Physical Chemistry

Ab initio investigation of tautomeric stability, molecular structure, and internal rotation of methylphosphonic dicyanide, methoxydicyanophosphine, and their isocyano analogs

L. S. Khaikin,[a] E. A. Zhilinskaya,[b] O. E. Grikina,[a] and L. V. Vilkov[a]*

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, Vorob'evy Gory, 119899 Moscow, Russian Federation. Fax: +7 (095) 939 0283*

[b] *Laboratoire de Physico-Chimie de l'Atmosphere, Centre d'Etudes et de Recherche Laser et Applications (CERLA), Universite du Littoral, F-59379 Dunkerque Cedex 1, France. Fax: (33) 28 23 7010*

The equilibrium geometric parameters and structures of the transition states of internal rotation for $MeP(O)(CN)_2$, $MeOP(CN)_2$, and their isocyano analogs, $MeP(O)(NC)_2$ and $MeOP(NC)_2$, have been calculated by the *ab initio* SCF method and with inclusion of electron correlation effects according to the second-order Müller—Plesset perturbation theory (MP2). At both levels the 6-31G* basis set has been used. The estimation of relative stability of these tautomeric forms depends largely on the calculation level. The total energies of the cyanides calculated by the MP2 method are 25—30 kcal mol^{-1} lower than those of the corresponding isocyanides. The oxo-tautomeric forms containing four-coordinate phosphorus are 15—25 kcal mol^{-1} more stable than the three-coordinate phosphorus aci-derivatives. The internal rotation potential curves of the aci-forms are characterized by a deep minimum for the *trans*-arrangement of the methoxy group and phosphorus lone electron pair. Two additional less clearly pronounced minima are located symmetrically on both sides of the weak maximum, which corresponds to the *cis*-arrangement. The equilibrium oxo-form structures have a staggered configuration of the methyl group with respect to the phosphorus atom bonds.

Key words: *ab initio* calculations; methylphosphonic dicyanide, methoxydicyanophosphine, methylphosphonic diisocyanide, methoxydiisocyanophosphine; relative stability of isomers, molecular structure, internal rotation.

The objects of our investigation — methylphosphonic dicyanide, $MeP(O)(CN)_2$ (**1**), methoxydicyanophosphine, $MeOP(CN)_2$ (**2**), and their isocyano analogs, $MeP(O)(NC)_2$ (**3**) and $MeOP(NC)_2$ (**4**) — are the most symmetrical of all the structural isomers of the ten-atomic $C_3H_3N_2OP$ system. For these compounds, four different tautomeric equilibriums are possible: between cyanides and isocyanides, and between phosphoryl oxo-forms and

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acidic aci-forms containing three-coordinate phosphorus (Fig. 1). The estimations of relative energies, which characterize thermodynamic stability of the tautomeric forms, and patterns in their molecular structure are important both from theoretical and practical points of view, since these rearrangements play an essential role in phosphorus chemistry.[1–4]

Stable isocyanides of the second-row elements (C, N, F) are rather rare, which is generally explained[5] by their rapid isomerization into the corresponding cyanides. But on going to the third-row element derivatives (Si, P, Cl), the energy difference between cyanides and isocyanides should considerably decrease according to *ab initio* post-Hartree—Fock calculations.[5–7]

Both oxo- and aci-tautomers of unsubstituted phosphinous acid ($H_3P{=}O$ and H_2POH) are unstable substances, which complicates their investigation. The data obtained by the IR matrix-isolation spectroscopy may indicate that the molecular structure of H_2POH is energetically more stable.[8–12] The *ab initio* calculations of $H_3P{=}O$ and H_2POH carried out both by the SCF method and with inclusion of electron correlation[13–24] leave no doubt that the aci-form H_2POH is more stable indeed (by 2—3 kcal mol^{-1} according to the best calculation estimates[21–24]). At the same time, it is well-known[2] that in the solutions of phosphinous acid derivatives oxo- rather than aci-forms usually prevail. Experimental studies of such equilibriums in the gaseous phase are rather scarce, and their results cannot always be interpreted unambigously.

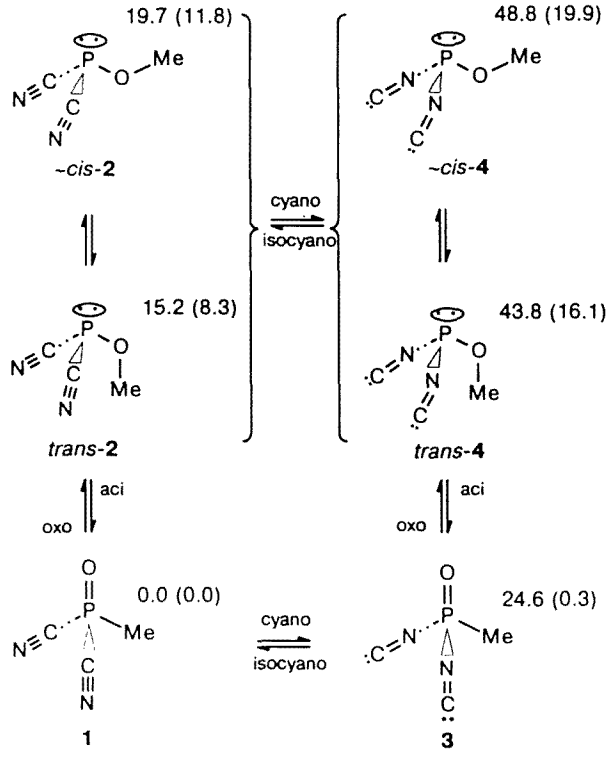

Fig. 1. Relative energies (in kcal mol^{-1}) of the structural and rotational isomers **1**—**4** calculated by the MP2 and RHF methods with the 6-31G* basis sets. The RHF energies are given in brackets.

The problem of conformational equilibrium for internal rotation about the P—O bond in $MeOPX_2$ molecules, to which the aci-forms **2** and **4** belong, are of great interest. A number of publications reported experimental data obtained in the gaseous phase for $MeOPF_2$,[25–27] $MeOPCl_2$,[28–29] and $MeOPMe_2$.[30] In the case of methoxydifluorophosphine, *ab initio* calculations with the 3-21G* and 6-31G** basis sets, including those that consider electron correlation, were also performed,[31] and Hartree—Fock calculations using the 3-21G* and 6-31G* basis sets were carried out for $MeOPMe_2$.[32] For the F- and Cl-substituted methoxyphosphines, it was established from the analysis of their microwave[25] and vibrational[26,28] spectra, and the electron diffraction data,[27,29] that under normal conditions the conformations with *trans*-arrangement of the O—Me bond with respect to the phosphorus lone electron pair prevail in the gaseous phase. At the same time, the presence of a second conformer is not excluded for $MeOPF_2$. *Ab initio* calculations[31] predict that the total energy for the *trans*-conformation of $MeOPF_2$ is 4.7 kcal mol^{-1} lower than for the *cis*-form. However, in the case of $MeOPMe_2$, the results of both the analysis of vibrational spectra[30] and the calculations[32] testify that under normal conditions the abundance of the *trans*-conformer in the gaseous phase is relatively low (although its presence in the liquid and solid phases succesively increases), and the conformation with near-*cis*-orientation of the methyl group is more stable. In the *cis*-configuration itself, the energy increases by only 0.03 kcal mol^{-1}, and thus, in the region of the prevailing conformation, the potential function of internal rotation about the P—O bond has a vast sloping part, where a large-amplitude torsional motion is possible. As the calculations[32] showed, the *trans*-conformer is 1.6 kcal mol^{-1} higher in energy than the prevailing conformation, and the barrier height for the passage to the latter, which characterizes kinetic stability of the *trans*-form, is 3.2 kcal mol^{-1}.

