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Phosphorus Compounds in Lower Coordination States Electrical Properties and Features of Structure

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PHOSPHORUS COMPOUNDS IN LOWER COORDINATION STATES. ELECTRICAL PROPERTIES AND FEATURES OF STRUCTURE

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Abstract P^I and P^{II} -derivatives have been investigated by electrical and electrooptical methods for the determination of the main parameters of multiple phosphorus bonds, polarity and polarizability, and on their basis spatial and electronic structure of these compounds has been studied. Experimental data on polarity and polarizability of phosphalkynes $P\equiv CR$, phosphalkenes $R^1P=CR^2R^3$, phosphazenes, diphosphenes, arsa- and stibaphosphenes $R^1P=ER^2$ ($E = N, P, As, Sb$) have been obtained. Polarities of $P\equiv C$, $P=C$ and $P=E$ bonds have been determined. Multiple $P\equiv C$ and $P=N$ bonds have considerable anisotropy of polarizability.

The progress obtained in the synthesis of P^I and P^{II} compounds contributes to the fact that in modern physicochemical investigations it is the study of the structural features and properties of these compounds, as well as learning the nature of the phosphorus multiple bonds, that are stressed. Our work is devoted to the research into P^I and P^{II} derivatives by means of dipole moments and the Kerr effect.

I. Phosphalkynes, one-coordinated phosphorus compounds

3,3-Dimethyl-1-phosphabutynes $(CH_3)_3C-C\equiv P$ (I) and 1-adamantylphosphacetylene $Ad-C\equiv P$ (II), have been studied by methods of dipole moments and the Kerr effect.

Analysis of experimental dipole moments (I) 1.24D, (II) 1.58D and literary data on polarity defined by microwave spectroscopy for P^I derivatives $R-C\equiv P$ $R=H, CH_3, F, CN, H_2C=CH, HC\equiv C$, results in the conclusion that the $P\equiv C$ triple bond is weakly polar, whereas the slight changing interval of this value (0.7 ± 0.2 D towards the carbon atom) indicates

its weak sensitivity to variation of the substituent R at C_{sp} -atom. We can only note a slight tendency of increasing $m(P\equiv C)$ within these limits with the growth of -I-effect of substituent R^{1,2}. The determination of experimental molar Kerr constants t-Bu-C \equiv P ($104 \cdot 10^{-12}$ e.s.u.) and Ad-C \equiv P ($110 \cdot 10^{-12}$ e.s.u.) has enabled to find molecular anisotropies of polarizability (γ): 5.30 (I) and 3.80 (II) A³.^{3,4} The calculated parameters of P \equiv C bond polarizability are: $\gamma(P\equiv C) = 5.31$ A³, $b_1 = 8.21$ A³. Thus, the anisotropy of the molecule t-Bu-C \equiv P (I) is determined mainly by the anisotropy of the P \equiv C triple bond. The comparison of P \equiv C and N \equiv C triple bonds (phosphaalkenes, nitriles) in the aspect of our research testifies that alongside with available analogs there are considerable differences expressed in the inverse polarity of these bonds [$m(C\equiv N) \sim 2D$] and in the greater polarizability of the P \equiv C bond. This, in its turn, is reflected in a different chemical behaviour of phosphalkynes and nitriles in reactions of electrophilic and nucleophilic addition and complex formation.⁵

II. Polarity, polarizability and conjugative effects in dicoordinated phosphorus compounds.

Polarity of P=C double bond has been determined from the literary data on dipole moments of simplest phosphalkenes and λ^3 -phosphabenzenes $H_2C=PH$, $F_2C=PH$, C_5H_5P , p-MeC₅H₄P. The bond is almost nonpolar in phosphalkenes (0.02D) and slightly polar in phosphabenzenes (0.5D). Thus, when the multiplicity of the carbon-phosphorus bond increases and the hybridization of both atoms from sp^3 to sp changes simultaneously, its polarity, which on the whole remains rather low, decreases and reaches the conversion of the moment to the C_{sp} atom in P^I compounds: $m(C-P) \sim 0.7 > m(C--P) \sim 0.5 > m(C=P) \sim 0 > m(C\equiv P) \sim -0.7D$.⁶

The combined analysis of dipole moments of phosphazenes (III-VI) and diphosphene (VII): (Me₃Si)₂N-P=N-Bu-t (III), (Me₃Si)₂N-P=N-SiMe₃ (IV), 2,4,6-t-Bu₃C₆H₂-P=N-Bu-t (V), 2,4,6-t-Bu₃C₆H₂-P=N-SiMe₃ (VI), 2,4,6-t-Bu₃C₆H₂P=PN(SiMe₃)₂

