Physical Chemistry

Ab initio study of molecular structure and internal rotation in methyldicyanophosphine and methyldiisocyanophosphine. The Raman spectrum of methyldicyanophosphine and its interpretation with the use of scaling of *ab initio* force fields

L. S. Khaikin,[a] O. E. Grikina,[a] B. I. Zhilinskii,[b] E. A. Zhilinskaya,[b] E. G. Baskir,[c] R. V. Nepomnyashchii,[a] O. A. Fomicheva,[a] and M. V. Proskurnina[a]*

[a]*Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory, 119899 Moscow, Russian Federation. Fax: +7 (095) 932 8846*
[b]*Littoral University, F-59140 Dunkirk, France.* Fax: (33) 28 65 8239*
[c]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5328*

The equilibrium geometric parameters and structures of transition states of internal rotation for the molecules of methyldicyanophospine $MeP(CN)_2$ and its isocyano analog $MeP(NC)_2$ were calculated by the RHF and MP2 methods with the 6-31G* and 6-31G** basis sets. At the MP2 level, the total energy of cyanide is ~35 kcal mol^{-1} lower than that of isocyanide and the barriers to internal rotation of methyl group for $MeP(CN)_2$ and $MeP(NC)_2$ are 2.2 and 2.7 kcal mol^{-1}, respectively. For both molecules, the one-dimensional *ab initio* potential functions of internal rotation approximated by a truncated Fourier series were used to determine the frequencies of torsional transitions by solving direct vibrational problems for a non-rigid model. The Raman spectrum of crystalline $MeP(CN)_2$ was recorded in the range 3500—50 cm^{-1}. The vibrational spectra of this compound were interpreted by scaling *ab initio* force fields calculated by the RHF and MP2 methods. The vibrational spectrum of methyldiisocyanophosphine was predicted with the use of the obtained scale factors.

Key words: methyldicyanophosphine, methyldiisocyanophosphine; *ab initio* calculations; molecular structure, internal rotation; vibrational spectra.

This work is a continuation of our previous studies[1,2] of the structure and tautomeric stability of cyano derivatives of phosphorus. Almost no experimental and theoretical data of such kind for methyldicyanophosphine have been reported in the literature. The X-ray diffraction study[3] was mostly dedicated to investigating the crystalline structure of methyldicyanophosphine. Later, the intermolecular P...N distance (3.05 Å) was calcu-

* Universite du Littoral, F-59140 Dunkerque, France.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 1703—1714, September, 1998.

1066-5285/98/4709-1653 $20.00

lated[4] on the basis of these data and appeared to be somewhat shorter than the sum of the van der Waals radii of the P and N atoms (3.4 Å).

The IR and Raman spectra of methyldicyanophosphine in the crystalline phase and its Raman spectra in melt, in acetonitrile solution, and in the gas phase were obtained in the most detailed spectral study.[5] However, problems arose when interpreting these data,[5,6] especially with the assignment of several weak bands in the low-frequency region of Raman spectra, for which attempts to measure depolarization ratios with adequate accuracy failed.

Using quantum-chemical calculations, we studied the thermodynamic stability and geometry of structural isomers in the $C_3H_3N_2P$ system and internal rotation of methyl group in these molecules. The Raman spectrum of methyldicyanophosphine in the crystalline phase was recorded again and the whole totality of experimental vibrational spectra was reinterpreted using quantum-chemical force fields, calculated intensities of the IR and Raman bands, and depolarization ratios. The vibrational spectrum of methyldiisocyanophosphine was predicted.

Procedure for Calculations and Experimental

The geometry of $MeP(CN)_2$ and $MeP(NC)_2$ molecules was optimized by the restricted Hartree—Fock (RHF) method and at the second-order Møller-Plesset (MP2) level of perturbation theory with inclusion of electron correlation using the 6-31G* and 6-31G** basis sets. To characterize stationary points, the results of calculations of the frequencies of normal vibrations were also used.

In the studies of the internal rotation of methyl group the potential energy values, in addition to stationary points, were calculated in each case at three fixed intermediate points along the coordinate of the corresponding motion with optimization of other geometric parameters. Such an approach makes it possible to take into account structural relaxation in the course of one-dimensional motion considered and, hence, to a certain extent, interaction of the motion in question with other internal vibrations.[7—9] As has been shown previously,[8] the consideration of geometry relaxation (the so-called non-rigid model) is often necessary for a correct determination of the shape of the potential function and the height of the barrier.

In order to predict the energy spectra and to estimate the frequencies of torsional transitions using theoretical potential functions, we solved the direct one-dimensional problems[9] in the framework of a non-rigid model. The dependence of calculated values of the potential energy on the angle of rotation (φ) was approximated by a truncated Fourier series

$$V(\varphi) = 0.5 \sum_{k=1}^{N} V_k (1 - \cos k\varphi),$$

where V_k is the maximum amplitude of the kth term of the expansion.

The functions $F(\varphi)$ characterizing the kinetic energy and required for solving the direct problems were calculated following the known procedure[10] using data of quantum-chemical calculations of geometric parameters for different points of the potential curves. These functions were also approximated by a truncated Fourier series.

The vibrational spectra were analyzed by scaling the *ab initio* force fields and refining a small set of scale factors by fitting theoretical vibrational frequencies to the experimental ones.

To meet the criteria for comparability of the force constants obtained in a series of related molecules, the harmonic force constants of the $MeP(CN)_2$ and $MeP(NC)_2$ molecules in the Cartesian system calculated for the equilibrium geometric parameters in the RHF/6-31G* and MP2/6-31G** approximations from analytical expressions for the second derivatives of the energy were transformed to a complete and non-redundant system of the internal coordinates of local symmetry. The corresponding sets of internal coordinates have been discussed previously.[11] Individual scale factors C_i were introduced for the groups of equivalent or similar (in the case of local symmetry) internal coordinates; the modification of quantum-chemical force constants F_{ij}^{theor} was defined as $F_{ij} = (C_i C_j)^{1/2} F_{ij}^{theor}$ (see Ref. 12).

All quantum-chemical calculations were carried out on an HP735 Work Station computer at the Littoral University (Dunkirk, France) using the GAUSSIAN-92 program package.[13] One-dimensional torsional problems were solved using the TORSIO program,[9] and the direct and inverse spectral problems were solved by a scaling procedure using the ANCO and SCALE programs.[14,15]

The Raman spectrum of $MeP(CN)_2$ in the crystalline phase in the frequency region 3500—50 cm^{-1} was recorded on a Bruker IFS-66 spectrometer equipped with a FRA 106 Raman accessory, a solid-state Nd/YAG IR laser (100 W, the exciting line at λ = 1.064 μm), and a D418-S detector cooled with liquid nitrogen. The resolution of the spectrometer was 4 cm^{-1}. The ^{31}P NMR spectrum was recorded on a Varian FT-80 spectrometer with 85% H_3PO_4 as external standard.

Methyldicyanophosphine $MeP(CN)_2$ was synthesized following the modified procedure[16] by the reaction of methyldichlorophosphine with hydrogen cyanide in ether in the presence of triethylamine. This procedure does not result in a high yield, but it is a one-step process, and, in addition, monitoring by ^{31}P NMR spectroscopy shows no traces of starting reagents.[16] Methyldichlorophosphine $MePCl_2$ was synthesized following the modified procedure[17] and hydrogen cyanide was synthesized following the conventional procedure.[18]

A solution of methyldichlorophosphine (5.6 g, 0.04 mol) in 80 mL of abs. diethyl ether was added dropwise to 4 mL of liquid hydrogen cyanide cooled to −10 °C, and the mixture was stirred for 30 min at −10 °C; then 13 mL of abs. triethylamine was added. The reaction mixture was stirred for 1 h at 0 °C and then the temperature was raised to room temperature, and the reaction mixture was stirred for an additional 4 h. Triethylamine hydrochloride precipitated was filtered off, washed with abs. ether, and the ethereal extracts were combined. The solvent was evaporated, and the residue was recrystallized from chloroform to give 3.2 g of methyldicyanophosphine (81%), m.p. 80—81 °C.[5] ^{31}P NMR ($CHCl_3$, δ): +81.4.[19]

Results and Discussion

Relative stability of methyldicyanophosphine and methyldiisocyanophosphine

Comparison of the results of theoretical and experimental studies of cyanide ⟹ isocyanide rearrangements available to date showed[1] that the inclusion of

electron correlation is of fundamental importance for reliable calculation of the energy difference of the isomers. Completeness of the basis set and the molecular geometry used in calculations are of lesser importance. The inclusion of electron correlation in the MP2 approximation usually leads to overestimation of the energy difference by no more than 3—5 kcal mol^{-1}, whereas in the case of the RHF method the errors do not exhibit such a regular behavior.[1] The results of MP2 calculations can be considered as the upper boundaries of the values of energy differences. Cyanides of non-transitional elements of Groups IV—VII of the Periodic system are always more stable than the corresponding isocyanides. At the same time, the relative stability of the isomers is strongly affected by electronegativity of the atom to which isomeric —C≡N and —N=C: groups in question are directly bonded, *viz.*, the isomerization energy increases as electronegativity increases.

