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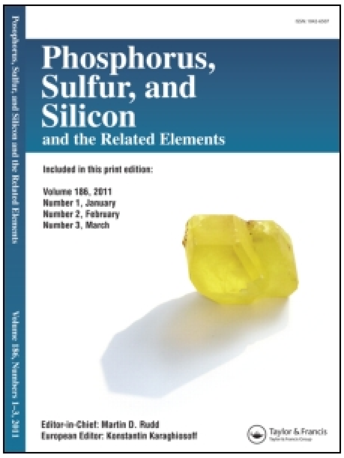

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Experimental and Theoretical Conformational Analysis of Methylene- and Cyanophosphines and Their Oxides

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EXPERIMENTAL AND THEORETICAL CONFORMATIONAL ANALYSIS OF METHYLENE- AND CYANOPHOSPHINES AND THEIR OXIDES

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The structure of a great number of methylenephosphine oxides ***1–11*** *and cyanophosphines and their oxides* ***12–18*** *was studied by semiempirical PM3 and ab initio RHF/6-31G*** *calculations. Obtained results are in good agreement with experimental data (dipole moments, Kerr effect, IR spectroscopy). In* ***12–18*** *the contribution of interactions of CN group or Ph ring with lone pair of electrons (LPE) of the P atom, d-orbitals of the P atom, or P=O group is absent.*

Keywords: Conformational analysis; cyanophosphines and their oxides; methylenephosphine oxides; quantum chemical calculations

Previously, a great number of phosphine oxides with alkyl and aryl radicals at the P atom were investigated by the complex of experimental methods (dipole moments, IR spectroscopy, Kerr effect) in Kazan State University. Regularities of the rotary isomerism were determined in methyl-substituted dialkyl- and diarylmethylphosphine oxides. In solution, these compounds exist in the conformational equilibrium of noneclipsed forms with g- and t-orientation of P=O and C—X (X=Cl, CN) bonds.[1] The theoretical basis of preference of either conformation in these compounds is practically absent in the literature. We performed the theoretical conformational analysis of a number of methylenephosphine oxides **1–11** and cyanophosphines and their oxides **12–18**:

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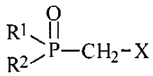

$R^1 = R^2 = Me$, X = Cl **1**; $R^1 = R^2 = Et$, X = Me **2**; $R^1 = R^2 = Et$, X = CN **3**; $R^1 = R^2$ = t-Bu, X = Cl **4**; R^1 = Me, R^2 = Ph, X = Cl **5**; R^1 = Et, R^2 = Ph, X = Cl **6**; R^1 = i-Pr, R^2 = Ph, X = Me **7**; R^1 = i-Pr, R^2 = Ph, X = Cl **8**; R^1 = t-Bu, R^2 = Ph, X = Cl **9**; $R^1 = R^2$ = Ph, X = CN **10**; $R^1 = R^2$ = X = Ph **11**; $MeOP(CN)_2$ **12**; $(MeO)_2PCN$ **13**; $(MeO)_2P(O)CN$ **14**; Ph–$P(CN)_2$ **15**; Ph_2PCN **16**; Ph(Et)PCN **17**; $Ph_2P(O)CN$ **18**.

The calculations with full optimization of geometry were conducted by PM3 method using VAMP 4.56 software. We have demonstrated that this method adequately reproduces structural characteristics derived from the gas electron diffraction and the X-ray analysis of $(RO)_3PY$ (Y=O, S, Se, Te). It is also in an agreement with the experimental data, including IR spectral data. The rotation about P—CH_2X bond for all investigated compounds was examined in terms of three stationary chess structures, one of them (t) had trans-orientation of P=O and C—X bonds, and two others (g^+, g^-) had gauche orientation of these bonds (Figure 1).

Only rotamers that had the relative energy values under 8.4 kJ/mol were examined.

