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# Polarity and Structure of Eight-Membered Organosilicon Compounds with Planar Fragments

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**Abstract**—For the first time is determined the polarity of eight-membered silocyns with planar fragments. By the methods of dipole moments and theoretical calculations (DFT B3LYP/6-31G*) of 1,3,2-dioxasilocyns is established that in these compounds occurs the conformational equilibrium of the forms *bath-chair* and distorted *bath* with the predominance of the first, in this case the bonds C($sp^3$)–S and C($sp^3$)–H of the exocyclic $MeSCH_2$ group are in the not eclipsed *gauche* orientation relative to each other.

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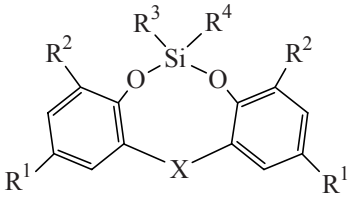
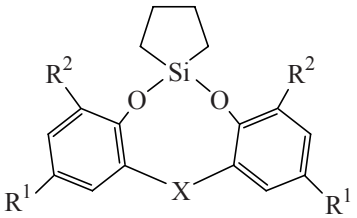
The spatial structure of some eight-membered heterocyclic systems containing silicon has been studied by the methods of X-ray diffraction and NMR spectroscopy, for example [1–3]. The search is carried out in the last decade of the new polyfunctional heterocyclic systems containing silicon, which are of the general theoretical interest and can possess useful properties [4–6]. The authors [7, 8] have obtained the eight-member silocyns with the planar aromatic fragments, which are the models for the study of the reactions of nucleophilic substitution at the silicon atom.

We realized an experimental and theoretical conformation analysis of similar silocyns (**I**–**IV**) by the methods of dipole moments and quantum-chemical calculations (DFT B3LYP/6-31G*).



**I–III**



**IV**

**I**, $R^1 = R^2 = R^3 = R^4 = Me$, X = $CHCH_2SMe$; **II**, $R^1 = R^2 = =$ *t*-Bu, $R^3 = R^4 = Me$, X = $CHCH_2SMe$; **III**, $R^1 = R^2 = Me$, $R^3 = R^4 = Ph$, X = $CHCH_2SMe$; **IV**, $R^1 = R^2 = Me$, X = $CHCH_2SMe$.

The planar unsaturated fragments in the positions 4, 5 and 7, 8 of eight-membered 1,3,2-silocyns **I**–**IV** fix their geometry, leaving a possibility for the realization of conformations *bath-chair* (*BC*), *bath-bath* (*BB*) or *twist-bath* (*TB*) [9, 10].

*BC* *BB* *TB*

In Table 1 are given relative energies, theoretical and calculated by vector-additive scheme dipole

moments of the conformers of compound **I** and its experimental dipole moment. According to the data of quantum-chemical calculations, in the gas phase the energetically advantageous conformation of the heterocycle of compound **I** is *BC*, which is realized in two degenerate forms, **Ia** and **Ib**, characterized by arrangement in the space of the bonds C($sp^3$)–S and C($sp^3$)–N relative to each other (Fig. 1): In the **Ia** conformation they are in $g^+$ orientation, in the conformation **Ib** in $g^-$ orientation; the value of $\mu_{calc}$ for the conformation **Ia** corresponds better to the

**Table 1.** Relative energy, theoretical and calculated dipole moments of the silocyn **I** conformers; $\mu_{exp}$ = 2.88 D

| Comp. no. | $\Delta E$, kcal mol$^{-1}$ | $\mu_{theor}$, D | $\mu_{calc}$, D |
|---|---|---|---|
| **Ia** | 0 | 2.10 | 2.44 |
| **Ib** | 0 | 2.10 | 2.28 |
| **Ic** | 1.92 | 0.92 | 1.39 |
| **Id** | 2.47 | 1.52 | 2.17 |
| **Ie** | 4.21 | 1.07 | 1.15 |
| **If** | 5.87 | 1.96 | 1.52 |

