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Dipole Moments and Structure of *ortho*-Diphenyl(diethyl)phosphinoyl-substituted Benzyl Alcohols, Phenols, and Their Derivatives

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Abstract—The method of dipole moments and DFT B3LYP/6-31G* quantum-chemical calculations were used to study the structures of *ortho*-substituted aryl- and arylmethyldiphenyl(diethyl)phosphine oxides. It was established that methyl ethers of phosphorus-containing benzyl alcohols and phenols exist as equilibrium mixtures of several conformers with prevalence of forms with the weakest steric interactions. Preferred conformers of *o*-[(diethylphosphinoyl)methyl]benzyl alcohol and *o*-[(diphenylphosphinoyl)methyl]phenol contain an intramolecular hydrogen bond between the hydroxyl hydrogen atom and phosphinoyl oxygen atom.

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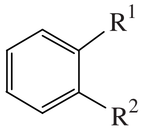
ortho-Substituted aryl- and arylmethyldiphenyl(diethyl)phosphine oxides are precursors of phosphorus-containing podands, acyclic analogs of crown ethers. Elucidation of the structure of such compounds is significant for studying complex formation with phosphorus-containing reagents. We measured the dipole moments of phosphine **I** and phosphine oxides **II**–**IX** in benzene (Table 1).



R^1 = CH$_2$OMe, R^2 = PPh$_2$ (**I**); R^1 = CH$_2$OMe, R^2 =P(O)Ph$_2$ (**II**); R^1 = CH$_2$OMe, R^2 = CH$_2$P(O)Ph$_2$ (**III**); R^1 = = OMe, R^2 = CH$_2$P(O)Et$_2$ (**IV**); R^1 = OMe, R^2 = CH$_2$P(O)Ph$_2$ (**V**); R^1 = CH$_2$OMe, R^2 = CH$_2$P(O)Et$_2$ (**VI**); R^1 = CH$_2$Br, R^2 = CH$_2$P(O)Et$_2$ (**VII**); R^1 = CH$_2$OH, R^2 = CH$_2$P(O)Et$_2$ (**VIII**); R^1 = OH, R^2 = CH$_2$P(O)Ph$_2$ (**IX**).

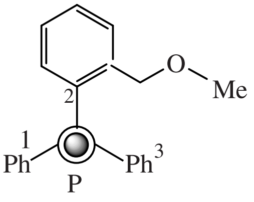
The dipole moments of these compounds fit the range of the dipole moments of tri- and tetracoordinate phosphorus compounds, listed in the handbook [1].

To interpret the experimental results, we performed DFT B3LYP/6-31G* quantum-chemical calculations of compounds **I**–**IX**. The calculated data are presented for those conformers whose relative energies are no higher than 3 kcal mol^{-1}.

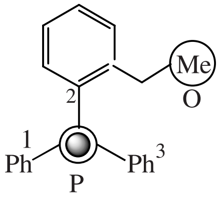
Below we depict the possible conformers of *o*-(methoxymethyl)diphenylphosphine (**I**) and *o*-(methoxymethyl)diphenylphosphine oxide (**II**).

Table 1. Coefficients of calculational equations, orientational polarizations, and experimental dipole moments of compounds **I**–**IX**

Comp. no.	α	γ	P_o, cm^3	μ_{exp}, D
I	1.269	0.315	54.987	1.63
II	5.671	0.319	324.691	3.96
III	6.162	0.264	373.803	4.25
IV	12.045	0.175	505.700	4.95
V	8.160	0.264	478.743	4.81
VI	8.629	0.115	385.670	4.32
VII	6.895	0.175	365.509	4.21
VIII	17.605	0.143	744.970	6.00
IX	13.369	0.221	666.449	5.68



a



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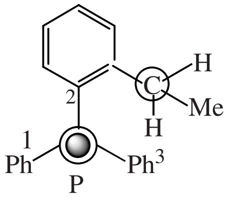

