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Quantum-Chemical Study of the Structure of Cyanophosphines and Their Oxides

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Abstract—The structure of cyanophosphines and their oxides was studied by ab initio (RHF/6-31G**) and semiempirical (PM3) methods. Both methods predict that $MeOP(CN)_2$, $(MeO)_2PCN$, and $(MeO)_2P(O)CN$ exist in noneclipsed antiperiplanar and synclinal conformations. The calculation results nicely agree with measured dipole moments and Kerr constants of these compounds. The phenyl and diphenyl derivatives $PhP(CN)_2$, Ph_2PCN, Ph(Et)PCN, and $Ph_2P(O)CN$ prefer forms in which the phenyl ring plane is eclipsing the phosphorus lone electron pair or the phosphoryl bond. The interactions of the phosphorus lone electron pair with the phenyl ring and with the cyano group are lacking in the title compounds.

Steric and electronic structures of organic phosphorus compounds are particularly interesting to study in cases where an electron-donor or an electron-donor substituent is directly attached to the phosphorus atom, since such compounds not infrequently possess an unusual and(or) a high reactivity. The highly reactive cyanophosphines and their oxides just belong to such compounds. Their structure in solutions has first been established by dipole moment and Kerr effect measurements [1, 2]. According to those works, irrespective of the coordination state of phosphorus [P(III) or P(IV)], number of cyano groups (one or two), and hydrocarbon chain length, alkoxy derivatives prefer noneclipsed *trans* (antiperiplanar) and *gauche* (synclinal) conformations. In P(III) and P(IV) cyano derivatives with one or two phenyl substituents, certain conformers have the phenyl rings eclipsing the lone electron pair (LEP) of the phosphorus atom or the phosphoryl group [2]. Consequently, experimental evidence was obtained to show that the strongly electron-acceptor and not very bulky cyano group has no effect on the conformational behavior of alkoxy and phenyl groups on P(III) and P(IV) and on intermolecular electronic interactions involving the phosphorus atom [2].

A deeper theoretical understanding and substantiation of the revealed experimental regularities can be gained by quantum-chemical calculations of phosphorus cyanides. Having experimental data (dipole moments and Kerr constants) for a wide range of cyanophosphines and their oxides, we perfomed semiempirical (PM3) and *ab initio* (RHF/6-31G**) calculations of $MeOP(CN)_2$ (**I**), $(MeO)_2PCN$ (**II**), $(MeO)_2 \cdot P(O)CN$ (**III**), $PhP(CN)_2$ (**IV**), Ph_2PCN (**V**), Ph(Et)·PCN (**VI**), and $Ph_2P(O)CN$ (**VII**).

It should be noted that semiempirical and *ab initio* (much less frequently) calculations of phosphines and their oxides has been reported in the literature [3–11]. The general opinion is that both semiempirical and *ab initio* methods rather well reproduce the molecular geometry (bond angles within 3–4° and bond lengths within 0.005–0.03 Å), whereas the rotation barriers, energetic characteristics, dipole moments, and some other physicochemical parameters may considerably differ from experimental, depending on the method and basis set. In this connection, further calculations at diifferent levels are needed.

First of all we considered it necessary to analyze how the PM3 and RHF/6-31G** methods reproduce the experimental geometric and polarity parameters of well-known simple P(III) and P(IV) compounds (trimethylphosphine, trimethylphosphone oxide, and trimethylphosphine sulfide) obtained by X-ray diffraction [12], gas-phase electron diffraction [12], and dipole moment measurements [13, 14]. The resulting data are listed Table 1. As seen, the molecular geometries of all the three compounds (Me_3P, Me_3PO, and Me_3PS) are fairly well reproduced by both the semiempirical and *ab initio* methods. Note that both the methods well reproduce the experimental dipole moments of trimethylphosphine and trimethylphosphine oxide, whereas the dipole moment of trimethylphosphine sulfide proves overestimated by 1–1.4 D (Table 1).