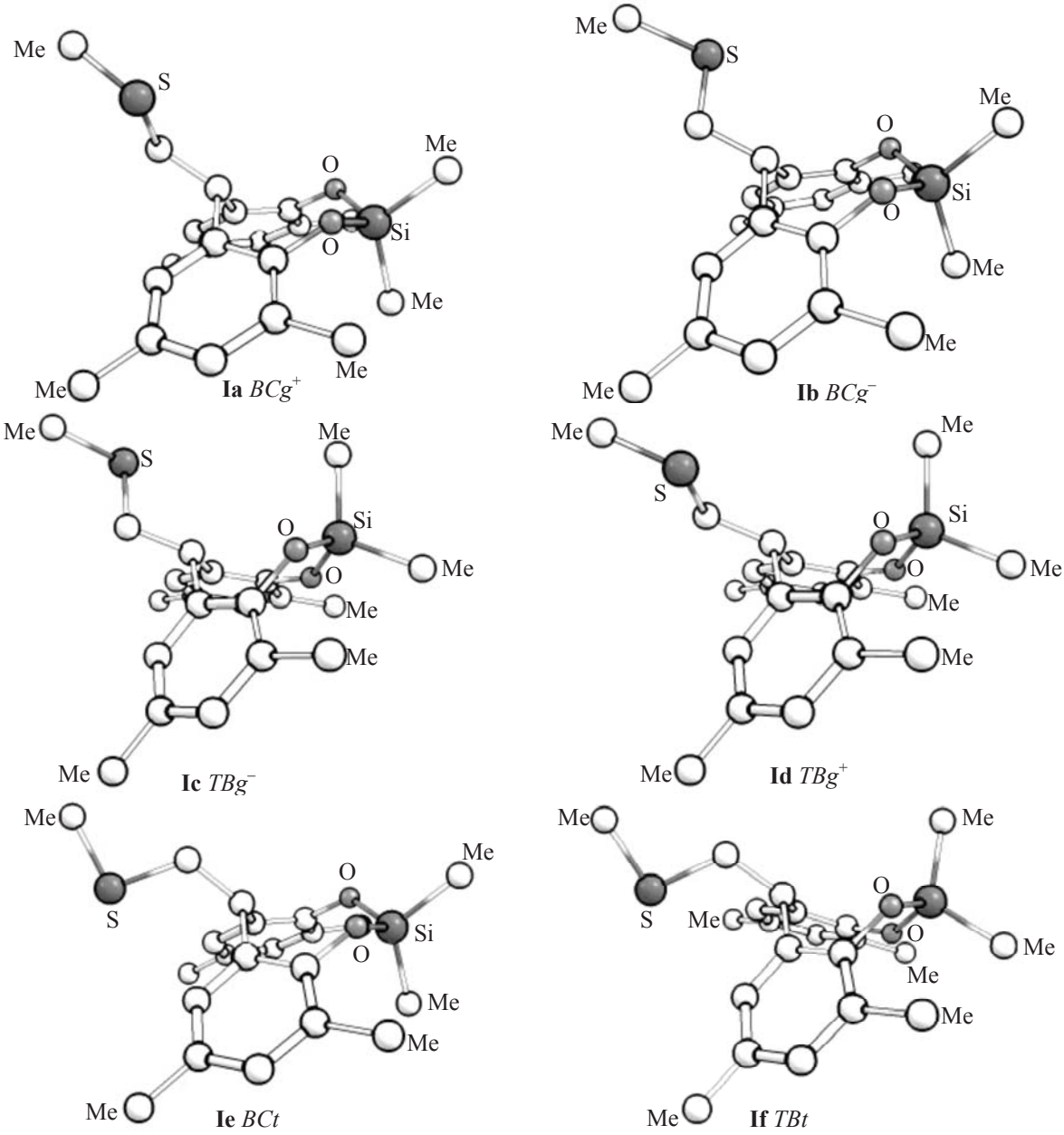
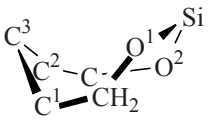