According to our *ab initio* calculations, the increase in the energy on going to the isocyano form in the $MeP(CN)_2 \rightleftharpoons MeP(NC)_2$ system is 14.4 kcal mol^{-1} and 34.8 kcal mol^{-1} for the RHF and MP2 approximations, respectively (Table 1). As for the energy difference for the $MeOP(CN)_2 \rightleftharpoons MeOP(NC)_2$ system we calculated previously (~30 kcal mol^{-1} in the MP2 approximation),[1] the values obtained are somewhat larger than in the case of the $H_2PCN \rightleftharpoons H_2PNC$ system (~20 kcal mol^{-1} in the same approximation).[20] However, it should be noted that each of the phosphines we studied contains two isomerizing groups. Thus, the thermodynamic stability of isocyano phosphines must be higher than that of H_2NNC in the $H_2NCN \rightleftharpoons H_2NNC$ amine system, in which the energy difference calculated by the MP2 method is ~50 kcal mol^{-1},[20] and be close to that of MeNC in the $MeCN \rightleftharpoons MeNC$ system (the corresponding energy difference is equal to 27 kcal mol^{-1}),[21] for which the results of calculations can be compared with the experimental data (23.7(1) kcal mol^{-1}).[22]

Equilibrium geometric parameters and their changes in the course of internal rotation

It can be seen from the data in Table 1 that RHF and MP2 calculations give close values for many geometric parameters of the phosphines studied. The main distinctions concern the bond lengths in conjugated $P(CN)_2$ and $P(NC)_2$ fragments. Previously,[20,23] it has been shown that the lengths of multiple bonds in cyano and isocyano groups are systematically underestimated in RHF calculations and overestimated in MP2 calculations and that averaging of the values obtained by both methods leads to a good agreement with the experiment. On this basis, the lengths of the C≡N and N=C: bonds in the H_2PCN and H_2PNC molecules were predicted to be 1.160 and 1.177 Å, respectively.[20] The analogous averaged values for the $MeP(CN)_2$ and $MeP(NC)_2$ molecules as well as for the molecules of compounds $MeOP(CN)_2$, $MeOP(NC)_2$, $MeP(=O)(CN)_2$, and $MeP(=O)(NC)_2$ calculated earlier[1] coincide with the estimates proposed in Ref. 20 with an accuracy of 0.002 Å, which may indicate a low sensitivity of the C≡N and N=C: bonds in phosphorus cyanides and isocyanides to the change in the coordination number of the P atom and to the influence of the substituents.

Variations of geometric parameters in the series of substituted phosphines calculated by the RHF and MP2 methods and found experimentally are in agreement within the limits of conventional accuracy of structural experiments (to 0.005 Å for the bond lengths and to 1° for the bond angles).[1] This makes possible discussing the calculated changes in the parameters of such compounds considering them analogously to the experimental data. It can be seen in Table 1 that the $P-C(H_3)$ bond is shortened by ~0.02 Å on going from $MeP(CN)_2$ to $MeP(NC)_2$. Analogous change in the length of the $P-C(H_3)$ bond also occurs when passing from $MeP(=O)(CN)_2$ to $MeP(=O)(NC)_2$.[1] In addition, in these derivatives of tetracoordinated phosphorus the $P-C(H_3)$ bonds are ~0.05 Å shorter and the $(H_3)C-P-C$ and $(H_3)C-P-N$ angles are ~5° larger than in the $MeP(CN)_2$ and $MeP(NC)_2$ molecules, respectively. The P—C (P—N) bonds and the C—P—C (N—P—N) bond angles also undergo similar changes, though to a somewhat lesser extent. This is in agreement with general regularities established in numerous experimental studies of phosphorus compounds,[24,25] according to which the lengths of ordinary bonds in the derivatives of tetracoordinated phosphorus are, as a rule, shorter and the bond angles between them are larger than those in analogous compounds containing a tricoordinated P atom.

The length of the $P-C(H_3)$ bond in the $MeP(CN)_2$ and $MeP(NC)_2$ molecules changes most pronouncedly in the course of internal rotation of the methyl group. In sterically less favored eclipsed form corresponding to the transition state of internal rotation (φ = 180°, see Table 1), this bond is lengthened approximately by 0.02 Å similarly to that observed earlier[1] for the $MeP(=O)(CN)_2$ and $MeP(=O)(NC)_2$ molecules. The axis of rotation of the methyl group deviates from the direction of the $P-C(H_3)$ bond by 2—4° so that one H atom (in the eclipsed form) or two H atoms (in the equilibrium staggered configuration) of this group approach a hypothetical position of the lone electron pair of the P atom (see Fig. 1). Changes in the bond angles at the P atom do not exceed 1°.

Mulliken atomic charges and electric dipole moments

The distributions of Mulliken atomic charges in the $MeP(CN)_2$ and $MeP(NC)_2$ molecules calculated by the RHF and MP2 methods are shown in Fig. 1 and the values of dipole moments of these molecules calculated by the same methods are listed in Table 1. These parameters change only slightly in the course of internal rotation.

Table 1. Results of *ab initio* calculations of equilibrium structures (ES) and transition states of internal rotation (TS) of the $MeP(CN)_2$ (**1**) and $MeP(NC)_2$ (**2**) molecules

Parameter[a]	RHF/6-31G*				MP2/6-31G**			
	1		**2**		**1**		**2**	
	ES	TS	ES	TS	ES	TS	ES	TS
Bond length, *r*/Å:								
P—C(H_3)	1.849	1.865	1.833	1.851	1.847	1.862	1.829	1.846
P—C (P—N)	1.801	1.800	1.708	1.708	1.788	1.786	1.719	1.719
C≡N (N=C:)	1.136	1.136	1.162	1.162	1.184	1.184	1.196	1.196
C—$H_{i,p}$	1.081	1.082	1.082	1.083	1.085	1.086	1.086	1.086
C—$H_{o,p}$	1.084	1.082	1.084	1.082	1.087	1.085	1.088	1.086
Bond angle, β/deg:								
C—P—C (N—P—N)	97.6	97.2	98.9	98.4	97.0	96.6	97.6	97.2
(H_3)C—P—C ((H_3)C—P—N)	99.7	100.6	98.9	99.8	99.1	99.8	97.9	98.7
P—C≡N (P—N=C:)	175.2	175.0	172.7	172.2	173.9	173.7	173.0	172.5
P—C—$H_{i,p}$	113.0	108.4	111.9	108.9	112.9	108.4	111.6	109.0
P—C—$H_{o,p}$	108.1	110.8	108.7	110.5	107.9	110.5	108.4	110.2
Dihedral angle, τ/deg:								
(H_3)C—P—C≡N ((H_3)C—P—N=C:)	±103.0	±103.1	±128.9	±131.1	±108.6	±109.3	±121.8	±125.3
$H_{i,p}$—C(H_3)—P—*A* (φ)	0.0	180.0	0.0	180.0	0.0	180.0	0.0	180.0
$H_{o,p}$—C(H_3)—P—*A*	±121.4	±60.4	±121.0	±60.3	±121.5	±60.3	±121.1	±60.2
Dipole moment:								
μ/D	4.46	4.55	3.39	3.48	4.50	4.59	3.31	3.38
α/deg[b]	30.0	30.1	22.1	22.5	29.8	29.8	22.1	22.3
Total energy,								
−(*E* + 564.0)/au	0.950433	0.946521	0.927561	0.923001	1.805934	1.802377	1.750447	1.746217

[a] The "*i,p*" and "*o,p*" indices correspond to H atoms located in the symmetry plane of the molecule and to those located out of this plane, respectively; and *A* is the point on the bisectrix of the C—N—C (N—P—N) angle.