As to the calculated geometry of cyanophosphines, we can note a certain nonlinearity of the P–C≡N group in nitrile **I**. The reported PCN angles vary within 174–175 (RHF/6-31G* [15, 16]), 172–174 (MP2–FULL/6-31G* [15, 16]), and 180° (CNDO/2 [17]). We obtained close values: 175 (PM3) and 174–175° (RHF/6-31G**). Consequently, higher level calculations result in smaller PCN angles. At the same time, the microwave [18] and electron diffraction data [19] point to a linear structure of the P–C≡N group in mono- and tricyanophosphines, whereas the X-ray diffraction analysis of tricyanophosphine $P(CN)_3$ showed that the PCN angle in crystal is reduced to 172° [20]. Miller *et al.* deduced a linear structure of the P–C≡N fragment in $P(CN)_3$ from the vibrational spectra of this molecule in solutions [21]. According to speculations in [20, 21], the deviation from the linearity in the crystal state derives from packing effects and, probably, specific intermolecular electronic interactions. Actually, the P···N distance in crystal (2.85 Å) is smaller than the sum of the van der Waals radii of P and N (3.4 Å) [20]. It is interesting to note that the PCN angle in the other compounds studied in this work is much larger. For instance, according to the RHF/6-31G** results, it is 176° in **II**, 178° in **V**, and 179° in **III** and **VII**, i.e. the P–C≡N group is almost linear.

Let us now consider the results of the theoretical conformational analysis of phosphorus cyanides. Figure 1 shows the Newman projections of all formally possible staggered conformers. We took the latter as starting structures in quantum-chemical calculations, knowing that organophosphorus compounds with P–O and P–S bonds characteristically exist in noneclipsed conformations [22]. Tables 2 and 3 list the torsion angles, relative energies, and dipole moments, calculated by the PM3 and RHF/6- 31G** methods for the possible conformers of phosphines **I**, **II**, and phosphonate **III**.

Both by the PM3 and RHF/6-31G** results, compoud **I** prefers the *trans* structure. This prediction is fully consistent with the experimental data [2], as well as with *ab initio* calculations with inclusion of electron correlation effects (MP2–FULL/6-31G*) [15] which show that the torsional potential curve has a deep well for a structure having the Me–O group *trans* to the phosphorus LEP. As to the polarity, the quantum-chemical calculations fail to reproduce the experimental dipole moment (4.16 D [2]). The deviation is

Table 1. Geometric parameters and dipole moments of Me_3P, Me_3PO and Me_3PS

Parameter	Experiment	RHF/6-31G**	RM3
Me_3P			
Bond length, Å:			
C–P	1.844^a	1.852	1.872
C–P	1.843^a	1.852	1.872
C–P		1.852	1.872
Bond angle, deg:			
CPC	98.8^a	100.1	100.6
CPC	98.9^a	100.1	100.7
CPC		100.1	100.7
Dipole moment, D:			
quantum-chemical calculation		1.38	1.08
vector additive scheme^b	1.16		
experiment^c	1.19		
Me_3PO			
Bond length, Å:			
C–P	1.809^d	1.817	1.824
C–P	1.809^d	1.817	1.824
C–P	1.809^d	1.817	1.824
P=O	1.476^d	1.474	1.482
Bond angle, deg:			
CPC	104.1^d	104.9	103.5
CPC	104.1^d	104.9	103.5
CPC	104.1^d	104.9	103.6
CP=O	114.4^d	113.7	114.9
CP=O	114.4^d	113.8	114.9
CP=O	114.4^d	113.8	114.9
Dipole moment, D:			
quantum-chemical calculation		4.67	3.92
vector additive scheme^b	4.40		
experiment^c	4.2–4.45		
Me_3PS			
Bond length, Å:			
C–P	1.818^d	1.823	1.831
C–P	1.818^d	1.823	1.831
C–P	1.818^d	1.823	1.831
P=S	1.940^d	1.966	1.944
Bond angle, deg:			
CPC	104.5^d	104.6	102.24
CPC	104.5^d	104.6	102.25
CPC	104.5^d	104.6	102.24
CP=S	114.1^d	113.9	115.96
CP=S	114.1^d	114.0	115.98
CP=S	114.1^d	114.0	116.02
Dipole moment, D:			
quantum-chemical calculation		5.84	6.20
vector additive scheme^b	4.78		
experiment^c	4.73, 4.87		

[a] Gas-phase electron diffraction [12]. [b] Calculated with data from [13] using the RHF/6-31G** geometry. [c] Data from [14]. [d] X-ray diffraction [12].