**Fig. 1.** Conformers of silocyn **I** by the data of B3LYP/6-31G* method.

**Table 2.** Relative energy, theoretical and calculated dipole moments of the silocyn **II** conformers, $\mu_{exp}$ = 2.58 D

| Comp. no. | $\Delta E$, kcal mol$^{-1}$ | $\mu_{theor}$, D | $\mu_{calc}$, D |
|---|---|---|---|
| **IIa** | 0 | 1.93 | 2.31 |
| **IIb** | 0 | 1.93 | 2.56 |
| **IIc** | 0.40 | 1.02 | 1.65 |
| **IId** | 1.17 | 1.75 | 2.41 |
| **IIe** | 3.97 | 0.77 | 0.55 |
| **IIf** | 4.77 | 2.16 | 1.61 |

experimental dipole moment.. The *trans*-orientation of bonds C($sp^3$)–S and C($sp^3$)–N (for example, in the conformer **Ie**) leads to an increase in the energy of molecule to 4.21 kcal mol$^{-1}$ (Fig. 1, Table 1). The conformation of the distorted *bath* is less preferable by the energy than *bath–chair* (Table 1, Fig. 1). The degree of distortion can be described in terms of the values of the torsion angles $C^1$–$C^3$···Si–$O^1$ and $C^2$–$C^3$···Si–$O^2$, which in the conformer **Ic** are equal to 40.8° and 15.9°, in the conformer **Id** –40.7 and 14.9° respectively.




In the conformations *TB* (**Ic**) and (**Id**) (Table 1) bonds C($sp^3$)–S and C($sp^3$)–N are respectively in $g^-$ and $g^+$ orientations relative to each other.

From the comparison of the data of Table 1 follow that in the compound **I** is realized the conformational equilibrium of forms **Ia**–**Id** with the predominance of conformation *bath-chair* (**Ia**). In all these forms the bond C($sp^3$)–S has an *gauche*-orientation with respect to the bond C($sp^3$)–N.

According to the data of quantum-chemical calculation, for the compound (**II**) energetically advantageous are two degenerate conformations *BC* (**IIa** and **IIb**), in which the bonds C($sp^3$)–S and C($sp^3$)–N are $g^+$ and $g^-$ oriented relative to each other (Table 2). With the experimental dipole moment better consisted $\mu_{calc}$ of the conformation **IIb**.

The conformations *TB* (**IIc** and **IId**) with $g^-$ and $g^+$ oriented bond C($sp^3$)–S relative to bond C($sp^3$)–N are respectively less preferable by the energy (Table 2). The *trans*-location of bonds C($sp^3$)–S and C($sp^3$)–N (**IIe** and **IIf**, Fig. 2) leads to a notable increase in the relative energy of molecule (Table 2). The torsion angles $C^1$–$C^3$···Si–$O^1$ and $C^2$–$C^3$···Si–$O^2$ of the forms **IIc** and **IId**) are equal to 34.8° and 15.3°, 32.9°, and 12.7°, respectively.