According to the IR matrix-isolation spectroscopy data,[8–12] unsubstituted phosphinous acid H_2POH exists in two conformations (*cis*- and *trans*-), the *trans*-conformer being hypothetically a little more stable. In agreement with the experiment, the calculations[24] show that the energy of the *trans*-conformation of H_2POH is only *ca.* 0.2 kcal mol^{-1} lower than that of the *cis*-conformation. The theoretical estimation[16–18] of the barrier height for mutual conversions between almost isoenergetic *trans*- and *cis*-forms of H_2POH gave the value of *ca.* 4 kcal mol^{-1} at the MP3/6-31G**//3-21G* level.

The stability of the observed conformations of quite a large range of compounds, in which adjacent atoms have lone electron pairs or polar bonds, corresponds to the empirical rules called the *gauche*-effect and the anomeric

Table 1. *Ab initio* optimized structures of the equilibrium (ES) and internal rotation transition (TS) states for $MeP(O)(CN)_2$ (**1**) and $MeP(O)(NC)_2$ (**3**)

Parameter	RHF/6-31G*				MP2=FULL/6-31G* [a]			
	1		**3**		**1**		**3**	
	ES	TS	ES	TS	ES	TS	ES	TS
Bond length, *r*/Å:								
P=O	1.4512	1.4516	1.4450	1.4452	1.4880	1.4884	1.4764	1.4766
P—C (P—N)	1.7966	1.7971	1.6757	1.6767	1.7889	1.7888	1.6967	1.6975
C≡N (N=C:)	1.1350	1.1351	1.1639	1.1638	1.1842	1.1842	1.1959	1.1959
P—CH_3	1.7973	1.8110	1.7915	1.8049	1.7961	1.8087	1.7873	1.7992
C—H	1.0834	1.0834	1.0825	1.0827	1.0927	1.0928	1.0911	1.0916
C—H′	1.0837	1.0826	1.0835	1.0822	1.0926	1.0917	1.0920	1.0909
Bond angle, φ/deg:								
C—P—C (N—P—N)	99.82	99.35	100.31	99.80	99.20	98.62	98.50	97.85
H_3C—P—C (H_3C—P—N)	103.74	104.56	104.01	104.78	103.22	103.96	103.19	103.94
C—P=O (N—P=O)	114.42	114.18	114.39	114.16	115.03	114.92	115.02	114.82
H_3C—P=O	118.41	117.88	117.66	117.22	118.59	118.02	119.15	118.77
P—C≡N (P—N=C:)	177.95	178.00	175.77	175.67	177.21	177.58	175.82	175.69
P—C—H	111.34	107.02	111.20	107.71	110.89	107.04	110.65	107.71
P—C—H′	108.70	111.07	108.82	110.77	108.77	110.95	108.76	110.44
Dihedral angle, τ/deg:								
H—C—P=O	180.0	0.0	180.0	0.0	180.0	0.0	180.0	0.0
H′—C—P=O	±59.16	±119.19	±59.18	±119.42	±59.30	±119.10	±59.32	±119.44
O=P—C≡N (O=P—N=C:)	±98.35	±100.12	±20.97	±11.59	±52.46	±50.15	±27.40	±24.11
Total energy,								
$-(E + 639)$/au	0.821338	0.817712	0.820832	0.817055	1.844715	1.841067	1.805465	1.801810

[a] All the electrons are included in the correlation energy calculation.

effect (see, *e.g.*, Refs. 33 and 34). However, the above mentioned differences in conformational behavior during internal rotation about the P—O bond cannot be unambigously explained, and therefore predicted *a priori* from these rules.

The *ab initio* calculations of the molecules **1**—**4** that we carried out give some additional information about tautomeric and conformational stability of the compounds in question. The calculations were performed using the GAUSSIAN-92 series of programs[35] on an HP735 work station at the Universite du Littoral (Dunkerque, France). The geometry optimization of the equilibrium molecular forms and transition states of internal rotation was carried out by the restricted Hartree—Fock method (RHF) and with inclusion of electron correlation effects according to the second-order Møller—Plesset perturbation theory (MP2) with the standard 6-31G* basis set. To characterize the stationary points of the internal rotation curves, the calculated normal-mode vibrational frequencies were also used.

The optimized geometric parameters and total energies (in au) for the oxo-forms **1** and **3** are shown in Table 1, and for the aci-forms **2** and **4** in Tables 2 and 3. The relative energies (in kcal mol^{-1}) between the equilibrium forms are given in Fig. 1.

The potential functions and barriers to internal rotation about the P—O bonds, in the aci-forms, and the barriers of rotation about the P—Me bonds in the oxo-forms also have been obtained. The potential curves shown in Fig. 2 were calculated by the MP2 method with complete optimization of geometric parameters except for the Me—O—P—E dihedral angle, the value of which has been fixed with the step of 30° (the E point in the symmetry plane of the $O—PX_2$ fragment characterizes a conditional arrangement of the phosphorus lone electron pair). The calculated energy values for the equilibrium and transition states have been used as well.

Results and Discussion

Cyanide ⇌ isocyanide isomerizations. The results of our calculations show that cyanides are more stable in comparison with isocyanides both in the **1** ⇌ **3** system with four-coordinate phosphorus and in the **2** ⇌ **4** one with three-coordinate phosphorus. In Table 4, these data are compared with those published earlier.

Up to the present, both theoretical and experimental investigations of cyanide ⇌ isocyanide rearrangements have been known only for a limited range of chemical systems. The best studied of them are the CHN and C_2H_3N systems, for which it is possible to compare the results of quite high-level calculations with the experimental data (see Table 4). Experimental methods give a rather large scatter in the estimates of the energy difference between the isomeric forms of the parent CHN system (see also the book by W. J. Hehre *et al.*[36]).