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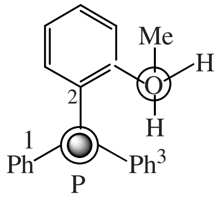

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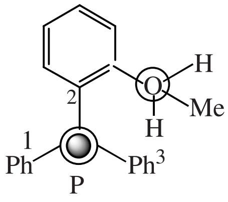


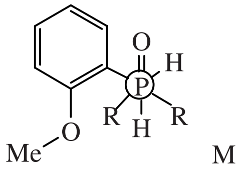
e

The relative energies of conformers of compounds **I** and **II** and their theoretical, vector-additive, and experimental dipole moments are listed in Table 2. Comparison of the experimental, vector-additive, and theoretical dipole moments of compounds **I** and **II** leads to a conclusion that in both cases we deal with a conformational equilibrium of several forms, but energetically preferable are conformers **Ia** and **IIa** with minimum steric interactions. Note that the difference in the dipole moments of the conformers is controlled by the steric arrangement of the $MeOCH_2$ group in the *ortho* position of the second benzene ring, since the dipole moment is insensitive to rotational isomerism at the P–C_{sp^2Ph} bond [2].

As follows from the data in Table 2, the energetically preferable conformer of phosphine **Ia** has all the three phenyl rings *synclinal* to the lone electron pair of P^{III}. The picture for phosphine oxide **II** is somewhat different. The conformer **IIa** with the energy 0 kcal mol^{-1} has only one phenyl ring arranged *gauche* to the P=O group (Table 2), while the other phenyl fragments are turned by 23°–25° from a position in which they are eclipsing the Ph and P=O groups.

We calculated possible conformers of *o*-[diphenylphosphinoyl)methyl]benzyl alcohol (**III**) and *o*-[diethylphosphinoyl)methyl]benzyl alcohol (**VI**). These calculations showed (Table 3) that compounds **III** and **VI** exist as equilibrium mixtures of conformers **a**–**c**, most contributed by conformers **IIIa** and **VIa**, respectively. In g^+g^+ conformer **VIa,** the ethyl groups are not eclipsing the P=O bond.

The data in Table 4 show that *o*-[(diethylphosphinoyl)methyl]anisole (**IV**) and *o*-[(diphenylphosphinoyl)methyl]anisole (**V**), too, are equilibrium mixtures of a series of conformers; therewith, the fractions of energetically (ΔE = 0 kcal mol^{-1}) preferred forms are **IV** 67.5 (**IV**) and 70% (**V**).



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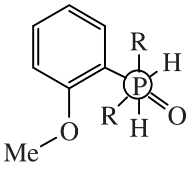

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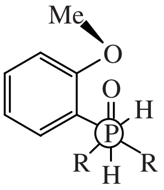

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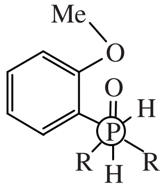

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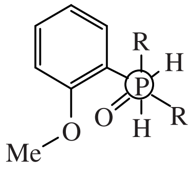

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Table 2. Relative energies, dipole moments (theoretical $\mu_{theor.}$, vector-additive $\mu_{calc.}$, and experimental $\mu_{exp.}$), and B3LYP/6-31G* dihedral angles C^1_{Ph}–C^2_{Ph}–P–Y (Y is the lone electron pair (**I**) or O atom (**II**)] for compounds **I** and **II**

Conformer	ΔE, kcal mol^{-1}	μ_{theor}, D	μ_{calc}, D	μ_{exp}, D	Dihedral angle, deg		
					$C^1_{Ph^1}$–$C^2_{Ph^1}$–P–Y	$C^1_{Ph^2}$–$C^2_{Ph^2}$–P–Y	$C^1_{Ph^3}$–$C^2_{Ph^3}$–P–Y
Ia	0	1.48	1.56	1.63	–34.3	–44.4	–36.1
Ib	0.10	1.63	1.51		–32.7	–48.4	–35.2
Ic	0.43	0.56	0.73		–37.4	–49.4	–27.9
Id	1.85	1.32	1.59		–27.1	–28.8	–60.2
Ie	2.23	1.93	2.31		–24.9	–30.3	–62.2
IIa	0	3.20	3.82	3.96	–23.4	–44.7	–25.4
IIb	0.54	3.71	4.27		–19.8	–53.7	–24.5
IIc	0.60	2.78	3.19		–26.4	–37.2	–30.4