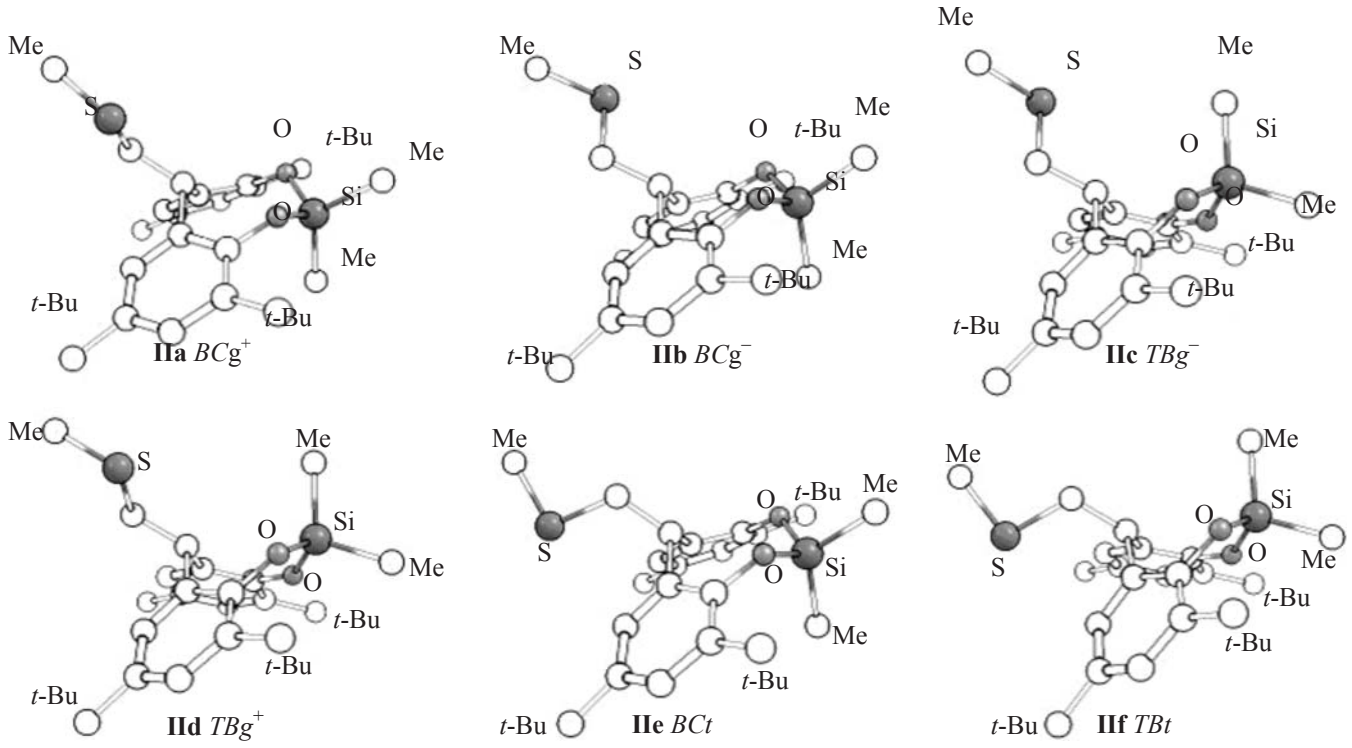



**Fig. 2.** Conformers of silocyn **II** by the data of B3LYP/6-31G* method.

From the analysis of the data of Table 2 follows that in the compound **II** is realized conformational equilibrium of the forms *BC* and *TB* with the predominance of the first; moreover, both the forms, like silocyn **I**, preferable appear with the *gauche* orientation of bonds C($sp^3$)–S and C($sp^3$)–N relative to each other.

In Table 3 are given the relative energies, theoretical and calculated according to vector-additive scheme dipole moments of the conformers, and experimental dipole moment of silocyn **III**. As can be

**Table 3.** Relative energy, theoretical and calculated dipole moments of the silocyn **III** conformers, $\mu_{exp}$ = 2.61 D

| Comp. no. | $\Delta E$, kcal mol$^{-1}$ | $\mu_{theor}$, D | $\mu_{calc}$, D |
|---|---|---|---|
| **IIIa** | 0 | 2.09 | 2.17 |
| **IIIb** | 0 | 2.09 | 2.30 |
| **IIIc** | 1.20 | 1.61 | 2.24 |
| **IIId** | 1.35 | 0.79 | 0.57 |
| **IIIe** | 4.13 | 1.19 | 1.54 |
| **IIIf** | 4.72 | 2.16 | 1.80 |

