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Conformational Analysis of 1,3,2-Dioxaphospholan-yl and 4,5-Benzo-1,3,2-dioxaphosphol-2-yl 2,2,2-trifluoroacetate

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Abstract—Conformational analysis of 1,3,2-dioxaphospholan-2-yl 2,2,2-trifluoroacetate and 4,5-benzo-1,3,2-dioxaphosphol-2-yl 2,2,2-trifluoroacetate was carried out using the method of dipole moments and quantum-chemical calculations (DFT B3LYP/6-31G*). Both compounds are found to exist as an axial conformer with preferably *syn* arrangement of the carbonyl group and the lone electron pair.

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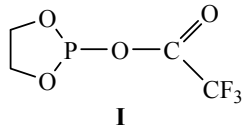
Despite the abundance of the data on the conformational analysis of compounds of three- and four-coordinated phosphorus with P–O and P–S bonds [1, 2], there is no information on the structure of the exocyclic acetate fragments $CH_3C(O)O$ and $F_3CC(O)O$ in 1,3,2-dioxaphospholanes and phosphorinanes. It is well known that in phosphorus heterocycles the exocyclic substituent with P(III) atom (both regular or irregular one) usually takes an axial position [2–4]. In addition, derivatives of tricoordinated phosphorus are stabilized typically as a single form, while the P(IV) compounds often contain several rotamers in an equilibrium [5]. It was interesting to see how the introduction of trifluoromethyl group into the acetate fragment would affect the structure of these compounds.

We determined the experimental dipole moments of 1,3,2-dioxaphospholan-2-yl-2,2,2-trifluoroacetate (**I**) and 4,5-benzo-1,3,2-dioxaphosphols-2-yl-2,2,2-trifluoroacetate (**II**) and calculated the moments of the possible conformers within the vector-additive scheme. The quantum-chemical calculations of the possible conformers was performed by the DFT B3LYP/6-31G* method.



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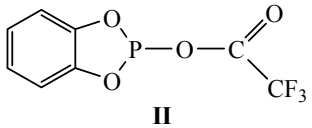


II

Table 1 shows the estimated coefficients of equations, the orientational polarization and experimental dipole moments of the trifluoroacyloxy derivatives **I** and **II**.

The results of quantum-chemical calculations show that both compounds exist as conformers with the axial orientation of the exocyclic $OC(O)CF_3$ fragment, the equatorial conformer is not realized.

The analysis of quantum-chemical calculations indicates that in both molecules the $F_3CC(O)O$ fragment is almost perpendicular to the plane of the phosphorus-containing ring. The dihedral angle OCCO of molecule **I** is 25.2º, the dihedral angle CCOP is 33.7º (for this conformation ΔE = 0.00 kJ mol^{-1}).

Table 2 lists the theoretical dipole moments of the possible conformations of compounds **I**, the values of relative energies, and dipole moments calculated by the vector-additive scheme.

As Tables 1 and 2 show, the experimental dipole moment of 1,3,2-dioxaphospholane **I** corresponds to the moments calculated by the vector-additive scheme taking into account the conformational equilibrium of

Table 1. Coefficients of calculation equations, orientation polarization, and experimental dipole moments of the trifluoroacyloxy derivatives **I** and **II**

Compound (solvent)	**I** (dioxane)	**II** (cyclohexane)
α	12.515	3.664
γ	–0.067	0.049
P_{or}, cm^3	422.415	219.344
μ_{exp}, D	4.54	3.26

Table 2. Possible conformers of compound **I**, their relative energies, the dipole moments calculated by the vector-additive scheme and theoretical dipole moments

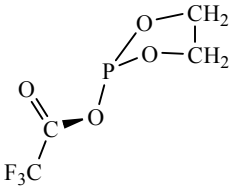
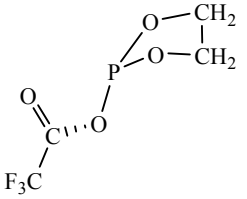
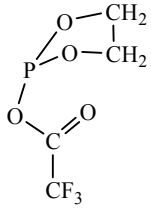
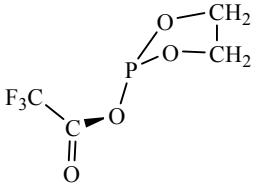
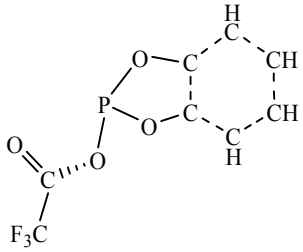
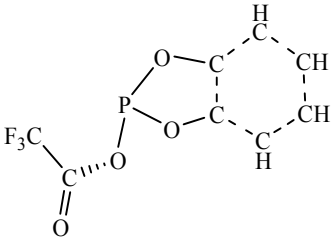
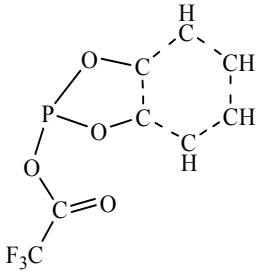
Comp. no.	Conformers	μ_{calc}, D	ΔE, kJ mol^{-1}	μ_{theor}, D
Ia		4.71	0.0	4.43
Ib		4.71	0.60	4.40
Ic		1.15	1.30	3.19
Id		3.31	18.60	4.29

Table 3. Possible conformers of compound **II**, their relative energies, the dipole moments calculated by the vector-additive scheme and theoretical dipole moments