The best of the *ab initio* methods used by the authors of the recent publication[5] to calculate the CHN

Table 2. *Ab initio* optimized structures of the equilibrium (ES) and internal rotation transition (TS) states for $MeOP(CN)_2$ (2)

Parameter	RHF/6-31G*				MP2=FULL/6-31G* [a]			
	TS1 (C_s)	ES1 (C_1)	TS2 (C_1)	ES2 (C_s)	TS1 (C_s)	ES1 (C_1)	TS2 (C_1)	ES2 (C_s)
Bond length, r/Å:								
P—O	1.6090	1.6087	1.6089	1.5948	1.6472	1.6477	1.6481	1.6303
P—C	1.8045	1.8000	1.8087	1.8170	1.7923	1.7867	1.7972	1.8054
	1.8045	1.8111	1.8167	1.8170	1.7923	1.8021	1.8033	1.8054
C≡N	1.1361	1.1359	1.1361	1.1365	1.1844	1.1840	1.1845	1.1846
	1.1361	1.1364	1.1366	1.1365	1.1844	1.1847	1.1847	1.1846
$O—CH_3$	1.4241	1.4230	1.4214	1.4246	1.4484	1.4467	1.4418	1.4464
C—H	1.0777	1.0778	1.0778	1.0778	1.0881	1.0880	1.0881	1.0880
C—H′	1.0821	1.0819	1.0808	1.0813	1.0924	1.0927	1.0921	1.0926
C—H″	1.0821	1.0829	1.0827	1.0813	1.0924	1.0935	1.0934	1.0926
Bond angle, φ/deg:								
C—P—C	96.14	96.20	95.26	94.87	95.39	95.54	94.32	93.86
O—P—C	99.99	98.33	99.11	102.05	99.68	97.04	98.96	101.84
	99.99	101.35	102.46	102.05	99.68	101.68	102.58	101.84
$P—O—CH_3$	119.76	119.93	126.24	126.54	115.68	115.43	121.48	121.63
P—C≡N	173.97	174.10	174.11	174.78	172.76	172.90	172.40	173.56
	173.97	173.63	173.78	174.78	172.76	171.86	172.19	173.56
O—C—H	106.06	106.31	105.98	106.23	105.12	105.49	105.21	105.69
O—C—H′	110.74	110.22	110.38	110.12	111.00	110.36	110.67	110.07
O—C—H″	110.74	110.92	110.84	110.12	111.00	111.18	111.12	110.07
Dihedral angle, τ/deg:								
$H_3C—O—P—E$ [b]	0.0	26.39	99.91	180.0	0.0	35.00	102.60	180.0
N≡C—P—O	−117.28	−122.65	−117.32	−105.15	−115.16	−121.78	−112.54	−99.75
	117.28	110.34	109.93	105.15	115.16	105.35	108.25	99.75
P—O—C—H	180.0	−164.29	−173.86	180.0	180.0	−166.62	−177.10	180.0
P—O—C—H′	61.09	76.98	67.03	60.88	61.38	74.98	63.95	60.87
P—O—C—H″	−61.09	−45.01	−55.01	−60.88	−61.38	−47.50	−58.47	−60.87
Total energy, $-(E + 639)$/au	0.802335	0.802526	0.798890	0.808084	1.813085	1.813405	1.809895	1.820580

[a] See footnote [a] to Table 1. [b] E denotes the position of the phosphorus lone electron pair.

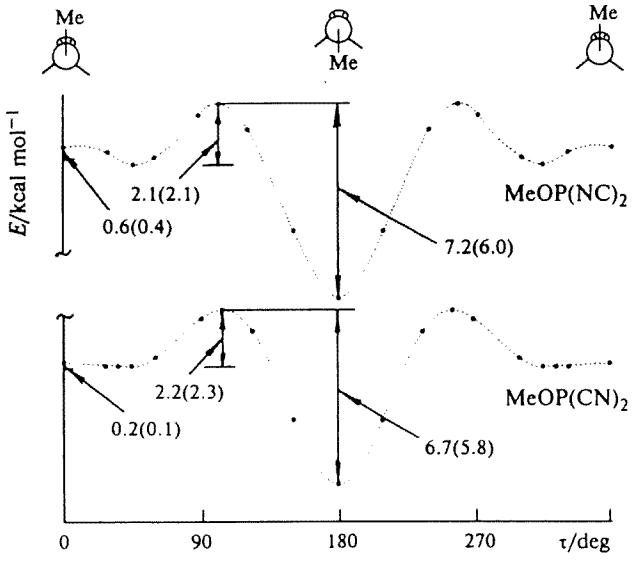

Fig. 2. Potential curves for internal rotation about the P—O bonds in $MeOP(CN)_2$ (**2**) and $MeOP(NC)_2$ (**4**) and barrier heights for their *trans*- and near-*cis*-forms calculated at the MP2/6-31G* level taking into account the geometry relaxation effects. The RHF/6-31G* barrier values are given in brackets.

system (CISDQ) reproduces well the value of 14.8±2.0 kcal mol^{-1}, which was experimentally obtained from the data of the ion-cyclotron resonance spectroscopy.[39] The results of the CCSD(T) calculations[41,42] carried out with various basis sets also agree with the experimental value. According to these results, the isocyanide HNC is 14.4±1.0 kcal mol^{-1} higher in energy than the cyanide HCN. Apparently, the MP2 calculations,[5] which were performed for three different cyanide ⇌ isocyanide rearrangements, systematically overestimate energy differences by 3—5 kcal mol^{-1}. The RHF estimates are of a more random nature. The analysis of the calculation data[5] also shows that the reliability of the estimates of energy differences between cyano- and isocyano-isomers is determined to a larger extent by the selected calculation method rather than by the completeness of the basis set used and by the chosen molecular geometry.

Therefore, the results of our MP2/6-31G* calculations (see Table 4) can be considered the upper limits (with possible decrease by no more than 5 kcal mol^{-1}) of the energy changes in going from cyanides to less stable isocyanides. The comparison of these data with the RHF ones demonstrates the importance of including the electron correlation in such calculations. The collation of the total energies for the equilibrium forms of the molecules

Table 3. *Ab initio* optimized structures of the equilibrium (ES) and internal rotation transition (TS) states for $MeOP(NC)_2$ (**4**)

Parameter	RHF/6-31G*				MP2=FULL/6-31G* [a]			
	TS1 (C_s)	ES1 (C_1)	TS2 (C_1)	ES2 (C_s)	TS1 (C_s)	ES1 (C_1)	TS2 (C_1)	ES2 (C_s)
Bond length, *r*/Å:								
P—O	1.6026	1.6030	1.6014	1.5875	1.6292	1.6306	1.6282	1.6121
P—N	1.7007	1.6931	1.7030	1.7154	1.7166	1.7075	1.7202	1.7327
	1.7007	1.7111	1.7158	1.7154	1.7166	1.7300	1.7318	1.7327
N=C:	1.1626	1.1627	1.1630	1.1629	1.1962	1.1960	1.1966	1.1964
	1.1626	1.1629	1.1632	1.1629	1.1962	1.1968	1.1967	1.1964
O—CH_3	1.4206	1.4189	1.4182	1.4224	1.4500	1.4475	1.4438	1.4496
C—H	1.0780	1.0781	1.0781	1.0780	1.0875	1.0875	1.0875	1.0873
C—H′	1.0824	1.0822	1.0802	1.0806	1.0919	1.0921	1.0904	1.0910
C—H″	1.0824	1.0837	1.0828	1.0806	1.0919	1.0938	1.0927	1.0910
Bond angle, φ/deg:								
N—P—N	97.07	97.54	97.15	95.96	95.23	96.08	95.44	93.87
O—P—N	99.35	97.22	98.56	101.24	98.83	95.85	98.15	101.06
	99.35	100.80	101.21	101.24	98.83	100.74	101.09	101.06
P—O—CH_3	120.06	119.86	126.90	126.80	116.58	115.82	123.26	122.74
P—N=C:	171.81	171.65	170.46	170.53	171.30	171.58	170.64	172.09
	171.81	170.88	170.30	170.53	171.30	170.02	171.22	172.09
O—C—H	106.25	106.59	106.12	106.26	105.12	105.68	105.15	105.52
O—C—H′	110.92	110.25	110.41	110.18	110.93	109.91	110.42	109.81
O—C—H″	110.92	111.10	111.00	110.18	110.93	111.26	110.95	109.81
Dihedral angle, τ/deg;								
H_3C—O—P—E[b]	0.0	38.49	99.29	180.0	0.0	44.62	100.79	180.0
:C=N—P—O	−125.38	−125.84	−117.78	−123.52	−119.23	−126.17	−114.72	−105.12
	125.38	119.91	131.32	123.52	119.23	103.82	109.48	105.12
P—O—C—H	180.0	−164.03	−172.50	180.0	180.0	−164.19	−176.89	180.0
P—O—C—H′	61.10	77.17	68.37	60.87	61.41	77.24	64.09	60.85
P—O—C—H″	−61.10	−44.75	−53.65	−60.87	−61.41	−45.02	−58.23	−60.85
Total energy,								
−(*E* + 639)/au	0.788924	0.789574	0.786266	0.795765	1.766007	1.766890	1.763481	1.774990

[a,b] See footnotes[a,b] to Table 2.

