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Dedicated to the 90th Anniversary of Corresponding Member of the Russian Academy of Sciences A.N. Pudovik

Conformational Analysis of Mono- and Bis(dimethoxyphosphoryl)benzenes

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Abstract—Conformational analysis of mono- and bis(dimethoxyphosphoryl)benzenes with substituents in the benzene ring was performed by the method of dipole moments, IR spectroscopy, and quantum-chemical calculations (DFT B3LYP/6-31G*). Comparison of all calculated and experimental data shows that the compounds studied exist as equilibrium mixtures of conformers with preferred *gg* orientation of the phosphoryl and methoxy groups.

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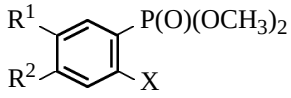
Correlation between the steric and electronic structure of molecules and their reactivity is one of the most important problems of organic and physical chemistry. Since most chemical reactions proceed in the liquid phase, of particular importance is to establish the structure of molecules in solutions. One of the most important physical methods of structural investigations in solution is the method of dipole moments. In combination with IR spectroscopy this method provides reliable and extensive information for conformational analysis of complex organophosphorus compounds [1]. At present a great deal of experimental evidence has been accumulated for these compounds. At the same time, there have been few works on theoretical substantiation of existing conformations, especially in polyfunctional organophosphorus compounds, even though the interest in this problem has quickened in recent years [2].

In this work we performed an experimental and a theoretical conformational analysis of mono- and bis(dimethoxyphosphoryl)benzenes **I**–**III** by means of dipole moment measurements, IR spectroscopy, and B3LYP/6-31G* hybrid density functional calculations.

The experimental dipole moments of compounds **I**–**III** and those calculated by the vector additive scheme are listed in Table 1. From a comparison of the experimental dipole moment of phosphonate **I** and those calculated by the vector additive scheme for all possible conformers (Table 1) it follows that in nonpolar solvents several conformational equilibria can take place: g_1g_1 and g_1g_2 forms with preference for the first one (70%), g_1g_1 and tg_1 (74 : 26), and g_1g_2 and tg_2 (56 : 44). In bis(dimethoxyphosphoryl)benzene **II**, three types of equilibria can exist: g_1g_1 and g_1g_2, tg_1 and tg_2, and g_1g_2 and tg_2. In bisphosphonate **III**, too, three types of equilibria involving *gauche* and *trans* conformers are possible. The dipole moments of possible conformers of compounds **I**–**III** were calculated using the bond moments presented in [1].



I–**III**

$R^1 = R^2 = CH_3$, X = Cl (**I**); R^1 = H, $R^2 = CH_3$, X = $P(O)(OCH_3)_2$ (**II**); $R^1 = R^2 = CH_3$, X = $P(O)(OCH_3)_2$ (**III**).

To find out whether monophosphonate **I** is conformationally homogeneous, we have studied its IR spectra recorded in KBr pellets (Fig. 1) and methylene

Table 1. Experimental (benzene, 25°C) and calculated dipole moments and orientation polarizations of compounds **I**–**III**[a]

Comp. no.	μ_{exp}, D	μ_{calc}, D				P_{op}	α	γ
		g_1g_1	g_1g_2	tg_1	tg_2			
I	3.38	3.59	2.90	4.48	3.91	233.511	5.058	0.062
II	3.90	4.05	2.97	4.53	3.55	310.221	5.513	0.158
III	3.81	4.24	3.10	4.61	3.54	297.307	5.287	0.373

[a] (α, γ) Coefficients of calculation equations.

chloride solution (Fig. 2). It follows from these spectra that P=O stretching vibrations are independent of the aggregative state. The P–O(C) group gives two ill-resolved bands (1060 and 1038 cm^{-1} in mineral oil and 1058 and 1034 cm^{-1} in CH_2Cl_2 solution). In the spectrum in CH_2Cl_2, these bands are resolved better, implying that the compound is present as an equilibrium mixture of two conformers.