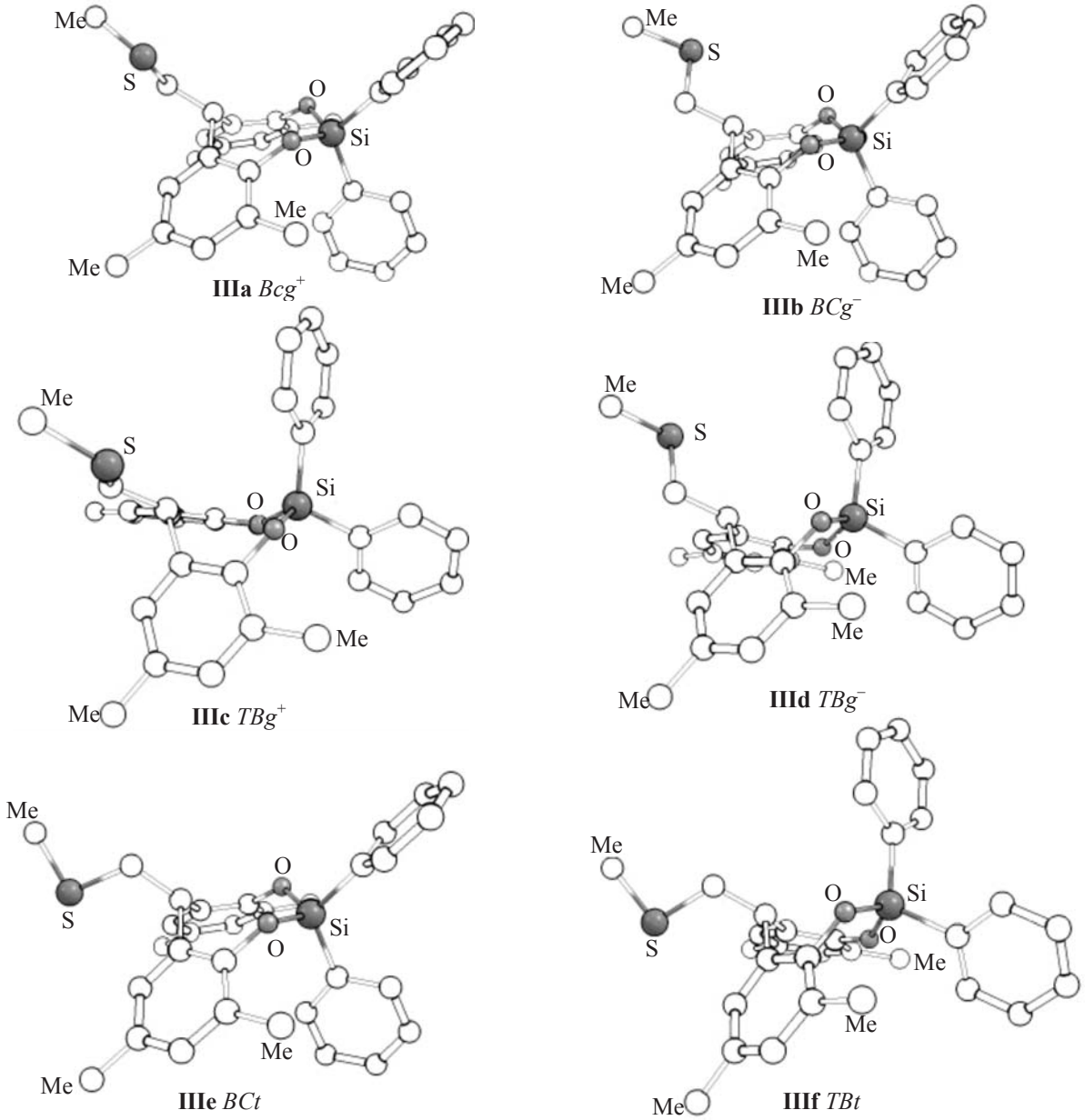



**Fig. 3.** Conformers of silocyn **III** by the data of the method of B3LYP/6-31G*.

seen, in the compound **III** and in silocyns **I** and **II**, to the global minimum correspond two degenerate conformations *BC* (**IIIa** and **IIIb**) with $g^+$ and $g^-$ orientation of the bond C($sp^3$)–S relatively to the bond C($sp^3$)–N, respectively. In these conformers the exocyclic axial and equatorial phenyl substituents at the silicon atom are located orthogonally relative to each other. In the conformations *TB* (**IIIc**) and (**IIId**) (Fig. 3), is observed analogous arrangement of C($sp^3$)–S and C($sp^3$)–N bonds, the dihedral angles $C^1$–$C^3$···Si–$O^1$ and $C^2$–$C^3$···Si–$O^2$ characterizing degree of distortions are equal to 41.2° and 15.1°, 43.3° and 15.5°, respectively.