1—**4** calculated by these two methods (see Tables 1—3), shows that the contribution of electron correlation to the structure stabilization is larger in the cyanides compared with the isocyanide forms. The authors of Ref. 43 came to an analogous conclusion in analysing the calculation results for the $H_2NCN \rightleftharpoons H_2NNC$ and $HCN \rightleftharpoons HNC$ isomerizations.

As was already noted, the relative stability of cyano- and isocyano-isomers depends on the influence of the chemical nature of the substituent. The earlier *ab initio* calculations predicted the total energy increases by *ca.* 45 kcal mol^{-1} for H_2NNC compared to H_2NCN,[5,43] and by *ca.* 70 kcal mol^{-1} for FNC compared to FCN.[7,37] This substantially exceeds the energy differences in the CHN and C_2H_3N systems with less electronegative substituents (*ca.* 15[5,36] and *ca.* 25[36] kcal mol^{-1}, respectively). A similar effect is also observed in the case of substituents containing the third-row elements (*e.g.*, SiH_3, PH_2, and Cl). However, the izomerization energies in such systems are much lower (*ca.* 8,[6] *ca.* 16,[5] and 35[7] kcal mol^{-1}, respectively) than in the case of substituents with the second-row elements.

Both these tendencies are confirmed by our calculations as well (see Table 4). Thus, the isocyanide $MeOP(NC)_2$ must show higher relative stability than H_2NNC, and approximately the same as MeNC. Although the MP2 method gives an increase in isomerization energy for the **1** $\rightleftharpoons$ **3** and **2** $\rightleftharpoons$ **4** systems in comparison with the corresponding energy difference[5] for the $H_2PCN \rightleftharpoons H_2PNC$ system, it should be taken into account that each of the molecules we investigate contains two isomerizing CN groups. It is significant that the isomerization energy in the four-coordinate phosphorus system $MeP(O)(CN)_2 \rightleftharpoons MeP(O)(NC)_2$ is smaller than that in the $MeOP(CN)_2 \rightleftharpoons MeOP(NC)_2$ system containing three-coordinate phosphorus.

Oxo- and aci-form isomerization. The performed calculations show that the **1** $\rightleftharpoons$ **2** and **3** $\rightleftharpoons$ **4** equilibriums for methyldicyano and methyldiisocyano derivatives of phosphinous acid are very similar from the point of view of the relative energy of the tautomers, and differ significantly from the equilibrium for the unsubstituted acid (Table 5). The considered substitutions lead to the inversion of relative stability of oxo- and aci-forms. In the MP2/6-31G* approximation, the total energies of the more stable oxo-forms **1** and **3** are 15—25 kcal mol^{-1} lower than the energies of the aci-forms **2** and **4**, while in the case of the $H_3P{=}O \rightleftharpoons H_2POH$ isomerization the

Table 4. Theoretical and experimental estimates of energy change (ΔE/kcal mol^{-1}) with the isomerization from cyano to isocyanoform[a]

System	ΔE calculation[b]						Experiment[h]
	RHF[c]	MP2[d]	MP3, MP4[e]	CISD[f]	CISDQ[f]	CEPA-1[g]	
HCN ⇌ HNC	12.4[36]	17.7—18.6[5]	13.9—16.0[5]	12.9—13.7[5]	14.0—14.8[5]		10.3[38], 14.8 (2.0)[39]
MeCN ⇌ MeNC	20.8[36]	27.4[36]	24.6—24.9[36]				23.7 (0.1)[40]
H_2NCN ⇌ H_2NNC	43.6—44.1[5]	47.7—49.1[5]	44.2—44.8[5]				
FCN ⇌ FNC	63.6[7]					69.5[37]	
H_3SiCN ⇌ H_3SiNC	−1.5[6]	7.8[6]					
$MeP(O)(CN)_2$ ⇌ $MeP(O)(NC)_2$	0.3	24.6					
H_2PCN ⇌ H_2PNC	11.5—19.9[5]	19.9—21.2[5]	16.3—17.9[5]				
$MeOP(CN)_2$ ⇌ $MeOP(NC)_2$							
trans-	7.7	28.6					
-cis-	8.1	29.2					
ClCN ⇌ ClNC	33.5[7]						

[a] The ΔE values that do not have any references were obtained in this work.

[b] RHF — spin-restricted Hartree—Fock method; MP*n* — *n*-order Møller—Plesset perturbation theory; CI and CC — methods of configuration interaction and coupled clusters (S, D, T, and Q symbols denote inclusion of single, double, triple, and quadruple excitations respectively); CEPA — coupled electron pair approximation.

[c] The calculations[5] were carried out with the 6-31G* and 6-31G** basis sets; the calculations[6] were performed using for Si/C, N/H atoms the (11s7p1d/9s5p1d/4s1p)/[6s4p1d/3s2p1d/2s1p] double-zeta basis set augmented by adding polarization functions; in the case of the CFN and CClN systems the (11s7p)/[6s3p] and (12s9p1d/9s5p)/[8s5p1d/6s3p] basis sets for Cl/C, N atoms respectively, were used[7]; in the calculations,[36] the improved energies were calculated as single points with the 6-31G* basis set and 3-21G optimized geometries.

[d] In the calculations,[5] four different approximations were used (ranging from the MP2/6-311++G**//MP2/6-311G** up to the MP2/6-311++G(2df,2pd)//MP2/6-311G** one) for the CHN system, and the same amount (ranging from the MP2/6-31G*//6-31G* up to the MP2/6-311++G**//MP2/6-311G** one) for the CH_2N_2 and CH_2NP systems; the energy refinements[6] were fulfilled by single point calculations with the (13s9p1d/10s6p1d/5s1p)/[6s4p1d/5s3p1d/3s1p] basis set for Si/C, N/H atoms using the geometries optimized by the RHF method; the calculations[36] were carried out in the MP2/6-31G**//3-21G approximation.

[e] In the four approximations of energy refinement[5] (ranging from the MP3/6-311++G** single point calculation up to the MP4(SDTQ)/6-311++G** one), the geometry optimized at the MP2/6-311G** level was used; the single point calculations[36] were fulfilled at the MP3/6-31G* and MP4(SDQ)/6-31G* levels for the geometries optimized with the 3-21G basis set.