The energies of possible conformers of compounds **I**–**III** and their theoretical dipole moments were obtained by B3LYP/6-31G* calculations (Table 2). For phenylphosphonate **I** the calculations give four conformers (Fig. 3) with noneclipsed orientation of the methoxy fragments with respect to the phosphoryl group. As to the relative orientation of the phenyl and P=O groups, the energetically most favorable conformer **Ia** (g_1g_1) has the aromatic ring coplanar to the P=O group. In conformers **Ib**–**Id**, the phenyl ring is eclipsing the P–O bond.

In conformation **Ia**, the C–Cl bond is *trans* to the P=O bond, and in conformations **Ib**–**Id**, the same orientation takes place with respect to the single P–O bond. This is evidently connected with the repulsive interaction of the chlorine and oxygen atoms.

For theoretical interpretation of the experimental IR spectra, we compared them with the calculated frequencies and vibration shapes of conformers **Ia**–**Id**, calculated by the B3LYP/6G* method (Table 3). The calculation fairly well fits the experimental spectral data. The theoretical frequencies differ from experimental by 1–20 cm^{-1}, which is 0.1–3.3% error.

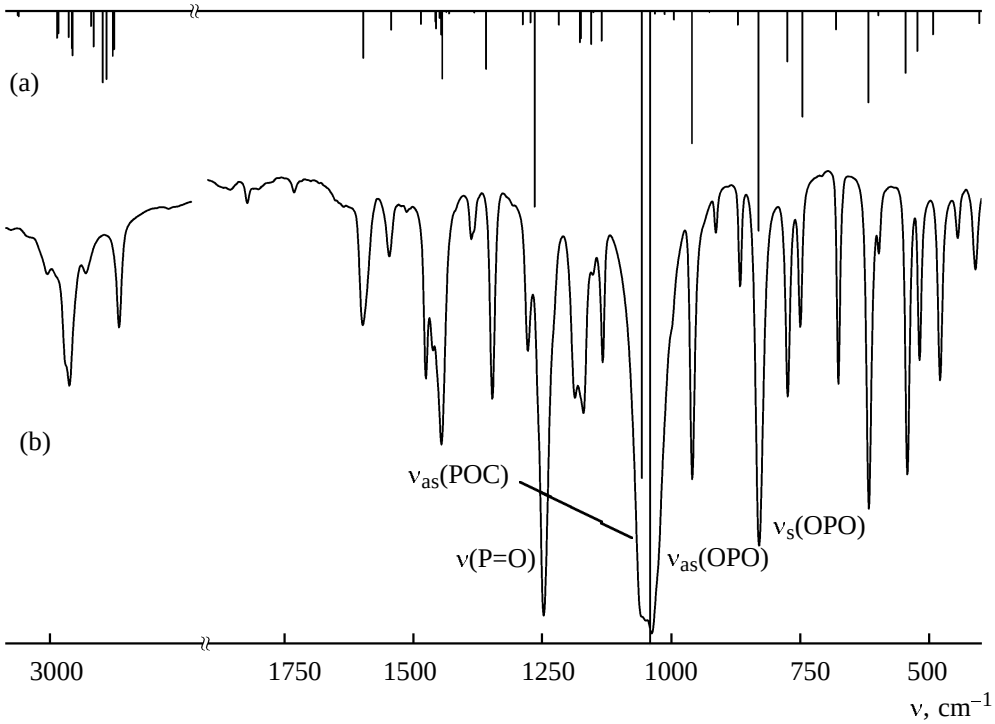


Fig. 1. IR spectra of compound **I**: (a) theoretical and (b) recorded in KBr.