Table 3. Relative energies and theoretical, vector-additive, and experimental dipole moments of compounds **III** and **VI**

Conformer	ΔE, kcal mol^{-1}	μ_{theor}, D	μ_{calc}, D	μ_{exp}, D
IIIa	0	3.54	4.21	4.25
IIIb	0.59	3.37	4.64	
IIIc	0.70	3.65	4.77	
VIa	0	3.58	4.32	4.32
VIb	1.88	3.42	4.74	
VIc	0.92	3.62	4.93	

Table 4. Relative energies and theoretical, vector-additive, and experimental dipole moments of compounds **IV** and **V**

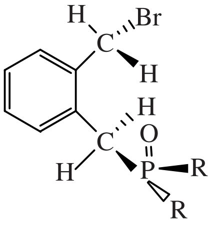
Conformer	ΔE, kcal mol^{-1}	μ_{theor}, D	μ_{calc}, D	μ_{exp}, D
IVa	0	4.85	4.74	4.95
IVb	0.56	5.29	5.36	
IVc	1.25	2.67	4.49	
IVd	1.33	2.27	4.37	
IVe	2.21	2.31	4.49	
Va	0	4.75	4.64	4.81
Vb	2.16	4.66	5.18	
Vc	1.54	2.85	4.23	
Vd	1.47	2.30	4.28	
Ve	1.49	2.30	4.23	

Table 5 Relative energies and theoretical, vector-additive, and experimental dipole moments of the conformers of compound **VII**

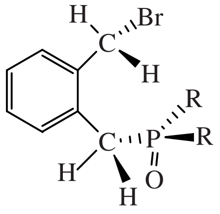
Conformer	ΔE, kcal mol^{-1}	μ_{theor}, D	μ_{calc}, D	μ_{exp}, D
VIIa	0.00	4.43	4.41	4.27
VIIb	1.58	2.76	4.52	

The energetically preferable conformer of *o*-[(diethylphosphinoyl)methyl)]benzyl bromide (**VII**) has the two bulky substituents at the neighboring carbon atoms of the benzene ring *trans* to each other (Table 5).

The results of quantum-chemical calculations for compounds **I**–**VII** are nicely consistent with the experimental dipole-moment data.

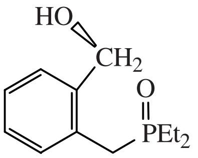


VIIa

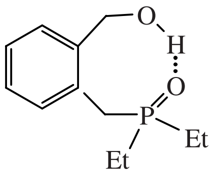


VIIb

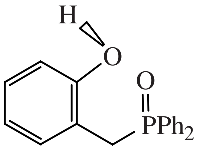
Previously Bondarenko [3] considered the IR spectra of phosphorus-containing *ortho* derivatives of benzyl alcohol **VIII** and phenol **IX** in CCl_4 and $CHCl_3$ solutions of varied concentration. The absence in the spectra of the free OH absorption band and the concentration independence of the intensity of the associated OH absorption band show that the only conformers of phosphine oxides **VIII** and **IX,** existing in the solutions, are those containing intramolecular hydrogen bonds between the OH and P=O groups, which close seven- and eight-membered rings (forms **VIIIb** and **IXb**).