[b] The values of the angle between the vector of the dipole moment lying in the symmetry plane of the molecule and the P—C(H_3) bond (see Fig. 1).

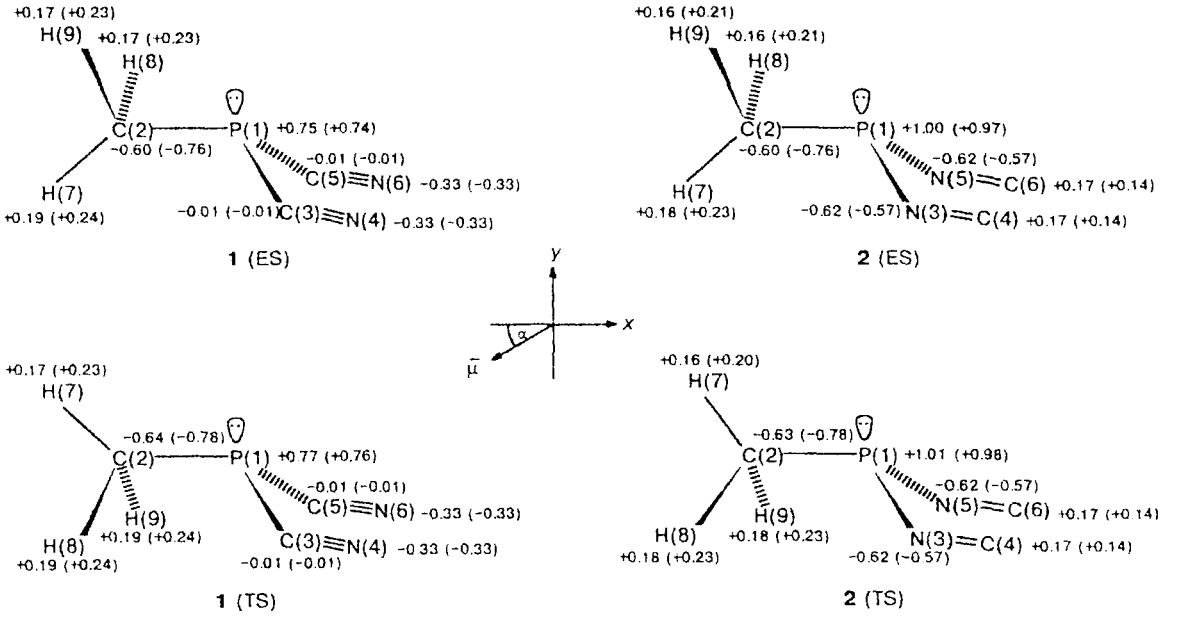

Fig. 1. Equilibrium structures (ES) and conformations of transition states of internal rotation (TS) of the $MeP(CN)_2$ (**1**) and $MeP(NC)_2$ (**2**) molecules: numbering of the atoms and Mulliken atomic charges calculated using geometric parameters optimized by the MP2 method (the results of the RHF calculations are given in parentheses). The H(7), C(2), and P atoms, and the hypothetical position of the lone electron pair of the P atom for each of the molecular forms are in its symmetry plane. The direction of the calculated vectors of dipole moments (the angle α, see Table 1) is shown in the center of the figure.

The positive charge on the P atom increases on going from the cyano to the isocyano form and in both molecules is approximately a factor of 1.5 less than in analogous methoxy derivatives $MeOP(CN)_2$ and $MeOP(NC)_2$.[1] The charges on the atoms of cyano and isocyano groups are nearly the same as in the methoxy derivatives, *viz.*, the negative charges on the N atoms in isocyanides are twice as large as those in cyanides, while carbon atoms in cyano groups are virtually neutral and those in isocyano groups have a small positive charge. Changes in the charges on the atoms of methyl groups caused by isomerization are minimum.

The calculated values of the dipole moments depend slightly on the method used and the μ value for cyanide is 1.2 D larger than that for isocyanide. The experimental value of the dipole moment of the $MeP(CN)_2$ molecule (4.92 D for solutions in cyclohexane and dioxane at 25 °C in an Ar atmosphere)[26] is only slightly larger than the calculated value (4.5 D). Therefore, the possible error of calculations is appreciably less than the calculated values, which makes it possible to consider the predicted directions of the dipole moments (in the symmetry plane of each of the compounds from the cyano or isocyano group to the methyl substituent, see Fig. 1 and Table 1) to be quite realistic too.

Potential functions of internal rotation of methyl group. Calculations of frequencies of torsional transitions

The study of internal rotation of methyl groups in the $MeP(CN)_2$ and $MeP(NC)_2$ molecules showed that the staggered conformation (the dihedral angle φ is 0°, see Table 1) is the most stable. According to the RHF calculations, the height of the barrier for the eclipsed forms of these molecules (φ = 180°) is 2.5 and 2.9 kcal mol^{-1}, respectively. The inclusion of electron correlation in the MP2 approximation affects slightly these values (2.2 and 2.7 kcal mol^{-1}, respectively). The calculated potential curves of internal rotation of the methyl group $V(\varphi)$ in both molecules are similar (Fig. 2) and are satisfactorily approximated by a truncated Fourier series with the three coefficients V_3, V_6, and V_9 (Table 2). The main contribution comes from the expansion term with coefficient V_3, which determines the height of the barrier to rotation.

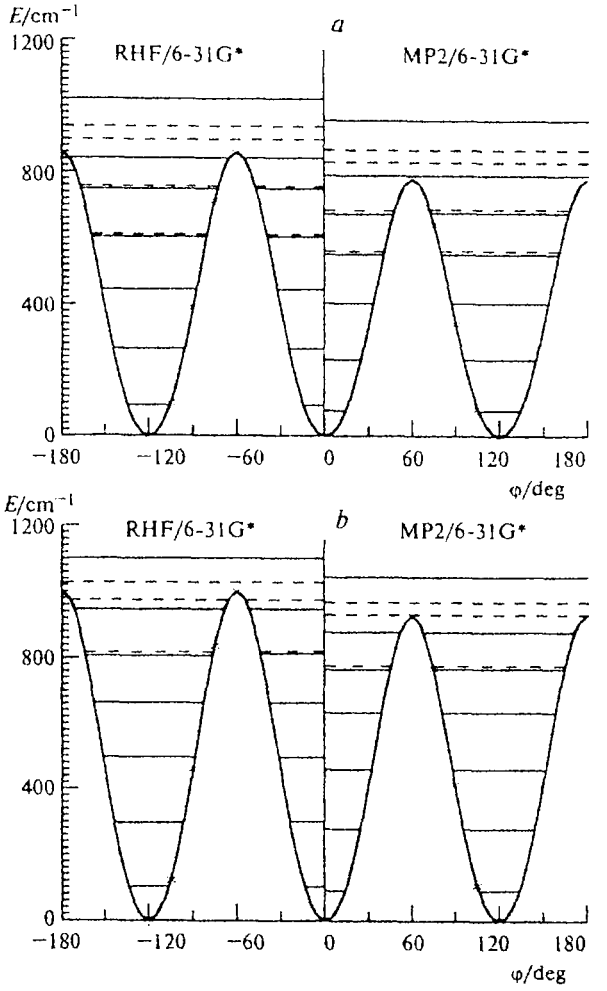

Fig. 2. Approximations of the potential functions of internal rotation of the methyl group in the $MeP(CN)_2$ (*a*) and $MeP(NC)_2$ (*b*) molecules by truncated Fourier series with the coefficients V_3, V_6, and V_9 according to the data of RHF and MP2 calculations. The values of the total energy obtained by quantum-chemical calculations are shown by asterisks. The torsional levels obtained on the basis of the solutions of the direct one-dimensional problem are shown.