Comparison of the calculated frequencies of conformers (Table 3) shows that the IR spectra are hardly sensitive to rotational isomerism in compound **I** about the P–C_{Ph} bond. At the same time, the vibration frequencies depend on the conformation of the methoxyl fragment. For example, the calculated ν(P=O) values for the *gg* and *tg* conformers significantly differ from each other (Table 3). However, the experimental IR spectra remain almost invariable in going from the solid aggregative state (KBr pellets, Fig. 1) to liquid (CH_2Cl_2 solution) (Fig. 2). Therewith, the ν(P=O) band remains singlet, implying that only of one of the two above groups of conformers is present in the solution. Evidently, they are the energetically more favorable (according to B3LYP/6-31G* calculations) *gg* conformers. The calculated spectra of

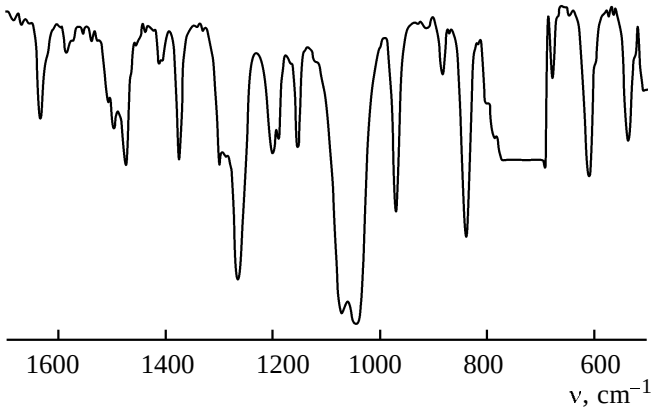


Fig. 2. IR spectrum of compound **I** in CH_2Cl_2.

Table 2. Relative energies and theoretical (μ_{theor}, B3LYP/6-31G*) and calculated by the vector additive scheme (μ_{calc}) dipole moments of conformers of compounds **I**–**III**

Conformers	ΔE, kcal mol^{-1}	μ_{theor}, D	μ_{calc}, D
Ia	0	2.22	2.31
Ib	1.48	3.26	4.21
Ic	1.49	4.00	4.82
Id	3.09	5.89	5.83
IIa	0	1.65	3.24
IIb	1.23	4.55	5.56
IIc	1.48	3.14	4.92
IId	1.97	1.77	2.38
IIIa	0	2.10	3.56
IIIb	1.16	4.43	5.47
IIIc	1.42	3.00	4.82
IIId	1.97	1.60	2.09