Table 2. Calculation results for possible conformers of $MeOP(CN)_2$ (**I**)

Parameter	*t*	g^-
PM3		
Torsion angle MeOP(LEP), deg	–179.95	–39.95
Relative energy (Δ*E*), kJ/mol	0	12.13
Dipole moment, D:		
PM3 method	2.66	4.57
vector additive scheme[a]	4.59	5.81
RHF/6-31G**		
Torsion angle MeOP(LEP), deg	180	–28.35
Relative energy (Δ*E*), kJ/mol	0	14.69
Dipole moment, D:		
RHF/6-31G** method	3.21	5.44
vector additive scheme[b]	4.63	5.99

[a] With the PM3 geometry. [b] With the RHF/6-31G** geometry.

Table 3. Calculation results for possible conformers of $(MeO)_2PCN$ (**II**)

Parameter	*tt*	g^-t	g^+t
PM3			
Torsion angle, deg:			
MeOP(LEP)	173.3	–25.7	44.7
MeOP(LEP)	–169.0	178.6	–178
Relative energy (Δ*E*), kJ/mol	0	7.74	7.78
Dipole moment, D:			
PM3 method	1.79	3.42	2.69
vector additive scheme[a]	3.81	4.60	3.68
RHF/6-31G**			
Torsion angle, deg:			
MeOP(LEP)	173.7	–28.3	43.1
MeOP(LEP)	172.8	–177.9	190.9
Relative energy (Δ*E*), kJ/mol	5.77	0	0.84
Dipole moment, D:			
RHF/6-31G** method	3.83	4.47	3.38
vector additive scheme[b]	3.71	4.53	3.73

[a] With the PM3 geometry. [b] With the RHF/6-31G** geometry.

0.4–1.5 D (Table 2). Fair agreement is attained only by the calculation by the vector additive scheme with both the PM3 and RHF/6-31G** geometries (Table 2). The *ab initio* calculations in [16] gave a value of 4.46 D for the dipole moment of (Δμ ~0.5 D at μ_{exp} 4.92 D [2]). It will be emphasized that, independent the basis set, PM3 and 6-31G** in the present work or 6-31G* and MP2–FULL/6- 31G* in [15], the *trans* form is always preferred for compound **I**. Since this result nicely agrees with experimental data, in calculations for the other cyanides we did not include electron correlation. Stabilization of the *trans* form of compound **I** is probably provided by two factors acting in one direction: electrostatic attraction of the opposite dipoles PA→CN and MeA→O and *gauche*-effect (maximal number of polar bond–polar bond interactions in the *trans* form). Apparently, the presence in phosphorus cyanides of a strongly polar fragment P–CN makes interactions of polar bonds the most important stabilization factor in preferred conformations.

In Table 3 we present the calculation results for those conformers of compound **II**, whose relative energies do not exceed 16–17 kJ/mol. The conformers are almost equally probable, which can be considered as an equilibrium of staggered forms with *gauche* and *trans* orientations of the alkoxy groups and phosphorus LEP. The same conclusion follows from a comparison of the dipole moments calculated quantum-chemically and by the vector additive scheme with the experimental value (3.64 D [2], Table 3).

