3 \cdot NH_3$ complexes*

Model	1				2				3			
X	LP	O	H^+	HO^+	LP	O	H^+	HO^+	LP	O	H^+	HO^+
R_{PN}, A	—	—	3.189	2.764	2.0	2.0	2.0	2.0	1.929	1.953	1.921	1.937
Δq, a.u.	—	—	0.006	0.040	0.200	0.197	0.296	0.302	0.289	0.293	0.392	0.381
ΔH_f, kcal mol^{-1}	—	—	−7.69	−7.47	48.53	39.55	4.89	−4.11	61.05	70.66	15.84	4.56
$\Delta H_f'$, kcal mol^{-1}	—	—	—	—	3.90	7.66	−24.18	−29.39	−26.32	−23.57	−45.96	−50.07

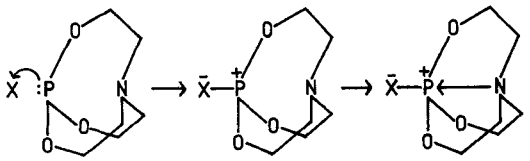
* Model 1—total optimisation of the bond lengths and bond angles; model 2—R_{PN} = 2.0 A; model 3—XPF = 90°.

series $PF_3 > OPF_3 \gg HOPF_3^+ \sim HPF_3^+$. The dependence of the total energy for the $XPF_3 \cdot NH_3$ complexes on the P←N distance (model 1) has minima for HPF_3^+ and $HOPF_3^+$. For PF_3 and OPF_3 the same dependence is repulsive. Qualitatively this finding is in good agreement with the data reported [6] concerning the P←N bonding in the protonated phosphatranes I and IV and the absence of a bond in the neutral molecules VII and IX. The optimized P←N distances obtained by calculation are well in excess of the experimental evidence for phosphatrane I. This may suggest an importance of the bicyclic structure in the hypervalent P←N bonding in the phosphatranes. Comparison of the results of calculations for the $XPF_3 \cdot NH_3$ complexes and the electronic characteristics of the XPF_3 molecules indicates that the low energy levels of the unoccupied MO in the case of HPF_3^+ and $HOPF_3^+$ may be used to rationalize the hypervalent P←N bonding.

The rôle of the bicyclic structure and the angular distortion in the P←N bonding can be understood by considering the results of calculations for model 2 ($R_{PN} = 2.0$ A). The optimized XPF bond angles in the $XPF_3 \cdot NH_3$ complexes are 14.2 to 14.6°, i.e. smaller then those in the isolated XPF_3 molecules. Thus variations in the bond angles at the phosphorus, resulting from the P←N bonding, are nearly independent of X. The distortion energies decreases with the ∠XPF values reduction. Despite the fact that the approach of the phosphorus and nitrogen to a distance of 2.0 A in all cases brings about a marked electron density transfer from NH_3 to XPF_3, the $\Delta H_f'$ values will be negative for HPF_3^+ and $HOPF_3^+$ only. For the neutral molecules the exchange repulsion energy exceeds the energy drop resulting from the donor-to-acceptor electron density transfer.

A more significant distortion of the acceptor molecule geometry when the phosphorus and fluorine atoms will be positioned in a plane (model 3, ∠XPF = 90°), leads to $\Delta H_f'$ becoming negative for all X's. For the neutral molecules these values are about one half those for the cations. Comparison of $\Delta H_f'$ and ΔH_d indicates that addition of H^+ to PF_3 and OPF_3 simultaneously strengthens the electronic effects associated with the P←N bonding ($\Delta H_f' =$ 19.6 kcal mol^{-1} for X = n_P and 26.5 kcal mol^{-1} for X = O) and reduces energy consumption for the distortion of the bond angles at the phosphorus ($\Delta H_d =$ 25.6 kcal mol^{-1} for X = n_P and 39.6 kcal mol^{-1} for X = O). In model 3, the ΔH_d differences between the neutral molecules and cations are even greater, exceeding the corresponding differences for $\Delta H_f'$. The equilibrium P←N distances in model 3 exceed the experimental values of the P←N covalent bond lengths in amidophosphites and amidophosphates, but they are smaller than that for phosphatrane I [6]. Comparison of R_{PN} with the other characteristics shown in Tables I and II indicates the absence a simple correlation between them.

Comparison of the quantum chemical results for the model complexes $XPF_3 \cdot NH_3$ with the experimental data on the hypervalent P←N bonding in phosphatranes [4–6] shows that model 2 fits best the experimental evidence. The hypervalent P←N bonding can be also discussed in qualitative terms as electron density transfer from the nitrogen lone pair to the antibonding orbital of the P—X bond.[9] With increasing electronegativity of X the electron-acceptor ability of σ_{PX}^* grows both due to the energy lowering of this orbital and the higher contribution of phosphorus to σ_{PX}^*. On the other hand the P—X bonds in phosphatranes can be regarded as belonging to the donor-acceptor type, i.e.,



SCHEME 3

resulting from the from the electron density transfer of the phosphorus lone pair to the unoccupied orbital of X (Scheme 3). The electronegativities of substituents X in phosphatranes representing quasiphosphonium compounds increase in the following series:

$$[O^-, S^-, BH_3] < [F_3BO^-, OP(OH)_3O^-] < [H, Et_3SiO] < (Et_3Si)_2O^+$$

This series indicates a magnitude and distribution of charge on X: negatively charged groups < negatively charged groups in a complex with the electron acceptors < neutral groups < postively charged groups. The order of the substituent electronegativities in the brackets depends on a number of factors which are hard to account for in a qualitative description (ability to the reverse electron transfer to the phosphorus to give the multiple P—X bond, interaction with the counterion, solvation). However, it can be assumed that the above order will remain generally valid when considering these factors.

The P←N bond is absent in phosphatranes VII to X, as could be expected based on the dependence of the acceptor properties σ^*_{PX} on the electronegativity. Concerning phosphatrane VII which has no exocyclic substituent ($X = n_P$), the qualitative approach under discussion renders the P←N bonding impossible due to the absence of the antibonding σ^*_{PX} orbital capable to accept the electron density of the nitrogen lone pair. As suggested by the model calculations using the MNDO method for the $PF_3 \cdot NH_3$ complex in the case of a planar PF_3 structure, the P←N bonding can take place at the expense of the σ^*_{PF} orbitals.

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