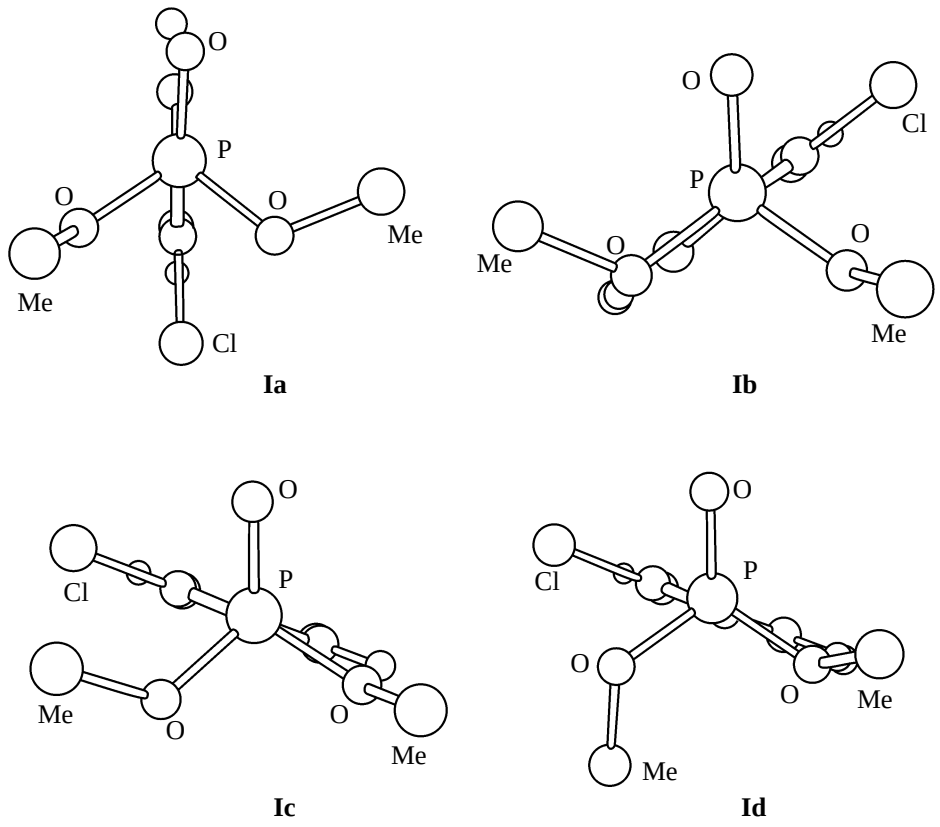


Fig. 3. Conformers of compound **I**.

Table 3. Vibration spectra of conformers **Ia, Ib**, and **Id**, calculated by the B3LYP/6-31G* method

Experimental frequencies ν, cm^{-1}		Calculated frequencies (B3LYP/6-31G*)			Assignment
solid phase (KBr), ν, cm^{-1}	CH_2Cl_2 solution	**Ia**	**Ib**	**Id**	
3060 sh	3056 sh	3071 (3)	3090 (2)	3085 (3)	$\nu_s(C_{Ar}–H)$
		3069 (4)	3071 (4)	3071 (4)	
3008 w	2984 m	2987 (18)	2984 (14)	2987 (12)	$\nu_{as}(CH_3)$ (O)
		2984 (15)	2983 (9)	2981 (21)	
2961 m	2968 m	2962 (18)	2965 (26)	2962 (21)	ν_{as}(CH2) (O)
		2955 (3)	2956 (21)	2955 (10)	$\nu_{as}(CH_3)$ (C_{Ar})
		2955 (25)	2954 (6)	2952 (22)	$\nu_{as}(CH_3)$ (C_{Ar})
		2954 (30)	2952 (26)	2946 (27)	$\nu_{as}(CH_3)$ (O)
2925 w	2900 w	2909 (24)	2910 (25)	2915 (9)	$\nu_{as}(CH_2)$ (C)
		2914 (10)	2914 (9)	2910 (24)	
		2889 (48)	2891 (62)	2888 (55)	$\nu_s(CH_3)$ (O)
		2881 (45)	2884 (49)	2879 (36)	
2854 m	2852 m	2868 (30)	2868 (32)	2868 (30)	$\nu_s(CH_3)$ (C_{Ar})
		2865 (26)	2866 (25)	2865 (24)	
1600 m	1600 m	1599 (31)	1600 (27)	1599 (29)	ν_{8a} [a]
1549 w	–	1545 (13)	1548 (8)	1544 (9)	ν_{8b} [a]
1478 m	1470 m	1487 (12)	1488 (10)	1485 (27)	$\delta_{as}(CH_3$ (C_{Ar})
1464 sh	1462 sh	1459 (9)	1460 (6)	1461 (8)	$\delta_{as}(CH_3)$ (O)
		1458 (7)	1457 (6)	1456 (7)	
		1451 (5)	1454 (8)	1450 (3)	
1447 m	1448 m	1449 (45)	1450 (7)	1450 (8)	$\delta_{as}(CH_3)$ (C_{Ar})
		1447 (16)	1447 (41)	1446 (7)	
		1446 (7)	1447 (7)	1446 (45)	$\delta_s(CH_3)$ (O)
		1440 (2)	1443 (5)	1442 (0)	
		1438 (1)	1437 (1)	1438 (3)	$\delta_{as}(CH_3)$ (C_{Ar})
		1433 (0)	1433 (0)	1432 (0)	
1390v.w	1388v.w	1394 (0)	1394 (0)	1394 (0)	$\delta_s(CH_3)$ (C_{Ar})
1384 sh	1380 sh	1384 (1)	1385 (2)	1385 (1)	$\delta_s(CH_3)$ (C_{Ar})
1349 m	1352 m	1361 (39)	1365 (40)	1364 (40)	ν_{19} [a]
1280 w	1280 w	1290 (9)	1282 (1)	1280 (2)	ν_{14} [a]
1249 v.s	1246 v.s	1275 (130)	1280 (98)	1304 (173)	ν(P=O)
		1267 (8)	1272 (12)	1270 (15)	$\gamma(C_{Ar}–H)$
		1220 (9)	1220 (50)	1220 (5)	$\nu(C_{Ar}–H)$
1189 m	1184 m	1179 (21)	1187 (17)	1176 (16)	$\rho(CH_3)$ (O)
		1177 (18)	1178 (18)	1175 (15)	
1172 m	1170 m	1166 (22)	1165 (12)	1166 (8)	$\nu(C_{Ar}–C)$
1155 sh	1153 sh	1157 (1)	1155 (2)	1156 (2)	$\rho(CH_3)$ (O)
		1153 (1)	1154 (2)	1155 (2)	
1135 w	1140 m	1137 (20)	1140 (42)	1138 (46)	$\nu(C_{Ar}–Cl)$
1060 sh	1058 sh	1059 (311)	1062 (426)	1058 (212)	$\nu_{as}(P–O–C)$
		1058 (0)	1058 (0)	1057 (0)	$\rho(CH_3)$ (C_{Ar})
1040 v.s	1034 v.s	1043 (422)	1039 (307)	1037 (386)	$\nu_{as}(P–O–C)$
		1034 (2)	1034 (7)	1034 (5)	$\rho(CH_3)$ (C_{Ar})
		1015 (2)	1016 (0)	1016 (1)	
		997 (6)	998 (9)	997 (8)	
961 s	978 s	962 (88)	955 (55)	957 (75)	$\nu(C_{Ar}–Cl)$, $\nu(C_{Ar}–P)$, ring [b]