With phosphonate **III**, we started with all the 6 formally possible staggered conformers shown in Fig. 1. According to the PM3 results, the possible forms are g^-t, g^-g^+, g^-g^-, and *tt* only, the former three being equally probable in terms of energy (Table 4). The PM3 dipole moments of these structures much differ from the μ_{exp} of an analog of this compound, diethyl cyanophosphonate (3.95 D in cyclohexane and 4.02 D in dioxane [2]). The difference in the dipole moments (Δμ) is more than 1 D. We consider it justified to compare phosphonate **III** and its diethyl analog, since its well known that experimental dipole moments of compounds of the same class, differing by the chain length of the hydrocarbon substituent (here Me and Et), are fairly close [14]. Based on the dipole moments calculated by the vector additive scheme (with the PM3 geometry) we can chose the only structure (g^-g^-), since the dipole moments of the other forms are much overestimated compared with experimental. In the RHF/6-31G** calculations we started with the same structures (Fig. 1). Unlike PM3, the *ab initio* calculation for this compounds results in only three equilibrium conformers (g^+g^-, g^-g^-, g^+t) with equal

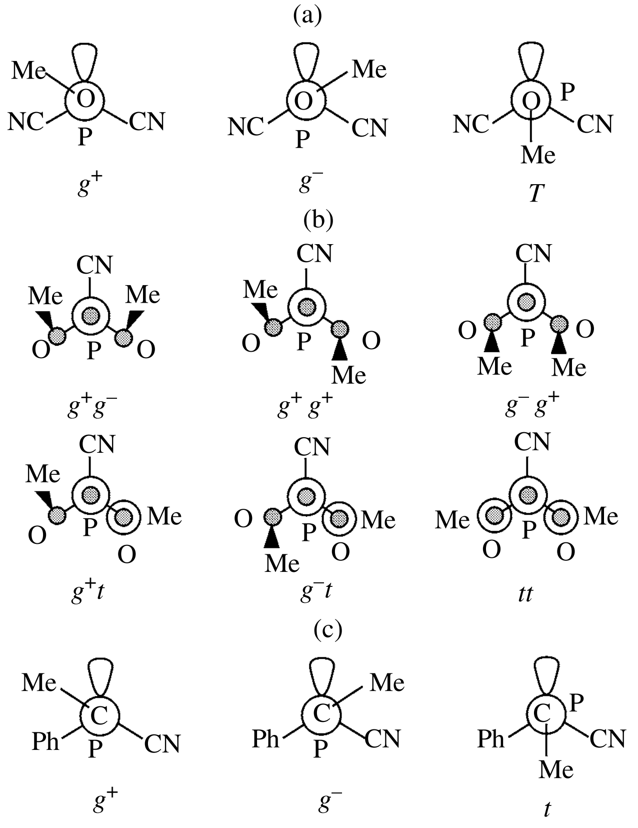

Fig. 1. Newman projections of possible conformers of (a) $MeOP(CN)_2$ (**I**), (b) $(MeO)_2PCN$ (**II**) and $(MeO)_2P(O)CN$ (**III**), and (c) Ph(Et)PCN (**VI**). Gray circles denote phosphorus LEP for compound **II** and phosphoryl oxygen for compound **III**.

energies. Therewith, only one of them (g^-g^-) was found by the PM3 method. Unlike what we have with phosphine **I**, the potential energy surface of phosphonate **III** is flatter. The relative energy of the transition states (saddle points) revealed by *ab initio* calculations are no higher than 4 kJ/mol. Most of the saddle points correspond to structures in which one methoxy groups is almost eclipsing the P=O bond (the C–O–P=O torsion angles are 0–10°) and the other is synclinal (the C–O–P=O torsion angles are 38–47°).

The dipole moments of equilibrium conformers, calculated both by the vector additive scheme (with the Hartree–Fock geometry) and quantum-chemically well reproduce the experimental dipole moment (3.95 D in cyclohexane [2]). Polarity analysis (Table 4) reveals equilibrium of three conformers, g^+g^-, g^-g^-, and g^+t, in phosphonate **III**. Thus, *ab initio* calculations and the method of dipole moments give consistent results.