[f] The energies of the CHN, CH_2N_2 and CH_2NP systems are improved[5] using the CISD and CISDQ methods with the 6-311++G** basis set, and with three more even larger basis sets, up to the 6-311++G(2df, 2pd) one, in the case of the CHN system; all the calculations used the geometries optimized at the MP2/6-31G** level.

[g] The CEPA calculations[37] are carried out using the (11s6p2d1f)/[8s4p2d1f] basis set.

[h] Obtained from the analysis of temperature dependence of band intensities in high resolution IR spectra,[38] by the ion-cyclotron resonance spectroscopy[39] and from studying a controlled thermic explosion in a calorimeter at 300 K.[40]

calculated oxo-form is 2—3 kcal mol^{-1} higher in energy.[23,24] The relative stability of the cyanide aci-form **2** is higher than that of the isocyanide aci-form **4** (see Fig. 1).

For methyldifluoro derivative of phosphinous acid a rough comparison between the total Hartree—Fock energies of the $MeP(O)F_2$ oxo-form (the 6-31G* basis set)[44] and the $MeOPF_2$ aci-form (the 6-31G** basis set)[31] is possible. This comparison shows about the same decrease in the oxo-form energy with respect to that of the aci-form (18—22 kcal mol^{-1}), as in the case of the **3** ⇌ **4** system.

The calculated energy differences between tautomers in the H_3OP system[23,24] depend insignificantly on the level of inclusion of electron correlation and change within a small interval of *ca.* 5 kcal mol^{-1}. Apparently, in this case, the energy change is overestimated by the MP2 method (considering its sign), similar to the calculations for the cyanide ⇌ isocyanide rearrangements (see Table 4). Weak influence of the geometric parameters used is confirmed by the comparison of the MP2/6-311G** and MP2/6-311G**//MP2/6-31G** energy changes, which differ by only 0.2 kcal mol^{-1} (see Refs. 23, 24). Therefore, the data of our MP2 calculations given in Table 5 can be considered the upper limits of the estimates of energy increases on going from oxo- to aci-form in the **1** ⇌ **2** and **3** ⇌ **4** systems (with a possible overestimation of not more than 5 kcal mol^{-1}).

Internal rotation. Energy differences for isodesmic processes, to which internal rotation belongs, are usually reproduced even by Hartree—Fock calculations satisfactorily, because of a rather small change of electron correlation contributions.[36] This is illustrated by the data of Table 6, in which the estimates of the total energy differences between the equilibrium *trans-* and near-*cis*-conformations of **2** and **4** are compared with the results of calculations for the related molecules.

The estimates of relative energies obtained by the MP2 method, taking into account the electron correlation, practically do not change in calculations at a substantially higher level, which indicates their good precision.

Table 5. Theoretical and experimental estimates of energy change (ΔE/kcal mol^{-1}) with the isomerization from oxo- to aci-form[a]

System	ΔE calculation[b]						Experiment[c]
	RHF	MP2	MP3	MP4 (SDQ)	MP4 (SDTQ)	CISD	
$H_3P{=}O \rightleftharpoons H_2POH$ [23,24]							
trans-	−7.6	−2.5	−7.7	−5.0	−3.1	−6.7	>−5 [9,10]
cis-	−6.9	−2.2	−7.3	−4.3	−2.9	−6.3	
$MeP(O)(CN)_2 \rightleftharpoons MeOP(CN)_2$							
trans-	8.3	15.2					
cis-	11.8	19.7					
$MeP(O)(NC)_2 \rightleftharpoons MeOP(NC)_2$							
trans-	15.7	19.1					
cis-	19.6	24.2					

[a,b] See footnotes[a,b] to Table 4. For the H_3OP system, RHF calculations[23,24] with the 6-31G** basis set, and MP2 calculations with the 6-311G** one were carried out; the other methods were employed to calculate the improved energies as single points with the 6-311G** basis set and with the use of the MP2/6-31G** optimized geometry.

[c] Obtained by the IR matrix-isolation spectroscopy for the products of gas-phase reaction and red visible photolysis in solid Ar.[9,10]

Table 6. Theoretical estimates of energy change (ΔE/kcal mol^{-1}) with the passage from *trans-* to *cis-* (or near-*cis-*) conformation[a]

Molecule	ΔE calculation[b]					
	RHF	MP2	MP3	MP4 (SDQ)	MP4 (SDTQ)	CISD
H_2POH [23,24]	0.7	0.2	0.4	0.3	0.2	0.4
$MeOP(Me)_2$[32]	−1.6					
$MeOP(CN)_2$	3.5	4.5				
$MeOP(NC)_2$	3.9	5.1				
$MeOPF_2$ [31]	4.4	4.7			4.7	

[a,b] See footnotes[a,b] to Tables 4 and 5. The calculations[32] were carried out in the RHF/6-31G* approximation. In the case of $MeOPF_2$,[31] the RHF calculations were fulfilled with the 6-31G** basis set, and the resulting geometry was further used for energy refinement at the MP2/6-31G** and MP4(SDTQ)/6-31G** levels.

From the data in Table 6 it follows that, although for the majority of the molecules studied the *trans*-conformation is more stable, the relative energies of *cis-* (near-*cis-*) forms can change significantly. Apparently, it partially depends on the polarity of bonds between the P atom and the substituents. In particular, the decrease of relative stability corresponds to the higher polarity (as shown below) of the P—N bonds in **4** compared to the P—C bonds in **2**. The prevalence of *trans*-conformation during the rotation about the P—O bond in the case of two polar bonds between the P atom and the substituents is in accordance with the notions of the *gauche-* and anomeric effects.[33,34] This conformation provides an optimal arrangement for each of the two P—C polar bonds in **2** or the P—N bonds in **4** relative to the two oxygen lone electron pairs: the *gauche*-arrangement with respect to one of the pairs, and the *trans*-configuration to the other.

The potential curves for internal rotation about the P—O bond in **2** and **4** calculated in the MP2/6-31G* approximation are very similar in shape (see Fig. 2). They are characterized by a deep minimum corresponding to the *trans*-arrangement of the methoxy group and phosphorus lone electron pair with the transition barrier of *ca.* 7 kcal mol^{-1}. The two less deep minima separated from the *trans*-form by the barriers of *ca.* 2 kcal mol^{-1}, are located symmetrically on both sides of the weak maximum corresponding to the transition *cis*-form. The barrier height in the *cis*-form is lower than 0.5 kcal mol^{-1}, and, therefore, a large-amplitude torsional motion in a wide range of the angles of rotation around the *cis*-form is possible. The potential curves have been calculated with full optimization of all the geometric parameters, except for the discretely fixed values of the internal rotation angle. Such an approach makes it possible to obtain in a relatively simple way the physically significant potential functions, which consider the effects of geometry relaxation during internal rotation (and, consequently, to a sufficient extent the contributions of torsional motion — normal mode interactions[45]). As was shown earlier,[45] the consideration of geometry relaxation is essential for proper determination of the shape of potential functions and barrier heights.