Table 3. (Contd.)

Experimental frequencies ν, cm^{-1}		Calculated frequencies (B3LYP/6-31G*)			Assignment
solid phase (KBr), ν, cm^{-1}	CH_2Cl_2 solution	**Ia**	**Ib**	**Id**	
916 v.w	914 v.w	928 (1)	910 (3)	911 (3)	$\gamma(C_{Ar}–H)$
869 w	876 w	873 (9)	872 (1)	874 (10)	$\gamma(C_{Ar}–H)$
832 s	836 s	833 (146)	821 (118)	818 (127)	$\nu_{as}(O–P–O)$
776 m	–	777 (71)	763 (117)	751 (138)	$\nu_{s}(O–P–O)$
752 m	Solvent[c]	748 (34)	752 (17)	758 (15)	Ar[b]
–		707 (0)	706 (1)	707 (0)	
678 m	680 w	683 (13)	689 (5)	685 (3)	$\nu(C_{Ar}–Cl)$, $\nu(C_{Ar}–P)$, Ar[b]
619 s	615 m	620 (61)	617 (51)	614 (19)	
600 sh	600 sh	601 (3)	600 (16)	601 (3)	Ar[b]
544 s	542 m	548 (41)	551 (43)	550 (41)	
521 m	Solvent[c]	525 (27)	530 (3)	514 (10)	
481 m		495 (16)	475 (9)	482 (23)	Deformation vibrations of the $P(O)(OMe)_2$ group
		452 (0)	467 (10)	439 (4)	

[a] The vibration shapes of the aromatic fragment were labeled by Whilson's indices [3]. [b] Vibrations of the aromatic fragment. [c] Complete solvent absorption.

the *gg* conformers are practically indistinguishable (Table 3).

Using of the method of dipole moments for a more detailed conformational analysis of compound **I** allows the following conclusions.