As follows from the experimental data in [2], the polarity and polarizability parameters of the P–CN group are almost insensitive to the nature of substituents at the phosphorus atom (oxygen or carbon atom). Phenyl-substituted cyanides **IV**–**VII** are convenient objects for studying intramolecular electronic interactions, since the information on the nature of electronic effects can be gained both from the interaction moment and from the orientation of phenyl rings in the molecules. The phosphorus atom in phenylcyanophosphines **IV**–**VII** can formally be involved in π conjugation both with phenyl rings and cyano groups. In the conformations of phosphine **IV** and phosphine oxide **VII**, deduced from experimental data (dipole moments and Kerr constants), the phenyl ring planes are almost eclipsing the phosphorus LEP (for **IV**, φ 7°) or the phosphoryl group (for **VII**, φ 6°). Both the calculation methods, too, give evidence in favor of almost bisector conformations. Thus, the orientation of the phenyl ring in compound **IV** precludes p_π–p_π overlap of the phosphorus LEP and the phenyl π system because of their orthogonality. The bisector conformation of phosphine **IV** is also preferred by the results of *ab initio* calculations in [23].

For phosphine **IV**, both the calculation methods prefer a conformation in which the phenyl ring is eclipsing the phosphorus LEP, in complete agreement with the experimental dipole moments and Kerr effect [2].

Table 4. Calculation results for possible conformers of $(MeO)_2P(O)CN$ (**III**)

Parameter	g^-t	g^-g^+	g^-g^-	tt
PM3				
Torsion angle, deg:				
MeOP(LEP)	–34.3	–32.9	–46.8	151.3
MeOP(LEP)	177.4	33.8	–45.1	177.6
Relative energy (ΔE), kJ/mol	0	0.71	1.80	6.65
Dipole moment,D:				
PM3 method	2.84	2.89	2.23	3.69
vector additive scheme[a]	5.21	5.40	4.67	5.21
RHF/6-31G**				
	g^+g^-	g^+t	g^-g^-	
Torsion angle, deg:				
MeOP(LEP)	38.5	37.8	–48.3	
MeOP(LEP)	–38.1	173.2	–36.6	
Relative energy (ΔE), kJ/mol	0	3.22	0.63	
Dipole moment,D:				
RHF/6-31G** method	2.70	5.01	4.78	
vector additive scheme[b]	3.91	4.84	4.89	

[a] With the PM3 geometry. [b] With the RHF/6-31G** geometry.

The experimental dipole moment of this compound (4.84 D) is fairly close to those calculated by the vector additive scheme with the PM3 (5.17 D) and RHF/6-31G** geometries (5.24 D). At the same time, the *ab initio* method overestimates the dipole moment by 0.8 D. According to the PM3 results, a conformer with the phenyl ring eclipsing one of the cyano groups can be realized, but this is not confirmed by the *ab initio* and experimental data.

For phosphine **V**, by both the PM3 and RHF/6-31G** results, energetically equally probable are structures in which the phenyl ring planes form torsion angles of ±40–50° with the phosphorus LEP. These results are consistent with experiment [1]. Note that the experimental dipole moment of compound **V** (4.12 D [1]) is well reproduced both by the vector additive scheme (4.20 D with the PM3 geometry and 4.19 D with the RHF/6-31G** geometry) and PM3 calculations (3.80 D). The *ab initio* calculation, like with compound **IV**, gives an overestimated value ($\Delta\mu$ 0.71 D).

In cyano(ethyl)phenylphosphine **VI** (Table 5), the phenyl ring is almost eclipsing the phosphorus LEP in *gauche* conformers (0–14°) which lack strong electronic interactions. This follows from both the PM3 and RHF/6-31G** results. In the *trans* conformer, the ethyl methyl group is *trans* to the phosphorus LEP and cannot be eclipsed by the phenyl ring plane by steric reasons. Had the $C_{ar}C_{ar}O$(LEP) torsion angle in this conformation been zero, the distances between atoms forming the methyl group and one of the *ortho*-carbon atoms would have been smaller than the sum of van der Waals radii by 0.2–0.4 Å. Therefore, this angle is increased to 18 (PM3) or 30° (RHF/6-31G**). The polarity of this compound (4.00 D [2]) is fairly well reproduced by the vector additive scheme and both the quantum-chemical methods.