From the comparison of the dipole moments of the considered conformers, calculated according to vector-additive scheme, as well as found by quantum-chemical calculation (Table 3), follows that in the

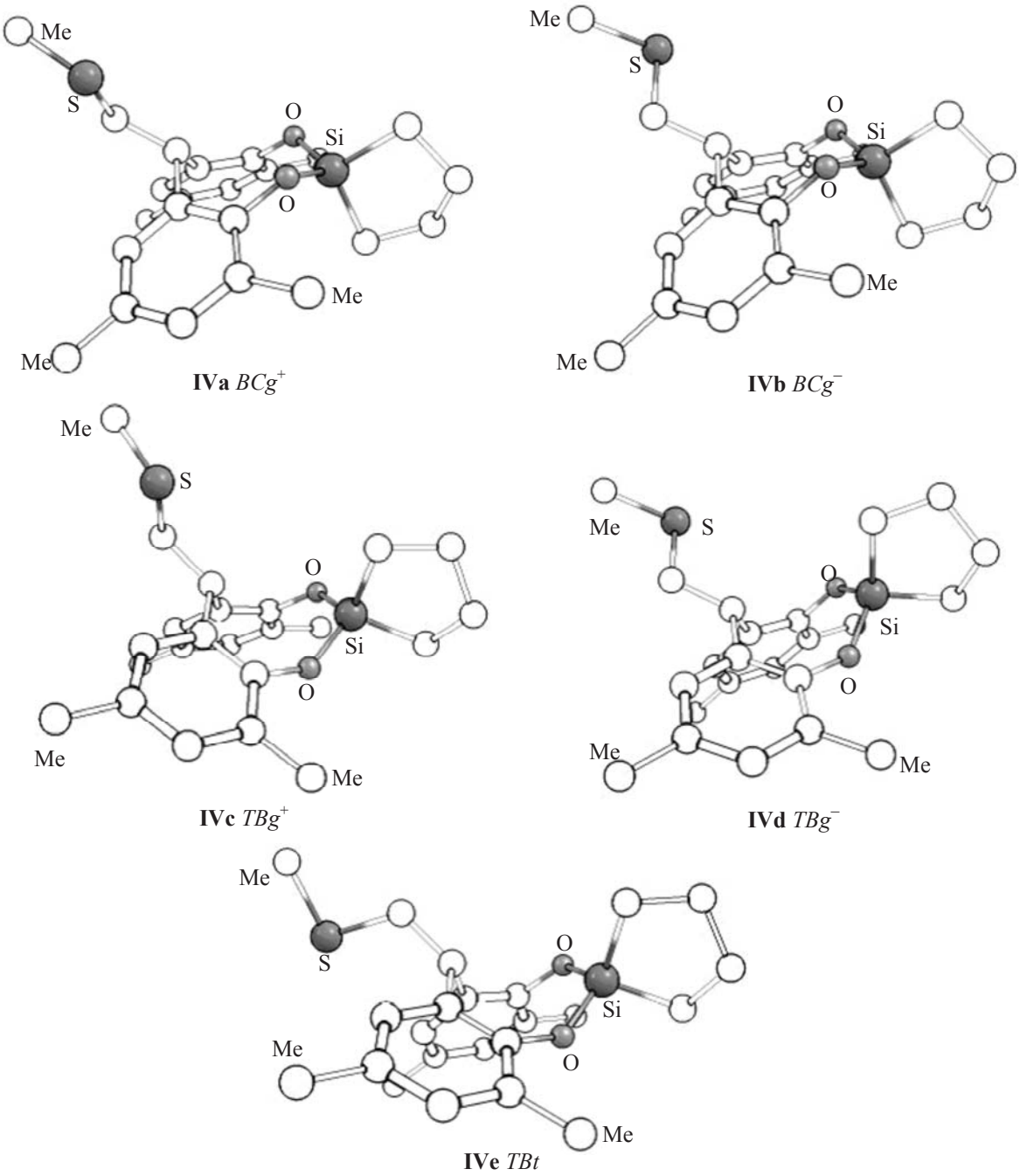



**Fig. 4.** Conformers of silocyn **IV** by the data of B3LYP/6-31G* method.

**Table 4.** Relative energy, theoretical and calculated dipole moments of compound **IV** conformers, $\mu_{exp}$ = 2.66 D