The dipole moments of conformers **Ia**–**Id** calculated quantum-chemically (μ_{theor}) and by the vector additive scheme (μ_{calc}) (Table 2) qualitatively agree with each other. Therefore, they both are suitable for comparisons with experimental values. The ratio of the possible conformers was calculated by Eq. (1). Since the relative energies of conformers **Ib** and **Ic** are close to each other (Table 2), they both can be present in the conformational mixture with equal probability. Therefore, the concentrations (*n*) of forms **Ib** and **Ic** can be assumed to be equal to each other.

$$\mu^2_{exp} = \mu^2_1(1 - n) + (\mu^2_2 + \mu^2_3)n. \quad (1)$$

Solving Eq. (1) with the experimental dipole moment of compound **I** and the dipole moments of conformers **Ia**–**Ic**, calculated by the vector additive scheme, leads us to a conclusion that conformer **Ia** is preferred.

$$11.42 = 5.33(1 - n) + (17.72 + 23.23)n,$$
$$\mu_1/(\mu_2 + \mu_3) = 80:20\%.$$

It is this conformer that is more favored by energy (Table 2). Solving Eq. (1) with the theoretical dipole moments obtained by the B3LYP/6-31G* method only slightly affects the conformer ratio in the mixture.

$$11.42 = 4.93(1 - n) + (10.63 + 16.00)n,$$
$$\mu_1/(\mu_2 + \mu_3) = 70:30\% \text{ (B3LYP/6-31G*)}.$$

Hence, the conformational equilibrium in monophosphonate **I** in solution and in the gas phase modeled by quantum-chemical calculations includes noneclipsed *gauche* forms differing from one another by the relative orientation of the aromatic fragment and the phosphoryl group.

Comparison of the available experimental and calculated evidence on the conformational behavior of molecule **I** points to a high predictive power of the B3LYP/6-31G* method. The same conclusion follows from the conformational analysis of compounds **II** and **III** (Figs. 4 and 5).

In all the conformers of molecules **II** and **III**, either g_1,g_1 or g_1,g_2 orientation of the methoxy groups with respect to the P=O bond is observed. But, like in **I**, the conformations of bis(dimethyl phosphonates) **II** and **III** differ from one another by the orientation of the dimethoxyphosphoryl groups with respect to the aromatic fragment.

In conformers **IId** and **IIId** with the energy 1.97 kcal mol^{-1}, the aromatic fragment and two di-