During the internal rotation of the methyl groups in **1** and **3** the stable conformation is the staggered one (the H—C—P=O dihedral angle is equal to 180°, see Table 1). According to the Hartree—Fock calculations with the 6-31G* basis set, the barrier height in the transition eclipsed configuration (the H—C—P=O angle is equal to

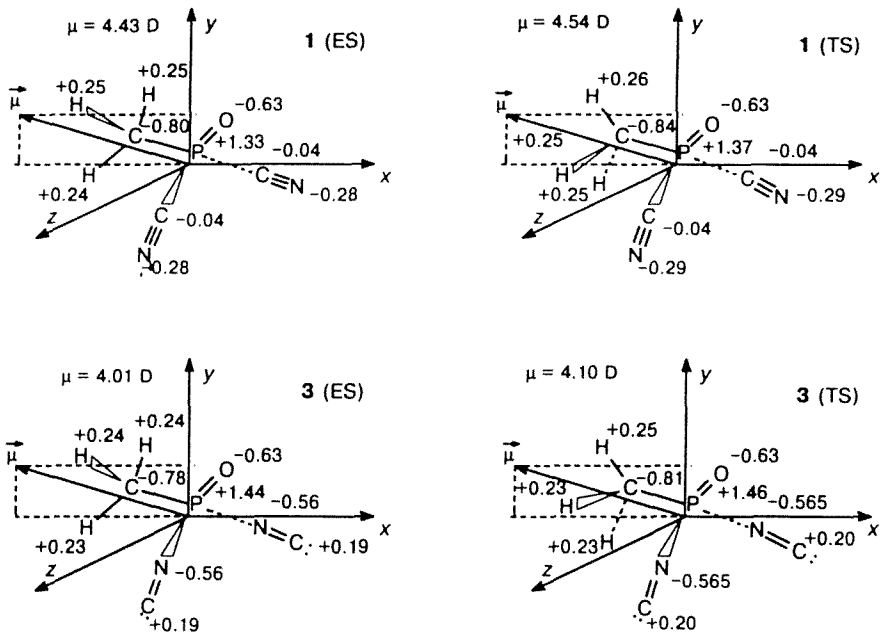

Fig. 3. RHF/6-31G* Mulliken atomic charges and electric dipole moments for the equilibrium (ES) and internal rotation transition (TS) states of $MeP(O)(CN)_2$ (**1**) and $MeP(O)(NC)_2$ (**3**) (see Table 1).

0°) is 2.3 and 2.4 kcal mol^{-1} for the molecules **1** and **3**, respectively. The inclusion of electron correlation at the MP2/6-31G* level does not change the estimates of this parameter (2.3 kcal mol^{-1} for both molecules). The RHF/6-31G* calculations show that the staggered conformation is stable for the $MeP(O)F_2$ and $MeP(S)F_2$ molecules as well, their rotational barriers being a little lower (1.9 and 2.1 kcal mol^{-1}, respectively).[44] The latter values, however, differ considerably from the experimental barriers obtained for the same molecules from the analyisis of microwave spectra (3.5—3.8 kcal mol^{-1}).[46—49] To find out the reasons for these distinctions, a special analysis should be undertaken.

Mulliken charge distributions on atoms and electric dipole moments. The theoretical prediction of Mulliken charge distribution on atoms and the dipole moment of a molecule, as well as of their changes with isomerization and internal rotation, may be essential for discussing chemical properties. For the molecules **1—4** such data derived from our RHF/6-31G* calculations are given in Figs. 3 and 4.

Since there is no unambigous theoretical definition of the notion of atomic charge, only the comparison between the calculated and experimental dipole moments makes it possible to estimate the capacity of the calculation method used to describe charge distribution in the molecule. To date there are no experimental data for the molecules **1—4**. However, it is well-known that the dipole moments calculated using the RHF/6-31G* optimized geometry are usually larger than the experimental values by 0.4—0.6 D,[22,36,44] except for the very polar systems. Our estimates of the dipole moments of the molecules **1—4** (2—6 D) exceed possible calculation errors by several times, and therefore not only the scalar magnitudes but also the obtained directions of the dipole moments seem to be rather realistic.

As can be seen from Figs. 3 and 4, the phosphorus atom in the molecules **1—4** has a large positive charge, which increases in going from the cyanides to the isocyanides. The negative charges of nitrogen atoms in the isocyanides become twice as large as in the cyanides. Carbon atoms are practically neutral in the cyano-substituents and have a small positive charge in the isocyano groups. Thus, the P—N bonds in **3** and **4** are essentially more polar than the P—C ones in the cyanides **1** and **2**. The change in charges of the rest of the atoms is minimal after such isomerization. The dipole moments of the cyanides are 0.5 to 1.5 D larger than those of the corresponding isocyanides.

The passage from oxo- to aci-forms causes a noticeable change in charges on the P, O and methyl C atoms. The positive charge of the phosphorus atom in the oxo-tautomers **1** and **3** is larger than in the molecules **2** and **4**. During the internal rotation about the P—O bond in the aci-forms **2** and **4** a small increase in phosphorus atom charge can be noticed on going from *cis*- to *trans*-conformations.

The negative charge of the oxygen atom in the oxo-forms **1** and **3** does not increase but somewhat decrease compared to the aci-forms **2** and **4**. This is of interest from the point of view of the possible nature of the phosphoryl bond, which has already been discussed for

several decades (*e.g.*, see Refs. 1, 13—17). The electronic structure of the phosphoryl group is described by the superposition of the ordinary semi-polar $P^+—O^-$ bond formed by the phosphorus lone electron pair and π-bonds with the participation of the oxygen lone electron pairs. The main subject of discussion is usually the actual extent of π-bonding interaction, which may change charge distribution considerably. The Mulliken population analysis showed[16] that the isomerization of phosphinous acid from the oxo-form $H_3P{=}O$ to the aci-form H_2POH leads to a noticeable decrease of π-contributions and, consequently, to an increase of electron density on the oxygen atom in the H_2POH molecule. The calculated changes in the oxygen atom charges in the molecules **1**—**4** may be