Table 5. Calculation results for possible conformers of Ph(Et)PCN (**VI**)

Parameter	g^+	g^-	t
PM3			
Torsion angle, deg:			
$C_{ap}C_{ap}OP$(LEP)	–0.3	–2.2	–18.1
$MeCH_2P$(LEP)	42.45	–51.7	177.45
Relative energy (ΔE), kJ/mol	0	0.54	2.18
Dipole moment, D:			
PM3 method	3.79	3.74	3.73
vector additive scheme[a]	4.21	4.24	4.21
RHF/6-31G**			
Torsion angle, deg:			
$C_{ap}C_{ap}OP$(LEP)	–9.7	–13.75	–29.6
$MeCH_2P$(LEP)	51.25	–51.25	–179.75
Relative energy (ΔE), kJ/mol	0.75	0	3.22
Dipole moment, D:			
RHF/6-31G** method	4.74	4.58	4.55
vector additive scheme[b]	4.17	4.19	4.20

[a] With the PM3 geometry. [b] With the RHF/6-31G** geometry.

Phosphine oxide **VII**, by the RHF/6-31G** results, has a conformation in which one of the phenyl rings is eclipsing the phosphoryl bond. The second phenyl ring may form torsion angles of 20–30° with the Ph and P=O groups. These results nicely agree with the experimental data in [2]. The dipole moments calculated by the vector additive scheme with the geometric parameters obtained by quantum-chemical calculations (5.15 D with the PM3 geometry and 5.11 D with the RHF/6-31G** geometry) almost coincide with μ_{exp} (5.20 D [2]). At the same time, the dipole moment resulting from Hartree–Fock calculations is overestimated over experimental by ~1 D.

Unlike the p_π–p_π conjugation of the phosphorus LEP with the benzene ring, similar interaction in the >P–C≡N systems has no steric restrictions. It is interesting to find out whether interactions of the cyano group with the phosphorus LEP or the phosphoryl group contribute into stabilization of preferred conformers of the cyanophosphines in study.

Figure 2 presents the correlation diagram of the energies of higher occupied MOs for preferred conformers of $MeOP(CN)_2$ (*t*), $PhP(CN)_2$ (*c*), $Ph_2P(O)CN$ (g^-c), $(MeO)_2P(O)CN$ (g^+g^-), and hydrogen cyanide. The latter was used as a model molecule, and its geometry was also optimized at the RHF/6-31G** level. The energy field in Fig. 2 is divided into five vertical sections (columns) containing the energy levels of the π(Ph), n_P, $p\pi_O$, and $\pi_{C\equiv N}$ orbitals for the above conformers. In the g^-c structure of phosphine oxide **VII**, the first four MOs (9.63, 9.66, 9.75, and 10.10 eV) are symmetric and antisymmetric combinations of π(Ph). The following two MOs (11.97 and 12.40 eV) are mostly localized on the symmetric and antisymetic (with respect to O=P–CN) components of the $p\pi_O$ orbital. The seventh and eighth MOs (13.28 and 13.34 eV) localized on the $\pi_{C\equiv N}$ orbitals have almost the same energy as the degenerate highest occupied MO of the model molecule H–C≡N (13.30 eV). On replacement of phenyl by methoxy groups, i.e. in the preferred g^+g^- conformer of $(MeO)_2P(O)CN$, stabilization of MOs is observed. The energies of the $p\pi_O$ orbitals decrease to 12.91 and