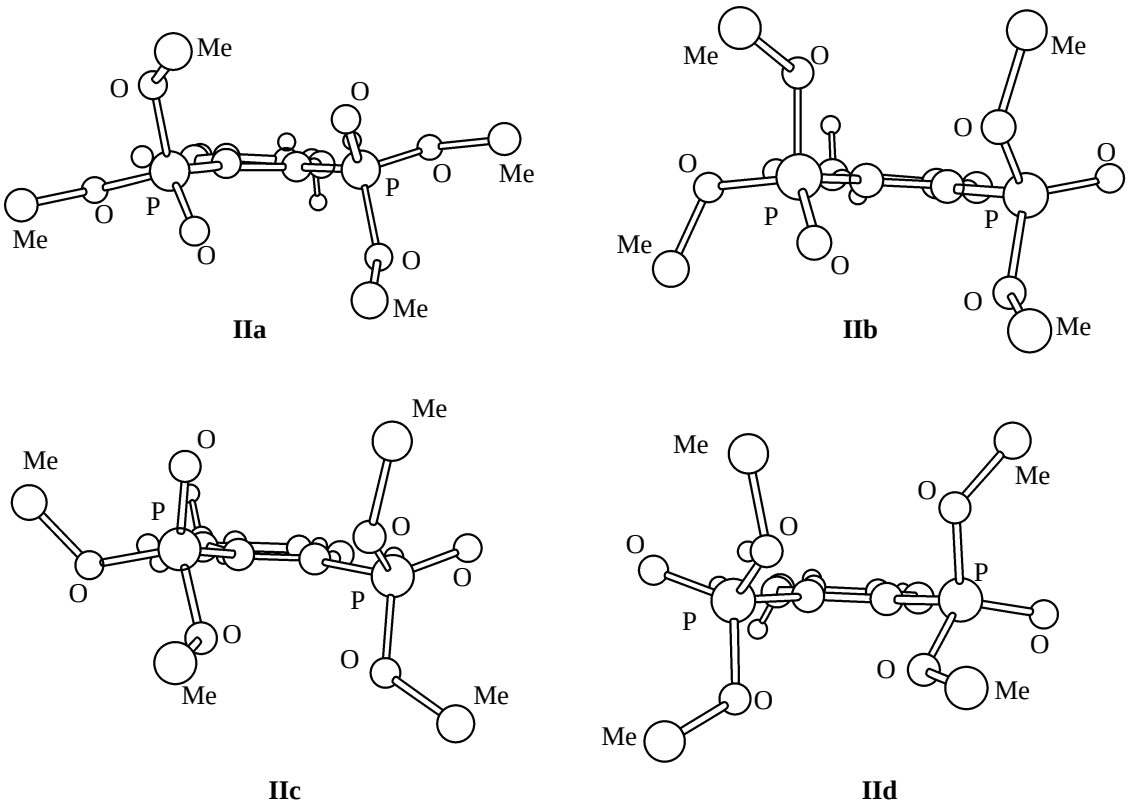


Fig. 4. Conformers of compound **II**.

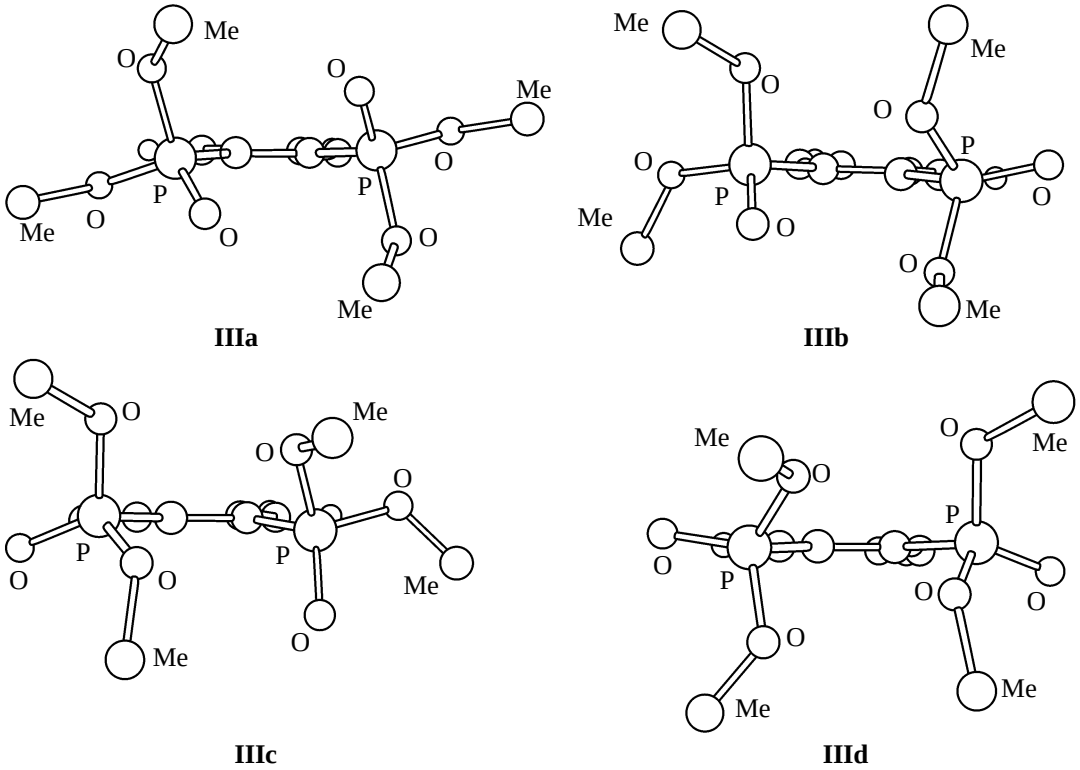


Fig. 5. Conformers of compound **III**.

methoxyphosphoryl P=O bonds are eclipsing each other. The dipole moments of the P=O bonds have opposite directions. In conformers **IIb, IIc, IIIb**, and **IIIc**, the aryl fragment is eclipsing the P=O bond of one of the dimethoxyphosphoryl groups. The other group is eclipsing the aromatic ring with its P–O bond with the C_{Ar}–C_{Ar}–P–O dihedral angle of 11° (Figs. 4 and 5).