Comp. no.	Conformers	μ_{calc}, D	ΔE, kJ mol^{-1}	μ_{theor}, D
IIa		4.47	0.00	3.43
IIb		3.04	16.54	3.25
IIc		0.93	6.67	2.27

the first three conformers with a significant (90%) prevalence of conformers **Ia** and **Ib** with zero or near zero energy. Carbonyl group and lone electron pair of phosphorus atoms in these conformers are *syn* arranged. Theoretical dipole moments of these conformers (4.43 D) practically coincide with the experimental value ($\Delta\mu$ = 0.11 D). The minor conformer (less than 10%) in principle can be conformer **Ia**, where the C = O group and the lone electron pair of the phosphorus atom are *anti*-located, but a fairly strong difference between the theoretical dipole moment of this conformer and the experimental moment (Table 1) is an additional evidence of its low presence in the conformational equilibrium. In addition, the *anti*-conformer **Ic** is less favorable in comparison with the *syn*-conformers **Ia** and **Ib** by steric reasons. Conformer **Id** should obviously be excluded from the consideration because of its high relative energy (Table 2).

In the molecule of 4,5-benzo-1,3,2-dioxaphosphol-2-yl 2,2,2-trifluoroacetate **II** the oxygen atoms lie almost in the plane of the benzene ring (dihedral angle is 178.3°), the atom P is a bit more deviated (dihedral angle is 171.8°).

According to the results of quantum-chemical calculations, the equatorial conformer of this compound is also nonexistent. As for the axial conformer, it seems that the forms where the relative energy at different relative orientation of the carbonyl group and lone electron pairs of the phosphorus atom and the nearest atoms of the heterocycle exceed 4–5 kJ mol^{-1} can be excluded from the consideration (Table 3, conformers **IIb** and **IIc**). Zero energy corresponds to the axial conformer, like the case of compound **I** with *syn*-orientation of the carbonyl group and lone electron pair of the phosphorus atom (Table 3, conformer **Ia**). Theoretical dipole moment of

this conformer (3.43 D) is close to the experimental one (3.26 D). However, the dipole moment calculated within the vector-additive scheme for zero-energy conformers (Table 3, conformer **IIa**) exceeds the experimental value by 1.21 D being equal to 4.47 D. If we accept that in solution this compound takes part in the conformational equilibrium, then first of all its equilibrium with the **IIc** conformer should be considered. Then the content of the two conformers is almost identical: 51 and 49%. This contradicts the published data on the preference of a single conformer in these compounds. In addition, steric hindrance in conformer **IIc** apparently is not favorable for its implementation. The participation in the equilibrium of conformer **IIa** and **IIb** leads to the predominance of the latter (almost 90%), but just this conformer is less favorable by the energy (Table 3, ΔE = 16.54 kJ mol^{-1}).

Considering the results as a whole, we can conclude that the structure of the compounds fit into the overall conformational picture for heterocyclic compounds with tricoordinated phosphorus. The introduction of trifluoromethyl group in the exocyclic non-regular substituent does not affect the fundamental conformational picture: in both compounds the preferred structure is that with axial orientation of the substituent like in similar heterocycles with the most exocyclic substituents.

In calculating the dipole moments by the vector-additive scheme we used the geometrical parameters obtained from quantum-chemical calculations. It is known that DFT methods (especially hybrid-type B3LYP) reproduce well the geometry of various classes of compounds. Indeed, for example, in an electron diffraction study of the structure of the pyrocathechol phospinate molecule it was concluded that the structure of the phenyl fragment of the heterocycle and two oxygen atoms at the atom of trivalent phosphorus were in the same plane, while the exocyclic chlorine was in the axial position [6].

We used the following values of the group and bond moments: μ_{exp} (CF_3) = 1.36 (calculated from μ_{exp} CF_3H [7]), m (C=>O) = 2.85 [8], m ($C_{sp^3} \rightarrow O$) = 1.1 (calculated from μ_{exp} ($CH_3)_2O$ [7]), m ($C_{sp^2} \rightarrow O$) = 0.66 [9], m ($C_{sp^3} \rightarrow C_{sp^2}$) = 0.78 (calculated from μ_{exp} propene [7]), m (O → P) = 0.51 [9], m ($H \rightarrow C_{sp^3}$) = 0.28 [10], m ($H \rightarrow C_{sp^2}$) = 0.70 D [10].

EXPERIMENTAL

The physicochemical measurements of quantitative characteristics of the electric properties of investigated compounds were performed for a series of eight or nine solutions of substances in dioxane and cyclohexane at 25±0.2°C in an argon atmosphere. Solvents were prepared just before measurements according to standard techniques given in [11]. To determine the experimental values of dipole moments, we used the second method of Debye, which is based on measuring the dielectric constant of dilute solutions of substances in non-polar solvent [12]. Dielectric constants of solutions were determined on the instrument IDM-2 [13] operating by the pulse method. The error in measuring the dielectric constant was ±0.5%. The refractive indices of solutions were determined on a IRF-23 refractometer (accuracy ±0.00001) for the sodium D-line. The accuracy of determination of the experimental dipole moments is ±0.05 D.

The DFT B3LYP/6-31G* quantum-chemical calculations with full geometry optimization of compounds **I, II** were performed with the Gaussian 09 software [14]. The compliance with the found stationary points of the energy minima in all cases was proven by calculation of second derivatives. The calculations were carried out in the Kazan branch of the Joint Supercomputor Center, Russian Academy of Sciences (http://wt.knc.ru).

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