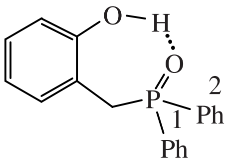
VIIIa



VIIIb

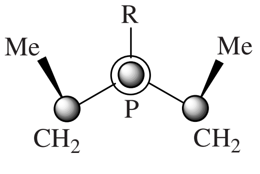


IXa

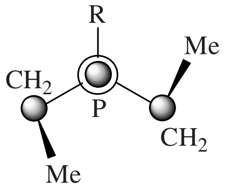


IXb

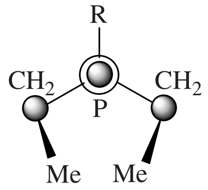
The presence of two ethyl groups at the phosphorus atom in *o*-(hydroxymethyl)phenyl-substituted phosphine oxide **VIII** complicates the conformational picture. Below are presented the Newman projections of the possible rotational isomers of compound **VIII**, R = $CH_2C_6H_4CH_2OH$.



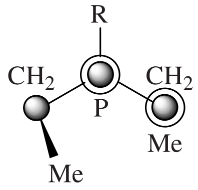
g^-g^+



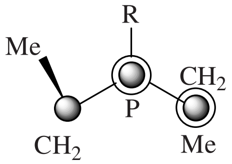
g^+g^+



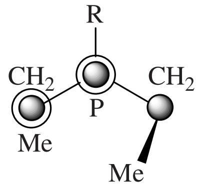
g^+g^-



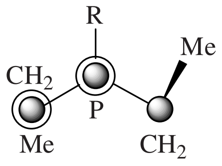
g^+t



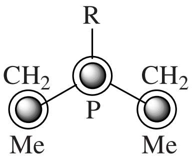
g^-t



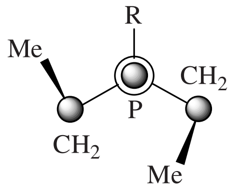
tg^-



tg^+



tt



g^-g^-

Table 6 lists the relative energies and experimental, theoretical, and vector-additive dipole moments of possible conformers of *o*-(phosphinoylmethyl)-substituted benzyl alcohol **VIII**. As seen from these data, the energy minimum corresponds to g^+g^+-conformer **VIIIb** with the eight-membered ring closed by an intramolecular H bond. The theoretical and vector-additive dipole moments the experimentally measured polarity of this compound (6.00 D). A similar situation, when intramolecular hydrogen bonding stabilizes specifically the same conformation, we observe earlier with 2-phosphinoyl-3-hydroxyacrylonitriles [4].

o-[(Diphenylphosphinoyl)methyl]phenol **IX,** too**,** exists as conformer **IXb** with an intramolecular H bond forming a seven-membered ring (Table 7). This conformer corresponds to an energy minimum, and the theoretical and vector-additive dipole moments fit the experimental dipole moment of this compound (5.68 D). According to the geometric parameters calculated by the DFT B3LYP/6-31G* method (Table 7), the phenyl rings at the phosphorus atom in **IXb** are almost eclipsing the P=O bond. Obviously, of key importance here are steric interactions, and preferred are the least sterically hindered conformations.

Thus, it was established by an analysis of the results obtained by the method of dipole moments and by quantum-chemical calculations that the preferable conformations of *o*-hydroxy-substituted aryldiphenyl- and aryldiethylphosphine oxides are those involving intramolecular hydrogen bonding the OH hydrogen and P=O oxygen atoms, forming a seven- or an eight-membered ring.

Table 6. Relative energies and theoretical, vector-additive, and experimental dipole moments of the conformers of compound **VIII**

Conformer	ΔE, kcal mol^{-1}	μ_{theor}, D	μ_{calc}, D	μ_{exp}, D
VIIIa (g^-g^+)	5.70	4.44	5.33	6.00
VIIIb (g^+g^-)	0.73	5.77	6.14	
VIIIb (g^+g^+)	0	5.81	6.17	
VIIIb (g^-g^+)	0.75	5.69	6.02	
VIIIb (g^-g^-)	0.64	5.68	6.04	
VIIIb (g^+t)	0.60	6.05	6.11	
VIIIb (tg^-)	0.64	6.03	6.14	
VIIIb (g^-t)	1.44	5.95	5.98	
VIIIb (tg^+)	0.80	6.01	6.16	
VIIIb (tt)	2.75	6.22	6.10	