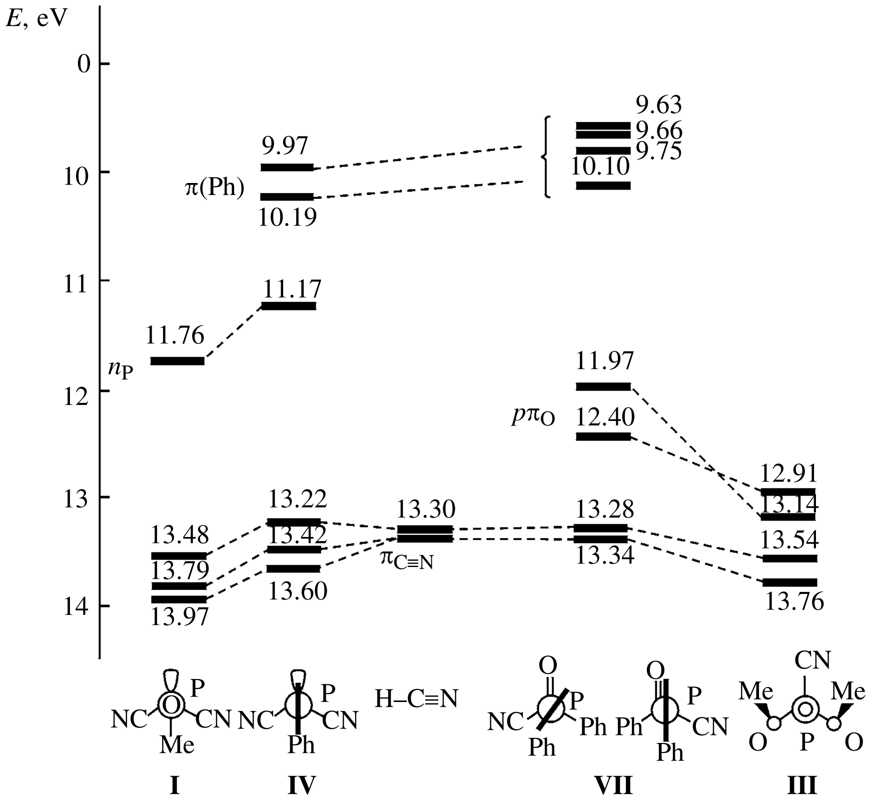

Fig. 2. Correlation diagram of the energies of higher occupied MOs of preferred conformers of **I, III, IV, VII** and HCN.

13.14 eV, and the energies of the $\pi_{\mathrm{C\equiv N}}$ orbitals, to 13.54 and 13.76 eV.

In the preferred *cis* conformer of $\mathrm{PhP(CN)_2}$, the highest two occupied MOs (9.97 and 10.19 eV) are phenyl π orbitals, and the third MO (11.17 eV) is mostly localized on phosphorus LEP orbitals (n_{P}). The two $\pi_{\mathrm{C\equiv N}}$ orbitals form symmetric and antisymmetric combination with respect to the O=P–C≡N plane. The fourth through sixth MOs (13.22, 13.42, and 13.60 eV) which are mostly localized on $\pi_{\mathrm{C\equiv N}}$ are close in energy to the highest occupied MO of the model molecule H–C≡N (13.30 eV). On replacement of the phenyl by methoxy group, i.e. in the preferred *trans* conformer of $\mathrm{MeOP(CN)_2}$, stabilization of MOs is observed. The energy of the n_{P} orbital decreases to 11.76 eV and the energies of $\pi_{\mathrm{C\equiv N}}$ orbitals, to 13.48, 13.79, and 13.97 eV. The $p\pi_{\mathrm{O}}$, being orthogonal to n_{P}, does not contribute into the highest occupied MO.