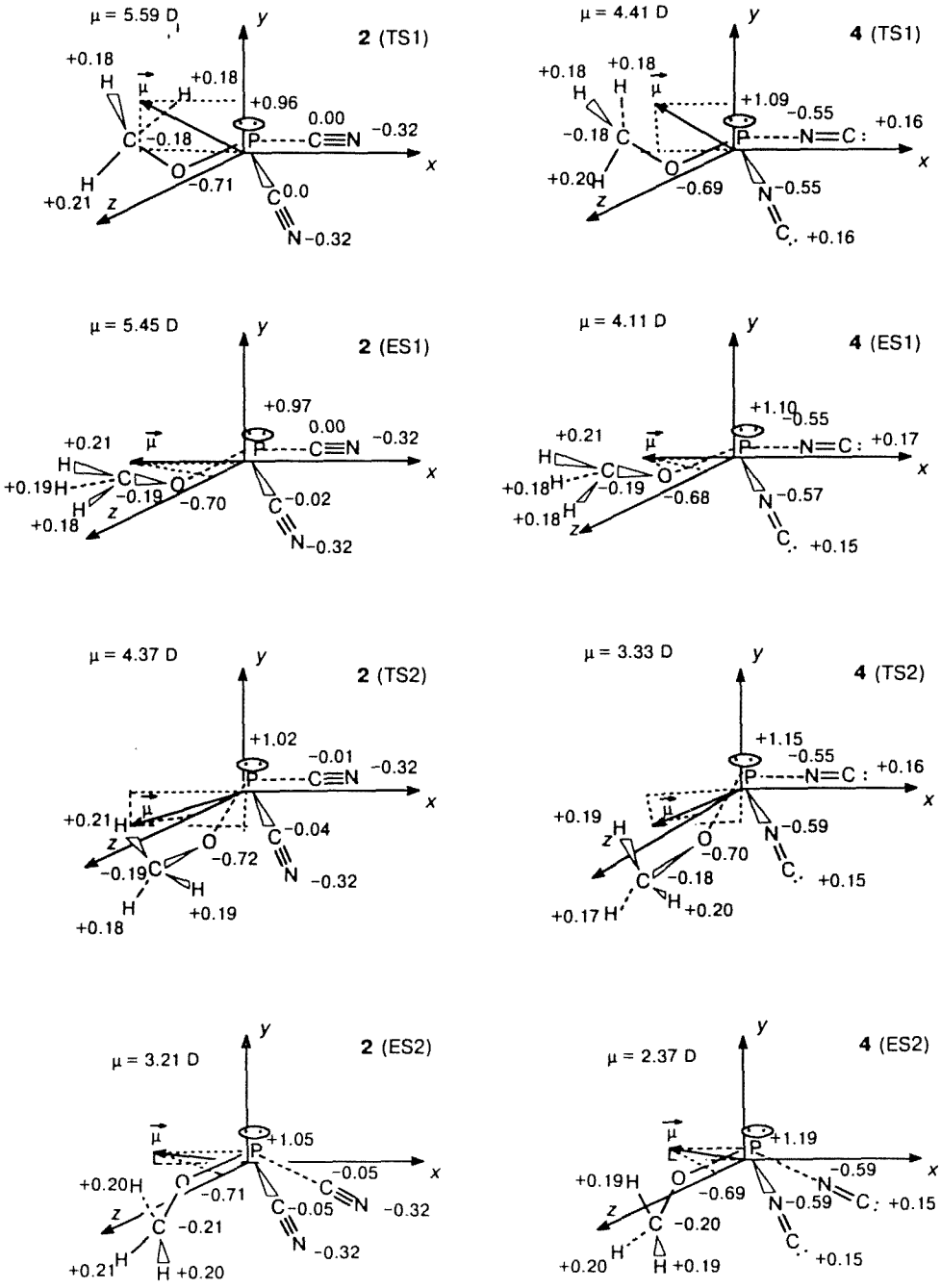

Fig. 4. RHF/6-31G* Mulliken atomic charges and electric dipole moments for the equilibrium (ES) and internal rotation transition (TS) states of $MeOP(CN)_2$ (**2**) and $MeOP(NC)_2$ (**4**) (see Tables 2 and 3).

Table 7. Theoretical and experimental structural parameters of the oxo-form of phosphinous acid and its derivatives[a]

Molecule	Basis set	r/Å		φ/deg[a]				Reference
		P=O	P—CH_3 (P—H)	H_3C—P=O (H—P=O)	H_3C—P—X (H—P—X)	X—P=O	X—P—X	
The RHF method with the 6-31G*(*1*) or 6-31G**(*2*) basis sets								
H_3P=O	*1*	1.465	1.393	117.0	101.0	117.0	101.0	50
	2	1.465	1.396	116.9	101.1	116.9	101.1	22
$HP(O)F_2$	2	1.433	1.372	118.2	102.1	116.1	99.4	22
Me_3P=O	*1*	1.474	1.820	113.8	104.8	113.8	104.8	50
$MeP(O)(CN)_2$	*1*	1.451	1.797	118.4	103.7	114.4	99.8	*b*
$MeP(O)(NC)_2$	*1*	1.445	1.792	117.7	104.0	114.4	100.3	*b*
$MeP(O)F_2$	*1*	1.438	1.786	118.5	103.6	114.9	98.8	44
The MP2 method with the 6-31G*(*1*), 6-31G**(*2*), or 6-311G**(*3*) basis sets								
H_3P=O	*2*	1.496	1.402	117.6	100.3	117.6	100.3	22
	3	1.485	1.406	117.7	100.2	117.7	100.2	24
$MeP(O)(CN)_2$	*1*	1.488	1.796	118.6	103.2	115.0	99.2	*b*
$MeP(O)(NC)_2$	*1*	1.476	1.787	119.2	103.2	115.0	98.5	*b*
Experiment								
$HP(O)F_2$	(r_s)[c]	1.437(6)	1.387(10)	117.9(20)	101.9(15)	116.3(10)	99.8(5)	51
Me_3P=O	(r_a)[c]	1.476(2)	1.809(2)	114.4(7)	104.1(8)	114.4(7)	104.1(8)	52
$MeP(O)Cl_2$	(r_a)[c]	1.448(5)	1.800(25)	117.4(10)	103.3(5)	114.5(5)	101.8	53
$MeP(O)F_2$	(r_0)[c]	1.442(9)	1.795(19)	118.2(15)	100.5(23)	117.5(20)	99.2(10)	47
	(r_{av})[c]	1.444(3)	1.770(5)	117.8(8)	103.7(8)	115.0(8)	99.2(2)	54

[a] X — H, Cl, F atoms, or C≡N and N=C: groups, respectively.

[b] This work.

[c] From the data of the microwave spectroscopy (r_s or r_0 parameters), gas electron diffraction (r_a) or their joint analysis (r_{av}); the physical sense of the parameters obtained by these methods was considered earlier.[55] The experimental errors are also indicated.

connected with an analogous effect.

The dipole moments of the oxo-forms **1** and **3** depend slightly on the methyl group internal rotation, while the rotation of the methoxy group about the P—O bond in **2** and **4** results in an almost double decrease in their dipole moments on going from *cis*- to *trans*-conformations. The values of dipole moments of the *cis*-conformations of **2** and **4** then exceed those obtained for the corresponding oxo-tautomers by 0.5—1.0 D. Due to a considerable difference in the dipole moments of the *cis*- and *trans*-conformations of **2** and **4**, their relative stability can essentially change depending on the medium polarity.

Equilibrium geometric parameters and their relaxation during internal rotation. The comparison of the calculation results for the molecules **1**—**4** and a series of related phosphorus derivatives with the available experimental structural data (Tables 7 and 8) shows that the electron correlation contributions to some geometric parameters are inadequately accounted for by the MP2 method. The MP2/6-31G* approximation, as well as the similar MP2/6-31G** one, significantly overestimates the P=O and P—O bond lengths (by 0.03—0.04 Å) and underestimates the P—O—C bond angle (by *ca.* 3°). According to the indirect assessments based on the results of the MP2 calculations[24] for the H_3P=O and H_2POH molecules using the three-exponent 6-311G** basis set, such an extension of the basis is still insufficient. At the same time, the RHF calculations with the considered basis sets show better agreement with experiment for the majority of geometric parameters of these compounds, except for the multiple bond lengths in cyano and isocyano groups (the deviations for bond lengths and angles lie within the limits of ±0.01 Å and ±1.5°, respectively).

Data in Tables 7 and 8 show that the changes in principal geometric parameters of the related molecules calculated by the RHF and MP2 methods and found experimentally agree with one another within the typical accuracy of experiment (up to ±0.005 Å for bond distances and up to ±1° for bond angles). Therefore, the use of *ab initio* calculation results along with experimental data for discussing structural regularities is quite reasonable.