Table 7. Relative energies and theoretical, vector-additive, and experimental, dipole moments, and dihedral angles (B3LYP/6-31G*) $C^1_{Ph^1}–C^2_{Ph^1}–P=O$, $C^1_{Ph^2}–C^2_{Ph^2}–P=O$ of the conformers of compound **IX**

Conformer	ΔE, kcal mol^{-1}	μ_{theor}, D	μ_{calc}, D	μ_{exp}, D	Dihedral angle, deg	
					$C^1_{Ph^1}–C^2_{Ph^1}–P=O$	$C^1_{Ph^2}–C^2_{Ph^2}–P=O$
IXa	8.09	2.48	3.98	5.68	–5.7	–15.3
IXb	0.00	5.65	5.76		–16.3	–18.3

EXPERIMENTAL

The dipole moments of phosphine **I** and phosphine oxides **II–IX** were measured in benzene at 25°C by the procedure in [5].

For calculation of the dipole moments of phosphine **I** and phosphine oxides **VIII, IX** the following bond and group moments were used, D: $m(H–C_{sp^3}) = 0.28$ [6]; $m(H–C_{sp^2}) = 0.70$ [6]; $m(C_{sp^2}–P) = 0.39$ [1]; $m(C_{sp^3}–P) = 0.83$ [1]; $m(P=O) = 3.40$ [1]; $m(Me–O) = 1.10$ calculated from the μ_{exp} of dimethyl ether [7]; $m(C_{sp^3}–O) = 1.02$ calculated from the μ_{exp} of MeOH [7]; $m(C_{sp^3}–C_{sp^2}) = 0.75$ calculated from the μ_{exp} of toluene [7]; $m(H–O) = 1.52$ calculated from the μ_{exp} of water [7]; $m(C_{sp^2 Ar}–O) = 0.37$ calculated from the μ_{exp} of phenol [7]; $m(C_{sp^3}–Br) = 1.51$ calculated from the μ_{exp} of CH_3Br [7]. In addition, the geometric parameters (Table 8) obtained by DTF B3LYP/6-31G* quantum-chemical calculations were used.

The coefficients of calculational equations, orientational polarizations, and experimental dipole moments are listed in Table 1. Solvents were purified by conventional procedures [8].

Synthetic procedures and analytical data for compounds **I–III** and **VI–VIII** are reported in [9], for compound **V** in [10], and for compound **IX** in [11].

***o*-[Diethylphosphinoyl)methyl]anisole (IV).** A mixture of 2.8 g (13 mmol) of *o*-[(diethylphosphinoyl)-methyl]phenol [12], 3.6 g (26 mmol) of anhydrous potassium carbonate, and 3.7 g (26 mmol) of methyl iodide in 7 ml of anhydrous acetonitrile was stirred unser reflux for 6 h, after which 15 ml of chloroform was added, and the precipitate was filtered off and washed with 10 ml of chloroform. The combined filtrates were washed in succession with 20% aqueous sodium hydroxide (10 ml), water (10 ml), dilute (1:10) hydrochloric acid (10 ml), and saturated sodium hydrocarbonate (10 ml), evaporated in a vacuum, and the residue was distilled to obtain 2.4 g (80%) of product **IV**, bp 163–165°C (2 mm Hg). Repeated distillation gave 1.9 g (66%) of the product, bp 152–153°C (1 mm Hg), n_D^{20} 1.5446, d_4^{20} 1.0964. Found, %: C 63.8, H 8.5, P 13.4. $C_{12}H_{19}O_2P$. Calculated, %: C 63.7, H 8.5, P 13.7.

All quantum-chemical calculations were performed in the Supercomputer Center for Collective Use, Kazan Research Center, Russian Academy of Sciences (http://wt.knc.ru).

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