| Comp. no. | $\Delta E$, kcal mol$^{-1}$ | $\mu_{theor}$, D | $\mu_{calc}$, D |
|---|---|---|---|
| **IVa** | 0 | 2.16 | 2.51 |
| **IVb** | 0 | 2.16 | 2.53 |
| **IVc** | 1.19 | 1.70 | 2.15 |
| **IVd** | 1.58 | 1.72 | 2.87 |
| **IVe** | 5.17 | 1.90 | 1.53 |

**Table 5.** Coefficients of equations and experimental dipole moments of compounds **I–IV** in benzene

| Comp. no. | α | γ | $P_{or}$, cm$^3$ | μ, D |
|---|---|---|---|---|
| **I** | 2.697 | 0.044 | 169.620 | 2.88 |
| **II** | 1.439 | 0.013 | 136.123 | 2.58 |
| **III** | 2.169 | 0.040 | 144.695 | 2.66 |
| **IV** | 1.803 | 0.059 | 139.307 | 2.61 |

compound **III** occurs conformational equilibrium of two forms, *BC* and *TB*, with the predominance the first. In these conformations are preferable the *synclinal* arrangement of bond C($sp^3$)–S relatively to C($sp^3$)–N and the orthogonal orientation of exocyclic aryl rings relatively to each other.

Optimized geometry of silocyn **IV** (Table 4) corresponds to two degenerate *bath-chair* conformations (**IVa** and **IVb**) with the *gauche* orientation of the bonds C($sp^3$)–S and C($sp^3$)–N relative to each other (Fig. 4). In the *twist-bath* (**IVc**) conformation the bonds C($sp^3$)–S and C($sp^3$)–N are $g^+$ oriented relatively to each other, in the conformer *TB* (**IVd**) they are $g^-$ oriented (Table 4, Fig. 4). The torsion angles $C^1$–$C^3$···Si–$O^1$ and $C^2$–$C^3$···Si–$O^2$ of conformers **IVc** and **IVd** are equal –18.5° and –35.8°, 17.2° and –34.3°, respectively.

Comparison of the experimental and calculated by vector-additive scheme dipole moments of the conformers **IVa**–**IVd** taking into account the value of their relative energies (Table 4) attests to the fact that in the compound **IV** is realized the conformational equilibrium of these forms with the predominance of energetically advantageous *BC* form.

Thus, the presence of planar fragments in the investigated eight-member cycles does not change the fundamental conformational picture of the cyclic part of the molecule. In this case the number of the possible conformers substantially decreases. Energetically more advantageous forms are realized, therewith the bonds C($sp^3$)–S and C($sp^3$)–H of exocyclic group $MeSCH_2$ occupy not eclipsed *gauche* orientation relatively to each other.

## EXPERIMENTAL

The physicochemical measurements of the quantitative characteristics of electric properties of the investigated compounds were carried out for the series of four to six solutions of substances in benzene at 25±0.2°C. The solvent was purified directly before the measurements according to the standard procedures, given in the monograph [11]. For determining the experimental values of dipole moments was used the second Debye method based on the measurement of the dielectric constant of dilute solutions of substances in a nonpolar solvent [12]. The dielectric constant of solutions was determined on an IDM-2 instrument [13] operating by the beat method. Error of the measurement of dielectric constant is ±0.5%.

The refractive indices of solutions were determined on the refractometer IRF-23 (accuracy ±0.00001) for the sodium D-line.

The coefficients of calculated equations and the experimental dipole moments of the investigated compounds are listed in Table 5. The accuracy of the determination of experimental dipole moments is ±0.05 D.

The quantum-chemical calculations with the complete geometry optimization of the investigated compounds **I–IV** are executed using Gaussian 03 program [14]. Correspondence of the obtained sta-tionary points to the minima in all cases was proved by the calculation of the second derivatives. Calculations are executed in the Collective Use Supercomputer Center of the Kazan Scientific Center of the Russian Academy of Sciences (http://wt.knc.ru).

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