Note that in the *trans* conformer of $\mathrm{MeOP(CN)_2}$, the MO mostly localized on n_{P} is additionally stabilized by hyperconjugation with $n(\mathrm{P}\text{-}\sigma^*)$ (O–C), which is lacking in $\mathrm{PhP(CN)_2}$. This is also evidenced by the decrease in the effective charge on phosphorus from 1.051 in compound **I** to 0.785 in compound **IV**. Analysis of the energies and compositions of frontier MOs revealed no n_{P}–$\overset{+}{\pi}_{\mathrm{C\equiv N}}$ interactions in $\mathrm{MeOP(CN)_2}$ and $\mathrm{PhP(CN)_2}$ and $p\pi_{\mathrm{O}}$–$\pi_{\mathrm{C\equiv N}}$ interactions in $\mathrm{Ph_2P(O)CN}$ and $\mathrm{(MeO)_2P(O)CN}$. A common feature of the preferred conformer of compounds **I**, **III**, **IV**, and **VII** are weakly populated phosphorus d_{π^*} AOs. This fact implies lack of interactions of these orbitals with symmetry-adopted substituent orbitals. In principle, accumulation of cyano groups (strong σ acceptors) in a molecule would be expected to contract phosphorus *d* orbitals, thus favoring transfer onto them of electron density from benzene rings or cyano groups. Apparently, this possibility is realized in part in $\mathrm{P(CN)_3}$, since, as follows from the electron density distribution in this molecule, estimated semi-empirically by the electronegativity equalization method [3], the phosphorus atom bears a partial negative charge (–0.148) and the cyano group, a positive charge (+0.304). Comparing data in [3] and our present results we can suppose that for phosphorus *d* orbitals in cyano derivatives to assume a shape favoring p_π–d_π interaction, the molecule should contain at least three cyano groups, which is the case in $\mathrm{P(CN)_3}$. The unique structure of this molecule is also manifested in an exceptionally small bond angle at the phosphorus atom (93°) [18]. This phenomenon cannot be explained in terms of reduced volume of the substituents on phosphorus, since in such molecules as $P(C{\equiv}CH)_3$ [24] and $P(C{\equiv}CPh)_3$ [25] the CPC angles have normal values (100–101°) and, therewith, the $P–C_{sp}$ bond in ethynylphosphines (1.75 Å) is even shorter than in $P(CN)_3$ (1.78 Å).

It thus can be concluded that in the phosphorus cyanides studied in the present work, the interaction of cyano groups with phosphorus LEP and *d* orbitals, or with the phosphoryl group contributes nothing into stabilization of preferred conformers. A possible explanation consists in that the cyano group in the P–CN fragment behaves as a σ acceptor and does not exhibit its π-acceptor properties. Evidence for this assumption comes from the photoelectron spectra of cyanophosphines $(CF_3)_nP(CN)_{3-n}$ (n = 0, 1, 2, 3) [26]. The referees concluded that the cyano group is cyanides exhibits exclusively a negative inductive effect similar to the *–I* effect of the trifluoromethyl group: The ionization potential of the phosphorus LEP almost remains almost invariable in going from $P(CN)_3$ to $P(CF_3)_3$ (12.04 and 11.60 eV, respectively). The above assumption allows us to explain the low sensitivity of the polarity and polarizability of the P–CN group to the environment of the phosphorus atom [1, 2]. It is interesting to note that the cyano group acts primarily as a σ-acceptor in compounds like Ar–X–CN (X = S, Se) also, because of the considerable difference in the orbital energetic characteristics of the heteroatom–C≡N system [27]. Most likely, such an energetic incompatibility is also characteristic of the P–C≡N fragment and explained the observed properties of the phosphorus cyanides studied.

The comparative study of quantum-chemical and experimental dipole moments, performed in the present work, shows that one should not fully confide in theoretical estimates. The dipole moments calculated by the RHF/6-31G** method for simple model compounds (trimethylphosphine and its oxide) and more complex molecules (phosphite **II** and phosphonate **III**) are nicely consistent with experiment. At the same time, the dipole moment of dicyanophosphine **I** which, unlike cyanophosphine **II**, has only one methoxy substituent, is not reproduced by theory. The quantum-chemical dipole moments of the other compounds, trimethylphosphine sulfide inclusive, too, fail to fit the experimental values. For practical use of the RHF/6-31G** polarities, one might introduce some scaling factor, since the theoretical dipole moments of compounds **IV**–**VII** and trimethylphosphine are overestimated by 0.6–1.0 D. However, this is prevented by an unexpectedly low (1.0 D lower than experimental) value resulting from the *ab initio* calculation. We believe that the polarities of possible conformers of organophosphorus compounds are best estimated by the vector additive scheme [13] with use of RHF/6-31G**geometric parameters.

Quantum-chemical calculations with full geometry optimization were performed using GAMESS (US) QC package [28].

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