We have determined that a population of the form with trans-orientation of C—X bond relative to the P=O group decreases as the volume of substituents at the P atom is increased in **1–4**. The increase of volume of the substituent X is enacted in the same manner. For phenylphosphine oxides **5–9**, in which the g^+ and g^- rotamers are not identical, the preferred rotamer is g^+, with the g-orientation of the alkyl group and the Cl atom. A plane of the Ph ring is close to eclipse of the P=O group for the energetically preferred conformations of the aromatic deravitives **5–11**. So, the results of semiempirical quantum chemical calculations adequately describe the experimental data for the examined phosphine oxides (dipole moments, Kerr constants, IR spectra of compounds in the different aggregate states and in the various solvents at the various temperatures) and give unconflicting conformational picture. We have also determined that a population of the form with transorientation of P=O and C—X bonds decreases as the

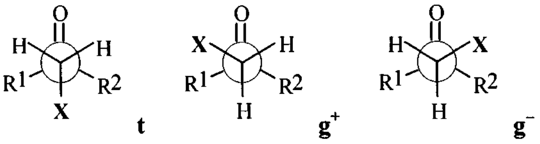

FIGURE 1 Orientation of P=O and C–X bonds (+, g^+, g^-) in investigated compounds.

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volume of substituents at the P atom and in the CH_2 group is increased. A plane of the aromatic cycle in crystal analogues is close to eclipse of the P=O bond.

For the first time the structure of high reactive cyanophosphines and their oxides with strong electron acceptor substituent at the P atom in solution was determined by the DM and Kerr effect methods.[2,3] For better theoretical understanding of our experimental data, we carried out quantum-chemical study of compounds **12–18** by semiempirical PM3 and ab initio RHF/6-31G** calculations. Independent of the method of calculations, the trans-structure for **12** is preferred. This conclusion is in a complete agreement with experimental data. For phosphonite **13** forms with g- and t-orientation of alkoxy groups and LPE of the P atom are realized. The structures, in which one of the methoxy groups is closed to eclipse of the P=O bond (torsion angles C—O—P=O are within 0–10°), and the second group, which have synclinal orientation (φ C—O—P=O are within 38–47°), are in phosphonate **14**. According to polarity analysis the equilibrium of g^+g^-, g^-g^-, g^+t conformers is realized in **14**. So, the results of unempirical calculations and data of DM and Kerr effect are in a good agreement with each other.

Polarity and polarizability of the P—CN group, which we determined earlier,[2] point to a low sensitivity of these parameters to a character of a substituent at the P atom. In phenylcyanophosphines **15–17**, the participation of the P atom conjugated with π-systems of Ph rings as well as C≡N groups is formally possible. Using the DM and Kerr effect methods, we found the conformations for **15** and **18**, in which the planes of Ph rings almost eclipse LPE at the P atom (**15**, $\varphi = 7°$) or the P=O group (**18**, $\varphi = 6°$). Carried-out calculations also point to an energy advantage of almost bissector conformations. Thus, orientation of the Ph ring in **15** excludes a possibility of p_π-p_π overlap of LPE at the P atom and π-system of the Ph ring due to their perpendicular arrangement. Structures, in which the planes of the Ph rings are in a range of torsion angles of ±40–50° relative to LPE at the P atom, are equally probable in **16**. This is in a good agreement with an experiment. In **17** Ph ring is closed to eclipse of LPE at P atom in g-conformations (0–14°), where there are no strong electron interactions. The results of both quantum chemical calculations point to that. According to ab initio calculations, conformation, in which a plane of one Ph ring eclipses P=O bond, is in **18**. The second Ph ring is in a range of torsion angles of 20–30° to the side of eclipse of Ph and P=O groups. These results are in a good agreement with experiment. In contrast to p_π-p_π conjugation of LPE at the P atom and Ph ring, this interaction does not have spatial limitations in the >P—C≡N system. The analysis of energies and constitution of frontal MO indicate the absence of interaction between the n_p and the $\pi^+{}_{C\equiv N}$

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orbitals in **12** and **15**, and between pπ_O and $\pi_{C\equiv N}$ orbitals in **14** and **18**. Small population of $d_{\pi *}$ AO of the P atom is general for the above preferred conformations of compounds **12**, **14**, **15**, **18**.

Therefore, we can conclude that neither interactions of cyano or phenyl group with lone pair of electrons or d-orbitals of the P atom, nor their interactions with the phosphoryl group contribute to stabilization of preferred conformers in studied phosphorus cyanides.

REFERENCES

[1] E. N. Strelkova, I. I. Patsanovskii, E. A. Ishmaeva et al., *Zh. Obshch. Khim.*, **54,** 1277 (1984).

[2] E. A. Ishmaeva, I. I. Patsanovskii, W. Stec et. al., *Dokl. AN SSSR*, **240,** 1361 (1978).

[3] I. I. Patsanovskii, E. A. Ishmaeva, G. V. Romanov et. al., *Dokl. AN SSSR*, **255,** 383 (1980).

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