Unlike compound **I** in which the energetically favorable conformer **Ia** has the P=O bond eclipsing the aromatic ring (Fig. 3), in compounds **II** and **III** in conformers with the energy 0.00 kcal mol^{-1}, there is an almost coplanar orientation of one of the dimethoxyphosphoryl P–O bonds and the aryl fragment, the C_{Ar}–C_{Ar}–P–O dihedral angles being 15° in conformer **IIa** and 6° in conformer **IIIa**. Evidently, the absence of eclipsed orientation of the P=O bond and phenyl fragment in the energetically favorable conformer of compounds **II** and **III** is connected with the steric repulsion of two bulky dimethoxyphosphoryl groups residing on the neighboring carbon atoms of the phenyl ring, as well as with interaction of bond dipole moments (Figs. 4 and 5).

EXPERIMENTAL

The IR spectra of phosphonates **I**–**III** in methylene chloride were registered on a Specord M-80 IR Fourier spectrometer. The thickness of the working layer was 0.01 cm, and the concentration of the solutions was 10^{-3} mM. The IR spectrum of phosphonate **I** in KBr was registered on a Bruker Vector-22 spectrometer.

Dimethyl (2-chloro-4,5-dimethylphenyl)phosphonate (**I**), 1,2-bis(dimethoxyphosphoryl)-5-methylbenzene (**II**), and 1,2-bis(dimethoxyphosphoryl)-4,5-dimethylbenzene (**III**) were prepared by the procedure in [4].

The experimental dipole moments of compounds **I**–**III** were measured in benzene at 25±0.2°C (Table 4) by the second Debye method based on the determination of the dielectric permeability of dilute solutions of compounds in a nonpolar solvent [5]. The solvent was purified by standard procedures [6] directly before measurements. The dielectric permeabilities of solutions were measured on an IDM-2 instrument [7] operating by the pulsation technique.

The refractive indices of solutions were measured on an IRF-23 refractometer with an accuracy of ±0.00001 for the D line of sodium.

The vibration spectra were calculated by Eq. (2) [8]:

$$GFL = L\Lambda, \quad (2)$$

where G is the kinetic energy matrix of the molecule in the pulse presentation; and F, potential energy matrix. Together the approximate character of the calculations and the harmonic approximation underlying Eq. (2) lead to appreciable systematic deviations of calculated frequencies from experiemntal. To correct these systematic errors, elements of the F matrix (force constants) were multiplied by correction scaling factors.

$$F_{ij}^{Scaled} = C_{ij}F_{ij},$$

where

$$C_{ij} = (C_{ii}C_{jj})^{1/2}.$$

The scaling factors empirically found for a series of phosphorus-containing molecules [9] were then used for calculation of vibrations of molecule **I** (Table 4).

Quantum-chemical calculations were carried out using the GAUSSIAN 98 program [12] by the B3LYP method with the 6-31G* basis set. The correspondence of stationary points to minima was always proved by calculating the second derivatives. The calculations were carried out on a computing cluster of 11 Althon 1200 processors (Kazan State Technical University) and a cluster of 9 Compac Alpha DS10L and DS 20E processors (Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences).

Table 4. Scaling factors for force fields used for calculation of the vibration spectra of molecule **I**

Vibrations	Internal coordinate	Scaling factor
Stretching	X–X	0.9207 [10]
	C_{Ar}–H	0.9150 [11]
	C_{aliph}–H	0.8890 [11]
	X–Y	1.0400 [10]
	P=O	1.0220 [9]
Deformation	X–C–H	0.9500 [10]
	H–C–H	0.9016 [10]
	X–X–X, X–X–Y	1.0144 [10]
	X–Y–X	1.0700 [9]
Out-of-plane	γ(CH)	0.9760 [10]
Torsion	All	0.9523 [10]
X = C, O; Y = P, Cl		

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