Table 2. Coefficients of the Fourier-series expansion (V_n/cm^{-1}) of the functions of potential energy of internal rotation of the methyl group in the $MeP(CN)_2$ (**1**) and $MeP(NC)_2$ (**2**) molecules calculated in the RHF/6-31G* and MP2/6-31G** approximations

Coefficient	1		2	
	RHF	MP2	RHF	MP2
V_3	864.0	784.6	1005.7	931.9
V_6	−41.7	−50.2	−40.8	−50.4
V_9	−6.3	−4.8	−5.6	−4.1
Standard deviation	2.1	1.9	1.9	1.8

Using the RHF- and MP2-optimized geometric parameters, *i.e.*, taking into account the effects of structural relaxation, we calculated the functions $F(\varphi)$ characterizing the kinetic energy (the definition of the function $F(\varphi)$ was given in Refs. 27 and 28) and obtained the coefficients F_0, F_1, and F_2 of their approximations by a truncated Fourier series (Table 3). The values of coefficients F_1 and F_2 in the Fourier expansions are very small and so taking into account the expansion terms after F_0 only slightly affects the final result. The functions $F(\varphi)$ and $V(\varphi)$ were used to calculate energy levels and frequencies of torsional transitions (Table 4, see Fig. 2) by solving the direct one-dimensional problem in the frame-

Table 3. Coefficients of the Fourier-series expansion (F_n/cm^{-1}) of the functions $F(\varphi)$ calculated for internal rotation of the methyl group in the $MeP(CN)_2$ (**1**) and $MeP(NC)_2$ (**2**) molecules using geometric parameters optimized in the RHF/6-31G* and MP2/6-31G** approximations

Coefficient	1		2	
	RHF	MP2	RHF	MP2
F_0	5.4473(6)	5.3969(3)	5.4398(5)	5.3881(4)
F_1	−0.0089(3)	−0.0096(2)	−0.0130(3)	−0.0122(2)
F_2	0.0113(7)	0.0120(3)	0.0174(6)	0.0163(5)

Note. The standard deviations are given in parentheses.

Table 4. The lowest energy levels (E/cm^{-1}) for internal rotation of the methyl group in the $MeP(CN)_2$ (**1**) and $MeP(NC)_2$ (**2**) molecules calculated in the RHF/6-31G* and MP2/6-31G** approximations

Excitation level	Symmetry type of the component	1		2	
		RHF	MP2	RHF	MP2
0	A_1, E	89.0	82.0	98.1	91.8
1	E	266.1	246.0	292.4	274.1
1	A_2	266.1	246.1	292.5	274.2
2	A_1	438.1	406.5	480.3	451.5
2	E	438.2	406.7	480.4	451.6
3	E	598.7	556.5	657.2	618.9
3	A_2	600.3	558.8	657.9	619.8
4	A_1	734.8	680.8	714.2	766.0
4	E	745.9	694.9	820.0	773.5
5	E	846.5	786.1	943.9	887.8
5	A_2	895.2	841.5	976.1	925.3
6	A_1	927.7	866.5	1031.7	972.1
6	E	1001.8	845.2	1092.0	1036.7

work of the non-rigid model of internal rotation.[8,9] The zeroth and the first energy levels are nearly triply degenerate, and the splitting of order 1—2 cm^{-1} appears only for the third level and then increases rather rapidly.

It follows from the solution of the direct one-dimensional problems obtained using data of quantum-chemical calculations that the fundamental frequencies of the torsional mode must be observed in the regions 165—180 cm^{-1} for $MeP(CN)_2$ and 180—195 cm^{-1} for $MeP(NC)_2$. This is in good agreement with the assignment of the torsional vibration of the methyl group in the $MeP(CN)_2$ molecule to the experimental band at 180 cm^{-1} resulting from the solution of the inverse spectral problems by scaling the quantum-chemical force fields (see below).

The use of quantum-chemical force fields for the interpretation of vibrational spectra of methyldicyanophosphine

The Raman spectrum of $MeP(CN)_2$ in the crystalline phase (Figs. 3 and 4) we obtained in this study is in good agreement with the reported data[5] (Table 5). Though the interpretation of these data has changed as time passed, it has not been completed as yet. Thus, it is argued[5,6] that no bands corresponding to the antisymmetric stretching mode of the C≡N bonds and to the torsional mode of the methyl group are observed in the spectra. The bands in the spectral region below 450 cm^{-1}, characteristic of the frequencies of most skeletal deformation modes and torsional mode of the methyl group, had no reliable assignment even to the symmetry types of normal vibrations. The results of the solution of the inverse spectral problem for $MeP(CN)_2$ obtained[6] taking into account the data of analogous calculations and reassignment of the frequencies of phosphorus and arsenic tricyanides[29,30] were the main reason for revising[6] the experimental assignment.[5] In addition, it has been pointed out[6] that the experimental assignment[5] could be complicated by non-reliability of depolarization measurements in the low-frequency region of the Raman spectra caused by the extremely high noise level and low scattering intensity in this spectral region. The absence of experimental spectra of methyldicyano-

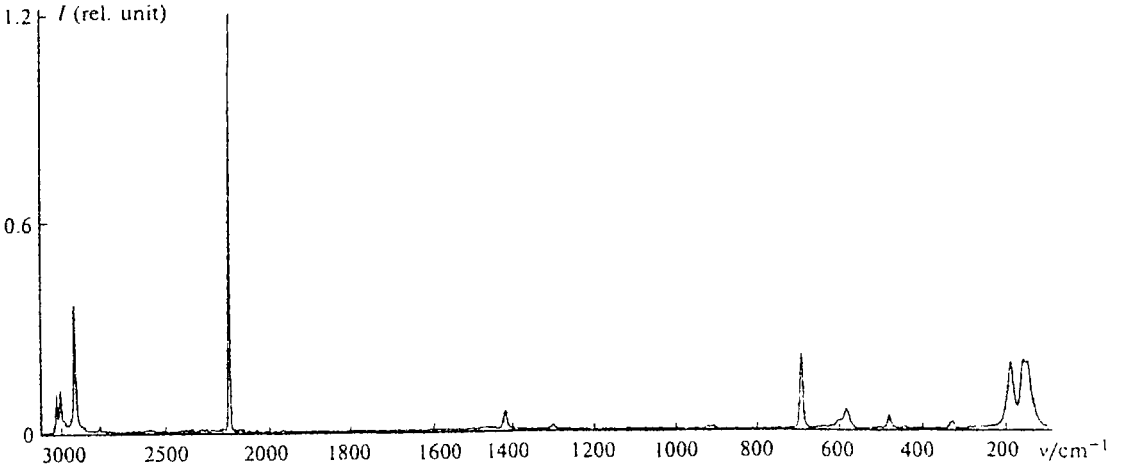

Fig. 3. General view of the Raman spectrum of methyldicyanophosphine in the crystalline phase.

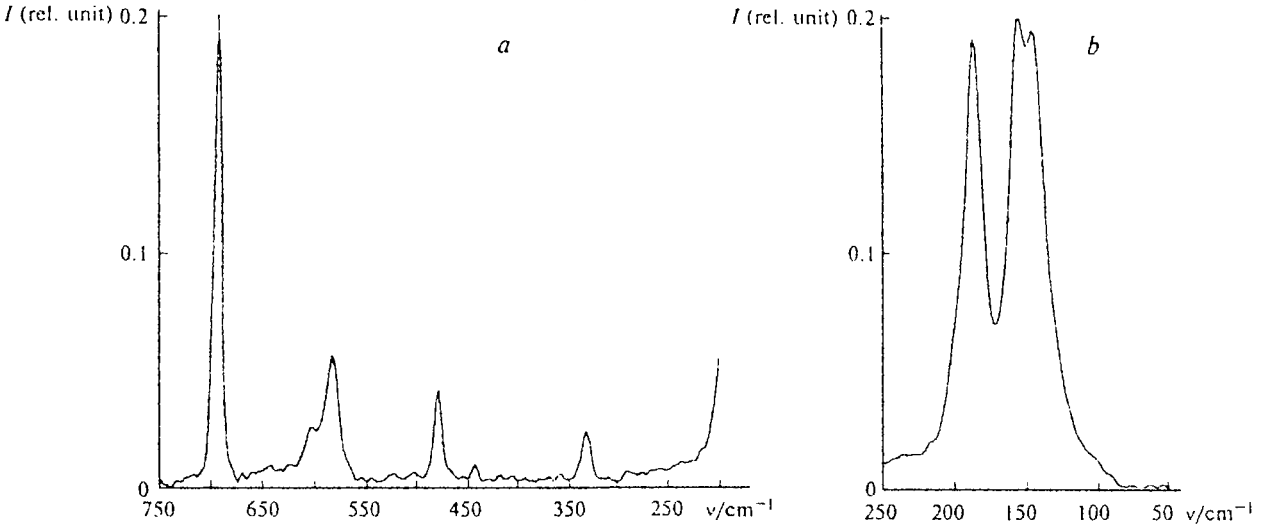

Fig. 4. Two regions of the Raman spectrum of methyldicyanophosphine in the crystalline phase: *a*, 200—750 cm^{-1}; and *b*, 50—250 cm^{-1}.

phosphine isotopomers is an objective obstacle to the analysis.