The changes in the equilibrium geometric parameters of the molecules **1**—**4** correspond to the general stereochemical patterns following from numerous experimental investigations of phosphorus compounds.[56,57] It was established that in the derivatives of four-coordinate phosphorus, the ordinary (single) bond lengths are, as a rule, smaller and the bond angles between them are wider than those in three-coordinate phosphorus compounds. This dependence is fulfilled well for many bonds formed by phosphorus atom, in particular for P—C bonds with different coordination numbers of carbon. According to our calculations, it is fulfilled in the molecules **1**—**4** as well (see Tables 1—3 and 7, 8).

The experimental data[56] show that the phosphoryl bond P=O becomes significantly shorter when more electronegative substituents attach at the phosphorus atom. This might indicate some intensification of π-interactions with the participation of the oxygen lone electron pairs. The results of our calculations correspond to this regularity, since the P=O bond lengths in **1** and **3** are

Table 8. Theoretical and experimental structural parameters of the aci-form of phosphinous acid and its derivatives[a]

Molecule	Conformation	Basis set	r/Å		φ/deg			τ/deg,[a]	Reference
			P—O	O—CH_3 (O—H)	O—P—X	X—P—X	P—O—CH_3 (P—O—H)	H_3C—O—P—E	
The RHF method with the 6-31G*(*1*) or 6-31G**(*2*) basis sets									
H_2POH	*trans-*	*2*	1.641	0.944	101.4	93.6	115.8	180.0	22
	cis-	*2*	1.648	0.943	99.5	94.3	111.2	0.0	22
$MeOPMe_2$	*trans-*	*1*	1.643	1.403	103.3	98.7	125.9	180.0	32
	-cis-	*1*	1.654	1.404	97.8;100.3	99.4	119.2	20.1	32
$MeOP(CN)_2$	*trans-*	*1*	1.595	1.425	102.1	94.9	126.5	180.0	*b*
	-cis-	*1*	1.609	1.421	98.3;101.4	96.2	119.9	26.4	*b*
$MeOP(NC)_2$	*trans-*	*1*	1.588	1.422	101.2	96.0	126.8	180.0	*b*
	-cis-	*1*	1.603	1.419	97.2;100.8	97.5	119.9	38.5	*b*
$MeOPF_2$	*trans-*	*2*	1.584	1.424	100.1	94.7	125.2	180.0	31
The MP2 method with the 6-31G*(*1*), 6-31G**(*2*), or 6-311G**(*3*) basis sets									
H_2POH	*trans-*	*2*	1.668	0.964	101.7	92.5	113.4	180.0	22
		3	1.658	0.959	101.6	92.3	113.6	180.0	24
	cis-	*2*	1.678	0.963	99.1	93.2	107.9	0.0	22
		3	1.671	0.957	99.1	92.9	107.6	0.0	24
$MeOP(CN)_2$	*trans-*	*1*	1.630	1.446	101.8	93.9	121.6	180.0	*b*
	-cis-	*1*	1.648	1.447	97.0;101.7	95.5	115.4	35.0	*b*
$MeOP(NC)_2$	*trans-*	*1*	1.612	1.450	101.1	93.9	122.7	180.0	*b*
	-cis-	*1*	1.631	1.448	95.9;100.7	96.1	115.8	44.6	*b*
$MeOPF_2$	*trans-*	*2*	1.614	1.445	100.3	95.0	120.8	180.0	31
Experiment									
$MeOPCl_2$	*trans-*	(r_a)[c]	1.585(12)	1.463(23)	101.4(10)	98.1(19)	124.5(37)	180.0[d]	29
$MeOPF_2$	*trans-*	(r_s)[c]	1.560(20)	1.446(5)	102.2(10)	94.8(6)	123.7(5)	180.0[d]	25
		(r_{av})[c]	1.574(4)	1.446(2)	101.6(1)	94.8(1)	123.9(1)	180.0[d]	27

[a,b,c] See the footnotes[a,b,c] to Table 7; the E point characterizes conventional position of the phosphorus lone pair of electrons.
[d] Fixed parameters.

0.01—0.03 Å smaller than those in the $Me_3P{=}O$ and $H_3P{=}O$ molecules, but exceed by roughly the same value the analogous bond lengths in the $HP(O)F_2$ and $MeP(O)F_2$ molecules. As can be seen from the data in Tables 7 and 8, the P=O, P—O and P—Me bonds shorten to a roughly equal extent (by 0.01—0.02 Å) on going from cyanides to isocyanides. We should also note the clear tendency to shortening of the P—O bond and simultaneous elongation of the O—C bond in the methoxy substituent with the increase in electronegativity of other substituents at the phosphorus atom.

As it was shown earlier,[5,58] the multiple bond distances of cyano and isocyano groups are systematically underestimated by the RHF/6-31G** calculations and overestimated at the MP2/6-31G** level. Nevertheless, the averaging of the estimates obtained by the RHF and MP2 methods provides good agreement with experiment. Proceeding from this, for the H_2PCN and H_2PNC molecules, which have not been synthesized yet, the C≡N and N=C: bond lengths were predicted to be 1.160 and 1.177 Å, respectively.[5] The analogous averaged values for the molecules **1**—**4** coincide with the suggested ones[5] to within 0.002 Å, which must demonstrate a low sensitivity of the C≡N and N=C: bonds to both the change in coordination number of phosphorus atom and the effect of other substituents. At the same time, the deviations from linearity of P—C≡N and P—N=C: fragments depend on the coordination number of the phosphorus atom, increasing by 3—4° in the aci-structures **2** and **4** containing three-coordinate phosphorus (see Tables 1—3).

The relaxation of geometric parameters during internal rotation can be estimated only by means of *ab initio* calculations. Our data for the molecules **1**—**4** (see Tables 1—3) show that such estimates obtained by the RHF and MP2 methods agree with each other to an even larger extent than the corresponding estimates of parameter changes in the series of related molecules. As a result of the minimal distinction of electron correlation contributions characteristic of isodesmic processes, the difference between the relaxation corrections estimated by the RHF and MP2 methods as a rule does not exceed 0.003 Å for distances and 0.5° for bond angles, while the correction values themselves may reach hundredths of an angstrom and several degrees. With rare exceptions, the use of even RHF relaxation corrections in the analysis of structural and spectral experimental data is quite reasonable.

During the internal rotation of the methyl group in **1** and **3** the P—Me bond length changes most noticeably. In the sterically less preferable eclipsed configuration corresponding to the transition state, it increases by more than

0.01 Å. The methyl group rotation axis tilts from the P—C bond direction by 3—4°, causing the approach of one (in the eclipsed configuration) or two (in the staggered configuration) hydrogen atoms of this group to the oppositely charged oxygen atom of the phosphoryl group. Bond angles at the phosphorus atom vary within the limits of ±1°.

The internal rotation about the P—O bond in the molecules **2** and **4** is accompanied by more essential relaxation changes of their geometric parameters (see Tables 2 and 3). Thus, the P—O—C bond angles of both the *trans*- and near-*cis*-conformers differ by 6—7°. The phosphorus atom bond angles and bond lengths change significantly as well. In particular, the P—O bond distance in the *trans*-conformers is ~0.02 Å shorter than that in the near-*cis* ones.

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