(VI) has permitted to determine the moments $m(R-P^{II})$ and $m(P=N)$. The values of $m(P=As)$ and $m(P=Sb)$ have been found in the dipole moments of the compounds (VIII-X) 2,4,6-*t*-Bu₃C₆H₂P=EN(SiMe₂Bu-*t*)₂, E=P (VIII), As (IX), Sb (X). Analysis of the dipole moments of the molecules (III-X) (their polarity is not high: 1.7-2.7D) testifies to the localization of the P=E double bond in these systems, and the $m(P=E)$ value decreases regularly in the row E = N, P, As, Sb, whereas the conversion of polarity is observed: $m(P=N) = 2.2 \pm 0.2$, $m(P=P)=0$, $m(As=P)=0.9 \pm 0.2$, $m(Sb=P)=2.4 \pm 0.2$.⁷ Many P^{II} compounds contain substituents able to conjugate. However, detection and study of np_{π} , and $p_{\pi}p_{\pi}$, conjugation with the P=E bond in these molecules encounter difficulties. Evidently conjugative effects are expressed in bis(dialkylamino)methylenephosphines (Alk₂N)₂C=PR, R=H, Ph, Me₃Si (their polarity increases to 3.5-4.0D), and especially in diphosphabutadiene (Me₂N)₂C=P=P=C(SiMe₃)₂ (5.0D). The conjugation of the nitrogen lone pair with the C=P double bond is revealed by dipole moment exaltation ($\Delta\mu \sim 2.5$ -3.0D and 5D for diphosphadiene) that corresponds to the electron transfer from Alk₂N-groups $\sim 0.2 e^-$.⁸ n, p_{π} -Conjugation is realized to such an extent in the recently studied trans-phosphaalkenes Alk₂N-C(R)=P(Ph), R=H, Me. The inverse polarization of the C=P bond in C-aminomethylenephosphines (C^{δ+} P^{δ-}), and bis(trimethylsilyl)methylenephosphines (Me₃Si)₂C=PR (C^{δ-} P^{δ+}), R = *t*-Bu, Ph, (Me₃Si)₂N ($\mu \sim 1.0$ -1.5D), Cl, Br, I ($\mu \sim 2.5$ D) is the result of differences in the character of electronic interaction in these compounds.

Conjugation in iminophosphines R₂N-P=N-PBu₂-*t* and R₂N-P=N-P(S)Bu₂-*t*, R₂N: (Me₃Si)₂N, *c*-2,2,6,6-Me₄C₅H₆N is not detected.

The discovered exaltation of dipole moments in diphosphenes *i*-Pr₂NP=PC₆H₂Bu₃-2,4,6-*t* and *c*-2,2,6,6-Me₄C₅H₆NP=PC₆H₂Bu₃-*t*-2,4,6 ($\Delta\mu \sim 0.9$ D) may be interpreted as a result of n, p_{π} -conjugation R₂N⁺-P=P⁻. However, this effect contributes but little to the stabilization of diphosphenes in compari-

son with that in C-alkylaminomethylenephosphines.

The study of some phosphazenes $RP=N\text{Bu-t}$, $R: (\text{Me}_3\text{Si})_2\text{N}$, $2,4,6\text{-t-Bu}_3\text{C}_6\text{H}_2$ and $R^1\text{P} = \text{NC}_6\text{H}_2\text{Bu}_3\text{-t-2,4,6}$, $R^1: (\text{Me}_3\text{Si})_2\text{N}$, $c\text{-2,2,6,6-Me}_4\text{C}_5\text{H}_6\text{N}$ by the Kerr effect has enabled us to state the value of the $P=N$ bond anisotropy of polarizability ($3.5\text{-}4.0 \text{ \AA}^3$), to detect cis-configuration $\text{Me}_2\text{NP}=\text{NC}_6\text{H}_2\text{Bu}_3\text{-t-2,4,6}$ in solution (as well as in crystal), and the orthogonal orientation of Ar-groups in these molecules.

Thus, for the first time polarities and polarizabilities of multiple phosphorus bonds in P^I and P^{II} compounds have been determined and regularities of their change have been analyzed. Conjugative effects, as well as steric factors, have been shown to be of importance in the stabilization of the P^{II} compounds.

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REFERENCES

1. I.I.Patsanovsky, E.A.Ishmaeva, J.Z.Stepanova et al., *Izv. AN SSSR. Ser. Khim.*, 415 (1984).
2. E.A.Ishmaeva, I.I.Patsanovsky, J.Z.Stepanova et al., *Dokl. AN SSSR*, 288, 160 (1986).
3. I.I.Patsanovsky, A.H.Pliamovaty, I.H.Shakirov et al., *Dokl. AN SSSR*, 290, 400 (1986).
4. I.I.Patsanovsky, E.A.Ishmaeva, J.Z.Stepanova et al., *Izv. AN SSSR. Ser. Khim.*, 1690 (1986).
5. E.A.Ishmaeva, I.I.Patsanovsky, *Usp. khim.*, 54, 418 (1985).
6. I.I.Patsanovsky, J.Z.Stepanova, E.A.Ishmaeva et al., *Zh. Obshch. Khim.*, 57, 1464 (1987).
7. J.Z.Stepanova, I.I.Patsanovsky, E.A.Ishmaeva et al., *Zh. Obshch. Khim.*, 57, 2449 (1987).
8. J.Z.Stepanova, I.I.Patsanovsky, E.A.Ishmaeva et al., *Zh. Obshch. Khim.*, 57, 2446 (1987).