Vibrational spectra of polyatomic molecules often cannot be unambiguously treated using traditional empirical methods of interpretation including the normal coordinate analysis. A correct choice and assignment of the fundamental frequencies are not evident without preliminary knowledge of at least the general structure

Table 5. The Raman and IR spectra (ν/cm^{-1}) of methyldicyanophosphine

Raman spectrum					IR spectrum, crystalline phase[5]
Crystalline phase		Solution in MeCN [5]	Melt[5]	Gas phase[5]	
This work	Ref. 5				
3022 w	3014 m		3020 s, p?		3016 sh
3001 w	2999 m		3006 s, dp?		2998 sh
2986 vw					
2932 s	2926 s		2933 vs, p	2929 m	
2889 vvw					
2812 vw					
2193 vvs	2188 vs	2189 vs, p	2189 vs, p	2187 vs, p	2186 m
2191 vvs					
1418 w	1419 s	1422 s, p	1423 m, p	1416 m	1423 vw
	1411 m				1414 s
1300 vw	1294 s		1300 m, p		1293 m
922 vw	924 w				922 m
911 vw	909 m				906 s
693 m	689 vs	693 vs, p	691 vs, p	687 s, dp?	690 vs
		628 s, p	633 s, p		646 w
600 vw	602 m	600 s, dp	606 vw, dp?		601 vs
581 w	580 vs	589 vs, p	588 vs, p	575 s, p	569 vs
477 w	478 s	459 s, p	468 m, p	476 w	471 w
440 vvw	438 w	430 vw	432 m, p (0.4)?		431 w
330 vw	328 m		316 m, dp		320 vw
186 m	183 m	177 vs, p	179 s, dp?	183 m, dp?	
155 m	152 m			151 m, dp	
145 m	140 m		132 s, p?	141 m, dp	
103 sh	95 w			93 w, p	
	61 m				
	40 m			45 s, dp	

Note. Hereafter p is polarized and dp is depolarized bands in the Raman spectrum; the measured depolarization ratio[5] is shown in parentheses.

Table 6. The nonredundant set of internal coordinates of local symmetry for the methyldicyanophosphine molecule[a]

Number	Notation of internal coordinate	Number	Notation of internal coordinate	Definition of internal coordinate
1	P—C(2) str	14	CH_3 s.str	0.5774 (C(2)—H(7) str) + 0.5774 (C(2)—H(8) str) + + 0.5774 (C(2)—H(9) str)
2	P—C(3) str			
3	C(3)≡N(4) str	15	CH_3 s.def	−0.4082 (PC(2)H(7) bend) − 0.4082 (PC(2)H(8) bend) − − 0.4082 (PC(2)H(9) bend) + 0.4082 (H(8)C(2)H(9) bend) + + 0.4082 (H(7)C(2)H(9) bend) + 0.4082 (H(7)C(2)H(8) bend)
4	P—C(5) str			
5	C(5)≡N(6) str			
6	C(2)PC(3) bend	16	CH_3 as.str	0.8165 (C(2)—H(7) str) − 0.4082 (C(2)—H(8) str) − − 0.4082 (C(2)—H(9) str)
7	C(2)PC(5) bend			
8	C(3)PC(5) bend	17	CH_3 as.def	0.8165 (H(8)C(2)H(9) bend) − 0.4082 (H(7)C(2)H(9) bend) − − 0.4082 (H(7)C(2)H(8) bend)
9	PC(3)N(4) bend			
10	PC(5)N(6) bend	18	CH_3 rock	0.8165 (PC(2)H(7) bend) − 0.4082 (PC(2)H(8) bend) − − 0.4082 (PC(2)H(9) bend)
11	P—C(3) tors (P—C(2), C(5); C(3)—N(4))	19	CH_3 as.str′	0.7071 (C(2)—H(8) str) − 0.7071 (C(2)—H(9) str)
12	P—C(5) tors (P—C(2), C(3); C(5)—N(6))	20	CH_3 as.def′	0.7071 (H(7)C(2)H(9) bend) − 0.7071 (H(7)C(2)H(8) bend)
		21	CH_3 rock′	0.7071 (PC(2)H(8) bend) − 0.7071 (PC(2)H(9) bend)
13	CH_3 tors (P—C(2) tors) (P—C(3), C(5); C(2)—H(7), H(8), H(9))			

[a] The numbering of the atoms is shown in Fig. 1. Hereafter the following notations of the vibrations are used: str is stretching; bend is bending for the bond angle; def is deformation vibration of local symmetry for the methyl group; rock is rocking; wag is wagging, twist is twisting; tors is torsional; s is symmetric; and as is antisymmetric vibration. The torsional coordinate is defined as the sum of the motions in the tetraatomic fragments.

of the potential energy matrix. This information can be obtained from quantum-chemical calculations of the force fields, scaling of which makes it possible to unequivocally solve the spectral problems.[12] Our experience shows that this approach is highly efficient.[31]

The use of the force fields calculated in the RHF approximation without inclusion of electron correlation can cause some uncertainty in the assignment of the spectral bands,[32] especially in the long-wave region for which experimental data (as in the case of methyldicyanophosphine) are often not sufficiently complete and reliable. For this reason we analyzed the vibrational spectra of $MeP(CN)_2$ using scaling of the force fields calculated both in the RHF approximation and by the MP2 method with inclusion of electron correlation.

The geometric parameters used in the spectral calculations and the definition of the nonredundant set of internal coordinates of local symmetry are listed in Tables 1 and 6, respectively, and the numbering of atoms in the methyldicyanophosphine molecule is shown in Fig. 1. Since, according to quantum-chemical calculations, the departure of the P—C≡N fragments from linearity is 5 to 6° (see Table 1), it was necessary to introduce the bending and torsional coordinates to reach the best description of the motions in these fragments. The obtained values of scale factors (Table 7) lie within the limits 0.70—0.85 and 0.85—1.10 for the force fields in the RHF and MP2 approximations, respectively, and are in good agreement with the values we found earlier for analogous fragments in other classes of compounds.[31,32]

The similarity of both force fields after their scaling (Table 8) and closeness of calculated vibrational frequencies (Table 9) may indicate that the suggested interpretation of methyldicyanophosphine spectra is unambiguous. This is also confirmed by the agreement between the experimental and calculated intensities of the fundamental bands in the IR and Raman spectra and the depolarization ratios (see Tables 5 and 9). The agreement achieved between the experimental vibra-

Table 7. Refined values of scale factors for the force fields of methyldicyanophosphine calculated in the RHF/6-31G* and MP2/6-31G** approximations[a]

Type of scale	Number of internal coordinate[b]	Factor	
		RHF	MP2
P—C(H_3) str	1	0.845	0.897
P—C(N) str	2, 4	0.812	0.841
C≡N str	3, 5	0.717	1.064
(H_3)CPC bend	6, 7	0.779	0.953
CPC bend	8	0.823	0.981
PCN bend	9, 10	0.787	1.083
P—C(N) tors	11, 12	0.769	1.063
CH_3 tors	13	0.798	0.914
C—H str	14, 16, 19	0.822	0.856
CH_3 s.def	15	0.754	0.867
CH_3 as.def	17, 20	0.778	0.869
CH_3 rock	18, 21	0.790	0.895

[a] See footnote "*a*" to Table 6.
[b] See Table 6.

