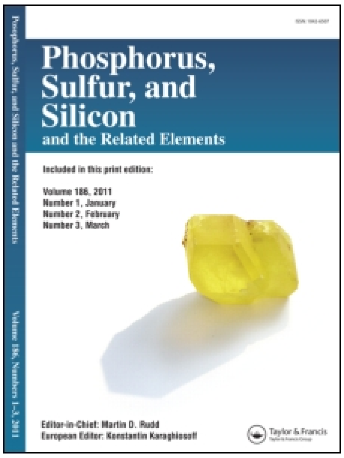

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Molecular and Electronic Structure of λ³-Iminophoshines

Alexander N. Chernega[a]; Anatoly A. Korkin[a]; Michael Yu. Antipin[a]; Yuri T. Struchkov[a]
[a] Institute of Organic Chemistry, Kiev, USSR; Nesmeyanov Institute of Organoelement Compounds, Moscow, USSR

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MOLECULAR AND ELECTRONIC STRUCTURE OF λ^3-IMINOPHOSHINES

ALEXANDER N. CHERNEGA, ANATOLY A. KORKIN,
MICHAEL YU. ANTIPIN, YURI T. STRUCHKOV
Institute of Organic Chemistry, Kiev, USSR; Nesmeyanov
Institute of Organoelement Compounds, Moscow, USSR

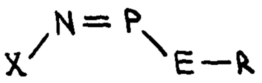
Abstract An analysis of main features of spatial and electronic structure of λ^3-iminophoshines has been carried out on the basis of experimental X-ray structural data and results of quantum chemical calculation

Recent advances in chemistry of bicoordinated phosphorus derivatives with a double P=N bond (λ^3-iminophosphines) have aroused interesting problems on spatial and electronic features of these compounds. X-Ray diffraction studies of a large number of different λ^3-iminophosphines X-N=P-Y (X = Ar, Alk, PR_2, $P(S)R_2$, $\overset{+}{P}R_3$; Y = Ar, Alk, NR_2, $N{=}PPh_3$, PR_2, OR, SR, Hlg et al.) synthesized in the Institute of Organic Chemistry in Kiev (L.N.Markovski et al.) together with our own and literature quantum chemical calculations of the model systems allowed to elucidate main structural features of these compounds.

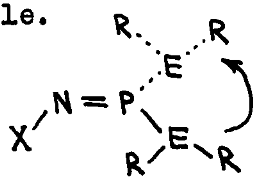
1. Experimental results show that without essential conjugation effects both in iminophosphines X-N=P-Y (I) and in iminophosphoranes $X{-}N{=}PY_3$ (II) the double P=N bond length varies in the same range of 1.50-1.57 Å. However, ab initio calculations with localization of MO for the model systems HN=PH (III) and $HN{=}PH_3$ (IV) show that electronic structure of the double bond in these two cases is essentially different. Thus for (III) π-system is of the type usual for unsaturated compounds, while in (IV) the double bond is essentially semipolar (partially triple). Another interesting result is a significant difference of the character of two lone pairs (LP) in (III): whereas LP(N) has mainly the p-character (p/s = 1.88), LP(P) is localized predominantly in the s-orbital (p/s = 0.31).

2. The central group of molecules considered involving the P=N bond almost in all cases is nearly planar (torsion angle XNPY ca. 0 or 180°). When X or Y is Ar steric effects force a benzene ring to become nearly normal to the central plane.

3. A compromise between electronic and steric effects in (I) can result in existence of trans- or stable cis-isomer.[1] For example, when Y = Hlg or ER with an "angular" bonding configuration (A) λ^3-iminophosphines exist as cis-isomers for any volume of R. However, when Y = ER_2 has a trigonal bonding configuration (B) the repulsion between X and one of two substituents R in the cis-form becomes more essential. As a result the cis-isomer has a lower energy only for a small R (e.g. R = Me); for a more bulky R trans-isomer becomes more favourable.



(A) E = O, S etc.



(B) E = N, P etc.

According to the quantum chemical calculations in stabilization of the cis-form an important role is played both by hyperconjugation effects $n_P-\sigma^*_{N-X}$ and (to the greater extent) $n_N-\sigma^*_{P-Y}$ and by the attractive interaction $\overset{\delta+}{X}...\overset{\delta-}{Y}$.

4. In trans-iminophosphines the bond angle NPY varies in the narrow range of 100.6-109.3° and the angle PNX in the broader range of 114.0-129.9°. On going from a trans-isomer to a sterically strained cis-form the NPY angle is somewhat increased to 109.0-115.9°, whereas the PNX angle undergoes a very strong increase up to 131.3-173.7°, showing its high flexibility. This effect, i.e. a significantly greater structural rigidity of the NPY angle may be explained by a weak tendency of the 3-rd period elements to rehybridization due to a significant difference in size of their outer s- and p-atomic orbitals.

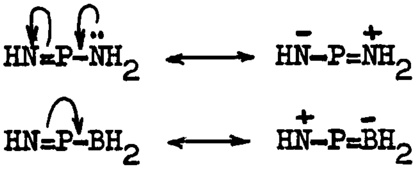
5. Increasing of the PNX bond angle on going from

trans- to cis-iminophosphines is accompanyed by shortening P=N bond from 1.55-1.58 Å to 1.50-1.55 Å. This shortening is mainly due to increasing of the s-character of the AO(N), participating in this bond formation. Increasing of the p-character of the LP(N), resulting in the stronger $n_N-\sigma^*_{P-Y}$ conjugation, can serve as an additional factor in the same direction.

6. X-Ray structural data show that in both (I) and (II) increasing of the PNX angle is accompanyed by shortening of the P=N bond. However, these bond length - bond angle relationships are different for these two classes of compounds. Ab initio as well as semiempirical calculations reproduce these empirical relationships with the corresponding curve for iminophosphoranes being much steeper. The correlation discussed seems to be due to two effects, viz. increasing of the s-component of the hybridized N atomic orbital, participating in the P=N bond formation, and strengthening of the $n_N-\sigma^*_{P-Y}$ conjugation with the increase of the PNX bond angle. However, if the first effect is practically the same both for (I) and (II), the second effect is more significant for (II) because in iminophosphoranes there are three (rather than one) acceptor σ^*_{P-Y} orbitals.

7. Specific peculiarities of conjugation effects in λ^3-iminophosphines should be stressed. In all studied compounds with the -N=P-N< group the $\pi_{P=N}$-system and LP(N) are almost parallel i.e. most favourably oriented for conjugation. However, such orientation does not lead to any significant structural manifistation of the $n_N-\sigma^*_{P=N}$ conjugation (increase of the N=P and decrease of the P-N distance). Our ab initio calculations of model iminophosphines XN=PH and HN=PX and, for comparison, of similar molecules $XN=CH_2$ and HN=C(H)X (where X is the donor group NH_2 or the acceptor group BH_2) in two extreme conformations (all-planar and with an X group normal to the double bond plane) have shown that the character of conjugation in XN=PH and HN=PX is essentially different. More-

over in the second case structural and energetic consequences of conjugation do not correspond to the common concept:



Specific character of conjugation effects in these systems as well as in molecules with the double C=P, Si=N and Si=C double bonds is determined by the decrease of efficiency of p_π-p_π-conjugation and increase of effects of bond polarization for atoms of the 3-rd period. As a result, polarization effects can overweight conjugation ones and change overall structural pattern.

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