Table 8. The force constants of methyldicyanophosphine calculated in the RHF/6-31G* and MP2/6-31G** approximations and those obtained by scaling (in internal coordinates)[a]

Notation of force constant	RHF		MP2		Notation of force constant	RHF		MP2	
	Calculation	Scaling	Calculation	Scaling		Calculation	Scaling	Calculation	Scaling
1—1	**3.39**	**2.86**	**3.21**	**2.88**	6—10, 7—9	−0.01	0.00	−0.01	−0.01
1—2, 1—4	0.10	0.08	0.09	0.08	6—11, 7—12[b]	±0.009	±0.007	±0.009	±0.009
1—3, 1—5	0.00	0.00	−0.01	−0.01	6—13, 7—13	∓0.03	∓0.02	∓0.02	∓0.02
1—6, 1—7	0.21	0.17	0.21	0.20	6—15, 7—15	−0.03	−0.02	−0.03	−0.03
1—8	0.02	0.02	0.02	0.02	6—16,7—16	−0.04	−0.03	−0.04	−0.03
1—9, 1—10	0.01	0.01	0.01	0.01	6—18,7—18	−0.13	−0.10	−0.11	−0.10
1—11, 1—12[b]	±0.002	±0.001	±0.002	±0.002	6—19, 7—19	±0.03	±0.02	±0.03	±0.03
1—14	0.08	0.07	0.04	0.04	6—21, 7—21	±0.18	±0.14	±0.16	±0.15
1—15	−0.33	−0.26	−0.30	−0.27	**8—8**	**1.23**	**1.01**	**1.06**	**1.04**
1—16	−0.02	−0.02	−0.02	−0.02	8—9, 8—10	0.10	0.08	0.08	0.08
1—17	−0.03	−0.02	−0.03	−0.03	8—11, 8—12[b]	∓0.002	∓0.02	∓0.003	∓0.003
1—18	0.07	0.06	0.06	0.05	8—16	−0.02	−0.01	−0.01	−0.01
2—2, 4—4	**3.80**	**3.09**	**3.63**	**3.05**	8—17	−0.01	−0.01	−0.01	−0.01
2—3, 4—5	0.00	0.00	0.03	0.03	8—18	−0.01	−0.01	−0.01	−0.01
2—4	0.08	0.06	0.07	0.06	**9—9, 10—10**	**0.33**	**0.26**	**0.25**	**0.27**
2—5, 3—4	0.01	0.00	−0.01	−0.01	9—10	0.01	0.01	0.00	0.00
2—6, 4—7	0.20	0.16	0.18	0.16	9—11, 10—12[b]	±0.002	±0.002	±0.001	±0.001
2—7, 4—6	0.06	0.05	0.05	0.05	9—21, 10—21	±0.01	±0.01	±0.01	±0.01
2—8, 4—8	0.23	0.18	0.20	0.19	**11—11, 12—12[b]**	**0.002**	**0.002**	**0.003**	**0.003**
2—9, 4—10	−0.01	−0.01	−0.01	−0.01	**13—13**	**0.08**	**0.06**	**0.07**	**0.06**
2—10, 4—9	0.03	0.02	0.02	0.02	13—19	−0.01	−0.01	−0.01	0.00
2—13,4—13	0.00	0.00	±0.01	±0.01	13—20	−0.01	−0.01	−0.01	−0.01
2—15, 4—15	−0.01	−0.01	0.00	0.00	13—21	0.01	0.00	0.01	0.01
2—16, 4—16	0.01	0.01	0.01	0.01	**14—14**	**6.04**	**4.96**	**5.73**	**4.91**
2—18, 4—18	−0.04	−0.03	−0.04	−0.03	14—15	0.13	0.10	0.12	0.10
2—19, 4—19	∓0.01	∓0.01	∓0.01	∓0.01	14—16	0.04	0.03	0.04	0.03
2—20, 4—20	∓0.01	∓0.01	∓0.01	∓0.01	14—18	−0.03	−0.03	−0.03	−0.03
2—21, 4—21	±0.04	±0.03	±0.04	±0.03	**15—15**	**0.67**	**0.50**	**0.59**	**0.51**
3—3, 5—5	**24.05**	**17.24**	**16.26**	**17.30**	15—16	0.01	0.01	0.01	0.01
3—5	0.00	0.00	−0.03	−0.04	15—17	0.01	0.01	0.01	0.01
3—6, 5—7	−0.01	−0.01	−0.02	−0.02	**16—16**	**5.96**	**4.90**	**5.75**	**4.92**
3—7, 5—6	−0.01	−0.01	0.00	0.00	16—17	−0.14	−0.11	−0.14	−0.12
3—8, 5—8	−0.01	−0.01	0.00	0.00	16—18	0.08	0.06	0.07	0.06
3—9, 5—10	0.05	0.03	0.05	0.05	**17—17**	**0.64**	**0.50**	**0.57**	**0.50**
3—14, 5—14	0.00	0.00	−0.01	−0.01	17—18	0.02	0.02	0.03	0.02
3—15, 5—15	−0.01	−0.01	−0.01	−0.01	**18—18**	**0.67**	**0.53**	**0.59**	**0.53**
3—19, 5—19	∓0.01	∓0.01	∓0.01	∓0.01	**19—19**	**5.90**	**4.85**	**5.70**	**4.88**
6—6, 7—7	**1.16**	**0.90**	**1.00**	**0.96**	19—20	−0.15	−0.12	−0.15	−0.13
6—7	0.04	0.03	0.01	0.01	19—21	0.13	0.10	0.12	0.11
6—8, 7—8	0.07	0.05	0.04	0.04	**20—20**	**0.65**	**0.50**	**0.58**	**0.50**
6—9, 7—10	0.05	0.04	0.04	0.04	**21—21**	**0.66**	**0.52**	**0.59**	**0.53**

[a] The notations of the force constants correspond to the numbering of internal coordinates in Table 6. The diagonal elements of the matrix of force constants are indicated in boldface print. The force constants of the stretching vibrations and interactions between them are given in mdyn Å^{-1}, the force constants of deformation vibrations and interactions between them are given in mdyn Å, and the force constants of interactions between the stretching and deformation vibrations are given in mdyn. The off-diagonal force constants, whose absolute values do not exceed 0.005 in all versions of scaling, are not given.

[b] The calculated force constants of torsional vibrations of the C≡N groups about the P—C bonds (**11—11** and **12—12**) are very small and therefore their values and the values of the constants of interaction of these vibrations with other vibrations of close absolute values are listed with an accuracy of the third decimal place.

tional frequencies and their theoretical estimates calculated in two approximations is characterized by mean deviations of 3 to 4 cm^{-1} (1.2 to 1.3%).

Since the equilibrium structure of the $MeP(CN)_2$ molecule has the C_s symmetry, all its normal vibrations must be active in both IR and Raman spectra; the bands in the Raman spectrum corresponding to 12 modes of the A′ symmetry type can be polarized and those corresponding to 9 modes of the A″ symmetry type must be depolarized (see Table 9).

Our analysis made it possible to introduce a number of important changes in the assignment of the bands as compared to those suggested earlier.[5,6] In particular, it was shown that the frequencies of symmetric and anti-

Table 9. Spectral parameters calculated in the RHF/6-31G* and MP2/6-31G** approximations and assignment of experimental frequencies for methyldicyanophosphine[a]

Symmetry type	Number of vibration	Quantum-chemical calculations						Frequency after scaling /cm^{-1}		Experimental frequency /cm^{-1}	Distribution of the potential energy of vibrations (%)[b]
		Frequency /cm^{-1}		Intensity			Depolarization ratio,				
				IR /km mol^{-1}		Raman /Å^4·(amu)$^{-1}$.					
		RHF	MP2	RHF	MP2	RHF	RHF	RHF	MP2		
A′	1	3334	3275	1.1	0.1	61.7	0.75	3023.6	3030.0	3022	CH_3 as.str (100)
	2	3227	3146	5.6	1.0	106.9	0.01	2926.7	2910.9	2929	CH_3 s.str (99)
	3	2575	2136	1.0	14.7	106.1	0.12	2186.0	2186.7	2187	C≡N s.str (94) PC(N) s.str (6)
	4	1602	1514	9.0	8.0	17.8	0.72	1413.8	1412.6	1416	CH_3 as.def (94) CH_3 rock (6)
	5	1498	1396	1.3	1.7	0.7	0.10	1300.0	1300.0	1300	CH_3 s.def (100)
	6	1037	972	26.0	23.0	3.9	0.59	921.8	921.0	922	CH_3 rock (87) CH_3 as.def (5) $PC(H_3)$ wag (5)
	7	749	726	12.4	12.7	21.3	0.33	687.2	687.0	687	$PC(H_3)$ str (92) PC(N) s.str (5)
	8	653	627	32.5	19.9	8.9	0.09	587.7	590.3	589	PC(N) s.str (63) CPC bend (14) PCN s.bend (11) $PC(H_3)$ str (7)
	9	511	459	0.2	0.4	2.6	0.57	458.0	455.9	459	CPC bend (37) PCN s.bend (30) PC(N) s.str (26) PC(N) s.tors (6)
	10	479	422	0.4	1.4	0.6	0.67	422.1	423.1	430	$PC(H_3)$ wag (46) PC(N) s.tors (42) PCN s.bend (8)
	11	186	160	13.2	9.4	3.9	0.64	163.8	161.4	155	$PC(H_3)$ wag (46) PC(N) s.tors (26) PCN s.bend (23)
	12	125	109	10.3	8.0	7.4	0.74	111.8	110.6	103	CPC bend (43) PCN s.bend (28) PC(N) s.tors (25)
A″	13	3310	3253	2.0	0.3	89.3	0.75	3001.6	3010.1	3001	CH_3 as.str′ (100)
	14	2573	2136	3.4	35.1	55.1	0.75	2188.0	2187.2	2187	C≡N as.str (95) PC(N) as.str (5)
	15	1607	1522	10.7	9.1	11.9	0.75	1418.2	1419.4	1416	CH_3 as.def′ (94) CH_3 rock′ (6)
	16	1026	962	29.1	26.4	1.0	0.75	911.2	912.0	911	CH_3 rock′ (85) $PC(H_3)$ twist (8) CH_3 as.def′ (6)
	17	670	648	59.3	31.7	1.3	0.75	601.0	599.8	600	PC(N) as.str (91) C≡N as.str (5)
	18	448	392	0.7	0.4	2.7	0.75	394.7	394.4	—	PC(N) as.tors (48) $PC(H_3)$ twist (34) PCN as.bend (11)
	19	355	305	4.3	2.4	0.2	0.75	314.3	315.4	316	PCN as.bend (83) PC(N) as.tors (12)
	20	203	187	0.1	0.1	0.4	0.75	181.5	179.9	179	CH_3 tors (88) PCN as.bend (5)
	21	176	156	0.00	0.01	4.3	0.75	154.9	155.7	145	$PC(H_3)$ twist (53) PC(N) as.tors (36) CH_3 tors (8)

[a] See footnote "*a*" to Table 6.
[b] The results obtained after scaling the force field calculated in the MP2/6-31G** approximation.

symmetric stretching modes of the C≡N bonds (ν_3 (A′) and ν_{14} (A″), respectively, see Table 9) are almost degenerate. The band at ~2190 cm^{-1}, which is of medium intensity in the IR spectrum and very strong and

Table 10. Spectral parameters of methyldiisocyanophosphine calculated in the RHF/6-31G* and MP2/6-31G** approximations and vibrational frequencies predicted after scaling procedure[a]

Symmetry type	Number of vibration	Quantum-chemical calculation						Frequency after scaling /cm^{-1}		Distribution of the potential energy of vibrations (%)[b]
		Frequency /cm^{-1}		Intensity			Depolarization ratio,			
				IR /km mol^{-1}		Raman /$Å^4 \cdot (amu)^{-1}$,				
		RHF	MP2	RHF	MP2	RHF	RHF	RHF	MP2	
A′	1	3321	3271	3.8	0.2	62.5	0.75	3012	3026	CH_3 as.str (100)
	2	3218	3142	5.6	0.4	106.5	0.01	2919	2907	CH_3 s.str (100)
	3	2368	2098	299.4	118.8	121.4	0.12	2012	2149	N=C: s.str (95) PN s.str (5)
	4	1600	1509	7.5	7.8	19.2	0.71	1412	1407	CH_3 as.def (94) CH_3 rock (6)
	5	1495	1394	8.4	9.3	0.6	0.18	1299	1298	CH_3 s.def (99)
	6	1029	968	41.7	36.0	4.3	0.58	915	918	CH_3 rock (82) $PC(H_3)$ wag (9) CH_3 as.def (5)
	7	769	740	46.8	33.9	18.6	0.36	703	700	$PC(H_3)$ str (90) PN s.str (5)
	8	696	659	73.6	60.7	8.2	0.08	627	615	PN s.str (77) NPN bend (9) $PC(H_3)$ str (5)
	9	452	423	13.3	8.3	0.7	0.54	406	419	NPN bend (45) PNC s.bend (23) $PC(H_3)$ wag (16) PN s.str (12)
	10	398	376	13.4	9.1	0.3	0.66	353	372	$PC(H_3)$ wag (49) PN s.tors (26) NPN bend (19)
	11	173	158	1.3	4.1	3.0	0.59	153	162	PNC s.bend (53) $PC(H_3)$ wag (24) PN s.tors (20)
	12	117	109	2.4	5.3	7.8	0.74	104	111	PN s.tors (53) NPN bend (23) PNC s.bend (22)
A″	13	3299	3252	5.3	0.5	88.3	0.75	2992	3009	CH_3 as.str′ (100)
	14	2344	2090	706.1	297.5	54.0	0.75	1990	2143	N=C: as.str (96) PN as.str (4)
	15	1602	1513	10.3	9.7	13.6	0.75	1414	1411	CH_3 as.def′ (94) CH_3 rock′ (6)
	16	1007	945	39.6	38.3	1.2	0.75	894	895	CH_3 rock′ (85) $PC(H_3)$ twist (9) CH_3 as.def′ (6)
	17	702	663	169.4	123.7	2.0	0.75	630	612	PN as.str (94) N=C: as.str (4)
	18	352	337	0.7	0.4	0.8	0.75	311	335	$PC(H_3)$ twist (53) PN as.tors (23) PNC as.bend (16) CH_3 rock′ (5)
	19	246	236	0.04	0.1	0.4	0.75	218	240	PNC as.bend (60) PN as.tors (22) CH_3 tors (15)
	20	212	199	0.02	0.2	0.5	0.75	189	195	CH_3 tors (81) PNC as.bend (18)
	21	168	156	0.000	0.002	4.2	0.75	148	157	PN as.tors (54) $PC(H_3)$ twist (35) PNC as.bend (6)

[a] See footnote "*a*" to Table 6.
[b] The results obtained after scaling the force field calculated in the MP2/6-31G** approximation.

polarized in the Raman spectrum, was assigned to both these motions. Since, according to quantum-chemical calculations, the ν_3 band in the Raman spectrum must be much more intense than the ν_{14} band, it is not surprising that the observed band at 2190 cm^{-1} remains polarized. We revised the assignment of antisymmetric stretching modes of the methyl group corresponding to the A′ and A″ symmetry types (ν_1 and ν_{13}, respectively) and that of a number of low-frequency modes. The band at ~180 cm^{-1} depolarized in the Raman spectrum was assigned to the ν_{20} torsional mode of methyl group, which is in good agreement with the estimate of the fundamental frequency of torsional transition obtained on the basis of the solution of the direct one-dimensional problem of internal rotation in the $MeP(CN)_2$ molecule using quantum-chemical data (see above).

The motions of the methyl group including its torsional mode, and the skeletal stretching modes, except for the symmetric stretching mode of the P—C bonds, exhibit virtually no mixing. On the contrary, according to our calculations, the skeletal deformation modes are strongly mixed with each other, and therefore traditional assignment of the four fundamental frequencies of the A′ symmetry type (ν_9 to ν_{12} vibrations) would be too conditional. The fact that a depolarized band in the gas-phase Raman spectrum[5] was recorded for one of them (ν_{11}) can be explained both by the high noise level discussed above,[6] which hampers experimental measurements, and by a fairly large depolarization ratio (the calculated value is 0.64, see Table 9).

One of the three fundamental frequencies of the A″ symmetry type corresponding to the skeletal deformation modes (ν_{18}, see Table 9) was not revealed in the experimental spectra of $MeP(CN)_2$. It is likely that one fails in detecting this frequency in the corresponding region of the Raman spectrum in the crystalline phase (~400 cm^{-1}) because of its low intensity against a background of the noise (see Fig. 4). The depolarized bands at ~320 cm^{-1} and at ~150 cm^{-1} in the Raman spectrum correspond to two other rather pure A″ modes (the ν_{19} antisymmetric bending mode of the nonlinear P—C≡N fragments and the ν_{21} twisting mode of the P—C(H_3) bond, respectively).

As has been suggested previously,[5,6] the band at ~630 cm^{-1}, which is strong and polarized in the Raman spectrum in the liquid phase, can be assigned to the intermolecular P...N interaction, and the peaks at 60 and 40 cm^{-1} in the Raman spectrum in the crystalline phase can be assigned to lattice vibrations (see Table 5).

Calculated spectral parameters of the $MeP(NC)_2$ molecule

The vibrational frequencies, intensities of IR and Raman bands, and depolarization ratios calculated for the methyldiisocyanophosphine molecule in the RHF and MP2 approximations are listed in Table 10. The quantum-chemical force fields were transformed to a system of internal coordinates of local symmetry, which is similar to that introduced for $MeP(CN)_2$ (see Table 6). Then, they were scaled using the refined values of scale factors for methyldicyanophosphine (see Table 7) under assumption of their transferability for analogous internal coordinates.

The approximate character of the scale factors introduced for internal coordinates of the P—N=C: fragment should affect the resulting frequencies. Nevertheless, considerable discrepancies (to 150 cm^{-1}) between the frequencies calculated for two versions of scaled force field (RHF and MP2, see Table 10) are observed only for the N=C: stretching modes (ν_3 and ν_{14}, see Table 10). The discrepancies in other frequencies are small and do not exceed 20—25 cm^{-1}. It should also be noted that as for $MeP(CN)_2$ the calculated frequencies of the ν_{20} torsional mode of the methyl group (189—195 cm^{-1}, see Table 10) agree well with the values obtained on the basis of the solution of the direct one-dimensional problem (182—194 cm^{-1}, see Table 4). Thus, most of the fundamental frequencies obtained in our calculations for the $MeP(NC)_2$ molecule except for those of the ν_3 and ν_{14} stretching modes can be considered to be rather reliable.

The same conclusion is also valid for the scaled force fields for the $MeP(NC)_2$ molecule. Their general structure is close to that of the force fields for the $MeP(CN)_2$ molecule considered in Table 8. The force constants of the vibrations of the methyl fragment and those of the torsional vibrations virtually coincide. The scaled force constants of the P—C(H_3), P—N, and N=C: stretching vibrations are equal to 3.0, 3.3—3.6, and 15—17 mdyn $Å^{-1}$, respectively, and the constants of the (H_3)C—P—N, N—P—N, and P—N=C: bending vibrations are equal to 1.1—1.2, 1.3, and 0.15 mdyn Å, respectively.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-32660a).

References

1. L. S. Khaikin, E. A. Zhilinskaya, O. E. Grikina, and L. V. Vilkov, *Izv. Akad Nauk, Ser. Khim.*, 1996, 1104 [*Russ. Chem. Bull.*, 1996, **45**, 1043 (Engl. Transl.)].
2. L. S. Khaikin, E. A. Zhilinskaya, O. E. Grikina, M. V. Proskurnina, and L. V. Vilkov, *J. Mol. Struct.*, 1995, **356**, 239.
3. L. Maier, *Helv. Chim. Acta*, 1963, **46**, 2667.
4. D. Britton, in *Perspectives in Structural Chemistry*, Wiley, New York, 1967, **1**.
5. H. G. M. Edwards, J. S. Ingman, and D. A. Long, *Spectrochim. Acta*, 1976, **32A**, 739.
6. H. G. M. Edwards and V. Fawcett, *Spectrochim. Acta*, 1989, **45A**, 147.
7. R. Meyer, *J. Mol. Spectrosc.*, 1979, **76**, 266.
8. A. V. Abramenkov and Yu. N. Panchenko, *Zh. Fiz. Khim.*, 1995, **69**, 1043 [*Russ. J. Phys. Chem.*, 1995, **69** (Engl. Transl.)].
9. A. V. Abramenkov, *Zh. Fiz. Khim.*, 1995, **69**, 1048 [*Russ. J. Phys. Chem.*, 1995, **69** (Engl. Transl.)].

10. M. A. Harthcock and J. Laane, *J. Mol. Spectrosc.*, 1982, **91**, 300.
11. P. Pulay, G. Fogarasi, F. Pang, and J. E. Boggs, *J. Am. Chem. Soc.*, 1979, **101**, 2550.
12. G. Fogarasi and P. Pulay, in *Vibrational Spectra and Structure*, Ed. J. R. Durig, Elsevier, Amsterdam, 1985, **14**, 125.
13. M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. J. Johnson, H. B. Schlegel, M. A. Robb, E. S. Peplogle, R. Gomperts, J. L. Anders, K. Raghavachari, J. S. Binkley, C. Gonzales, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, *GAUSSIAN 92, Revision C*, Gaussian Inc., Pittsburgh (PA), 1992.
14. S. V. Krasnoshchekov, A. V. Abramenkov, and Yu. N. Panchenko, *Zh. Fiz. Khim.*, 1997, **71**, 497 [*Russ. J. Phys. Chem.*, 1997, **71** (Engl. Transl.)].
15. S. V. Krasnoshchekov, A. V. Abramenkov, and Yu. N. Panchenko, *Vestn. Mosk. Univ., Ser. 2: Khimiya*, 1985, **26**, 29 [*Moscow Univ Bull., Ser. 2, Chem.*, 1985, **26** (Engl. Transl.)].
16. B. Uznanski and W. J. Stec, *Synthesis*, 1975, 735.
17. E. N. Guryanova, I. P. Goldshtein, and I. P. Romm, *Donorno-aktseptornaya svyaz'* [*Donor-Acceptor Bond*], Khimiya, Moscow, 1973 (in Russian).
18. *Preparativnaya organicheskaya khimiya* [*Preparative Organic Chemistry*], Ed. N. S. Vul'fson, Khimiya, Moscow, 1964 (in Russian).
19. C. E. Jones and K. J. Coskran, *Inorg. Chem.*, 1971, **10**, 1536.
20. M. T. Nguen, P. J. Groarke, S. Malone, and A. F. Hegarty, *J. Chem. Soc., Perkin Trans. 2*, 1994, 807.
21. W. J. Hehre, L. Radom, P. V. R. Schleyer, and J. A. Pople, *Ab initio Molecular Orbital Theory*, J. Wiley, New York, 1986.
22. M. H. Baghal-Vayjovee, J. L. Collister, and H. O. Pritchard, *Can. J. Chem.*, 1977, **55**, 2634.
23. M. T. Nguen, *Chem. Phys. Lett.*, 1989, **157**, 430.
24. L. S. Khaikin and L. V. Vilkov, *Usp. Khim.*, 1971, **40**, 2174 [*Russ. Chem. Rev.*, 1971, **40** (Engl. Transl.)].
25. V. A. Naumov and L. V. Vilkov, *Molekulyarnye struktury fosfororganicheskikh soedinenii* [*Molecular Structures of Organophosphorus Compounds*], Nauka, Moscow, 1986 (in Russian).
26. I. I. Patsanovskii, E. A. Ishmaeva, G. V. Romanov, V. N. Volkova, E. N. Strelkova, and A. N. Pudovik, *Dokl. Akad. Nauk SSSR*, 1980, **255**, 383 [*Dokl. Chem.*, 1980 (Engl. Transl.)].
27. R. Meyer and Hs. H. Gunthard, *J. Chem. Phys.*, 1968, **49**, 1510.
28. J. D. Lewis, T. B. Malloy, T. H. Chao, and J. Laane, *J. Mol. Struct.*, 1972, **12**, 427.
29. H. G. M. Edwards, J. S. Ingman, and D. A. Long, *Spectrochim. Acta*, 1976, **32A**, 731.
30. H. G. M. Edwards and V. Fawcett, *Spectrochim. Acta*, 1987, **43A**, 1345.
31. L. S. Khaikin and O. E. Grikina, *17th Austin Symposium on Molecular Structure*, Austin (Texas, USA), 1998, 115, S11.
32. L. S. Khaikin, O. E. Grikina, V. I. Perevozchikov, V. A. Shlyapochnikov, and J. E. Boggs, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1557 [*Russ. Chem. Bull.*, 1998, **47**, 1514 (Engl. Transl.)].

Received February 25, 1998