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Steric and Electronic Structure of Complexes of Pyrylium and Thiopyrylium Cations with Borabenzene Anion

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Abstract—The coordination of pyrylium and thiopyrylium cations with borabenzene was studied by DFT [B3LYP/6-311++G(d,p)] calculations. The structures of charge-transfer molecular complexes formed by the aromatic ions were predicted. The stabilization is due both to electron density transfer and to covalent bonding.

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Recently there has been much interest in systems with unusual π–π contacts between conjugated systems, in particular, between aromatic rings. Studies of such systems allow better understanding of the structure of important protein systems, mechanisms of many biochemical processes, and crystal packing (see references in [1–3]).

Recent studies [1–3] demonstrated on a high level of theory that, in all the systems considered (benzene dimers, complexes of benzene with benzene heteroanalogs or aromatic cations), the most stable structure or one of the most stable structures is a complex with almost parallel arrangement of two aromatic rings with a small shift relative to the center of one of them.

On the other hand, it was shown (see references in [4]) that properties of aromatic molecules existing in the charged state strongly depend on the nature of counterions. As a rule, complexes with inorganic anions were considered, whereas virtually no attention was given to mutual influence of charged aromatic rings in molecular charge-transfer complexes. Studies of such complexes are interesting in the context of the development of systems with nonlinear optical properties [5].

In this study we examined by DFT [B3LYP/6-311++G(d,p)] [6] calculations the coordination of organic pyrylium and thiopyrylium cations with borabenzene anion in the gas phase and in a polar aprotic solvent, DMSO. Our goal was to determine the structure of the stable complexes and evaluate how the mutual coordination affects the aromatic properties of the components.

All the calculations were performed by DFT methods (B3LYP) in the valence-split 6-311++G** basis set using the Gaussian-03 program package [7]. Full optimization of the geometry of the molecular structures corresponding to the energy minima (λ = 0, here and hereinafter λ is the stationary point index denoting the number of negative eigenvalues of the Hesse matrix in this point) and saddle points (λ = 1) on the potential energy surface were performed in the "tight" mode. Structures corresponding to the energy minima on the potential energy surface were found by the method of the steepest descent (movement along gradient line) from a saddle point to a neighboring stationary point (saddle point or minimum). To compare the parameters of coordination bonds in the complexes with the parameters characteristic of covalent bonds, we calculated the covalence factor χ [8] by the formula

$$\chi = \frac{\sum\limits_{i=\mathrm{X,Y}} R_i - l_{\mathrm{XY}}}{\sum\limits_{i=\mathrm{X,Y}} R_i - \sum\limits_{i=\mathrm{X,Y}} r_i},$$

where $\sum\limits_{i=\mathrm{X,Y}} R_i$ is the sum of the van der Waals radii [9] of atoms X and Y; $\sum\limits_{i=\mathrm{X,Y}} r_i$, sum of the covalent radii [9] of atoms X and Y; and l_{XY}, distance between the corresponding atoms.

To analyze the structures obtained and the electron density distribution in them, we used the natural bond

Table 1. Calculation results[a] for structures **I–XI**

Structure	E_{tot}	λ	ZPE	ω_1	ΔE	ΔE_{ZPE}
I	–487.795970	0	0.183692	30	102.62	101.36
II	–487.794459	0	0.183750	34	101.67	100.38
III, C_s	–487.792065	0	0.183741	29	100.18	98.89
IV, C_s	–487.791669	1	0.183270	–75	98.42	97.43
V, C_s	–487.789262	1	0.183282	–69	99.93	98.93
VI	–810.773607	0	0.180018	29	97.87	96.72
VII	–810.774556	0	0.180109	18	98.47	97.26
VIII, C_s	–810.768719	0	0.179747	19	94.81	93.83
IX, C_s	–810.771968	0	0.180162	31	96.85	95.60
X, C_s	–810.767735	1	0.179557	–61	94.20	93.33
XI, C_s	–810.767745	1	0.179629	–68	94.21	93.30

[a] (E_{tot}) Total energy, au, 1 au = 627.5095 kcal mol^{-1}; (λ) number of negative eigenvalues of the Hessian; (ZPE) zero-point harmonic vibration energy, au; (ω_1) smallest harmonic vibration frequency (or imaginary frequency for transition states), cm^{-1}; (ΔE, ΔE_{ZPE}) complexation energies (without and with taking into account ZPE), calculated as the difference between the total energy of the complex and the sum of the total energies of the cation and counterion, kcal mol^{-1}; the same for Table 2.

orbital (NBO) scheme [10]. The degree of aromaticity was evaluated for the calculated structures using NICS indices [11]. The solvent effect for the polar (DMSO) solvent was taken into account using the Tomasi continual model (IEFPCM) [12].

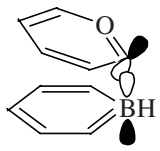
Pyrylium complexes in the gas phase. Calculations for the gas phase revealed three stable asymmetric π complexes of the pyrylium cation with the borabenzene anion (structures **I–III**, Table 1, Fig. 1). The systems obtained have close energies (the difference does not exceed 2.5 kcal mol^{-1}) and are the most stable minima in the corresponding areas of the potential energy surface. Structure **I** is the most stable. The π complexes revealed are characterized by strong electron density transfer (~0.4–0.5 e) from the organic anion to the cation, leading to distortion of the pyrylium ring plane by 7°–13°. The total dipole moment of the system, however, remains high (~6 D).

As in the previously considered complexes of pyrylium with inorganic anions [4], counterions are coordinated exclusively at the *ortho* and *para* positions of the aromatic cation, with the boron center predominantly oriented toward the carbon atom of the aromatic pyrylium cation.

The structures revealed show high stereochemical nonrigidity. The stereoisomerization barriers for systems **I** and **II**, corresponding to symmetrical transition states **IV** and **V**, do not exceed ~3 kcal mol^{-1}.

It should be noted that the energy of interaction between the rings is so high that the planar structure of the π complex is not noticeably distorted even on adding counterions ($LiBF_4$).

The covalence factor χ for the C···B intermolecular contacts in systems **I–III** vary in the range from 0.50 to 0.60, which means that the coordination bond approaches a single bond in strength. An NBO analysis shows that the major contribution to stabilization of the complex is made by the C···B intermolecular contact provided by *p–p* donor–acceptor interactions of the carbon and boron centers.



It should be noted that there also can be nonclassical B–H···H–C interaction between hydrogen atoms at the boron center of the heterocyclic anion and at the nearest carbon center of the pyrylium cation. The possibility of such interaction is supported by fairly large (~0.1–0.3 e) charges of opposite signs, localized on the above-mentioned hydrogen atoms, and by relatively short distance between the centers, ~2.5 Å.

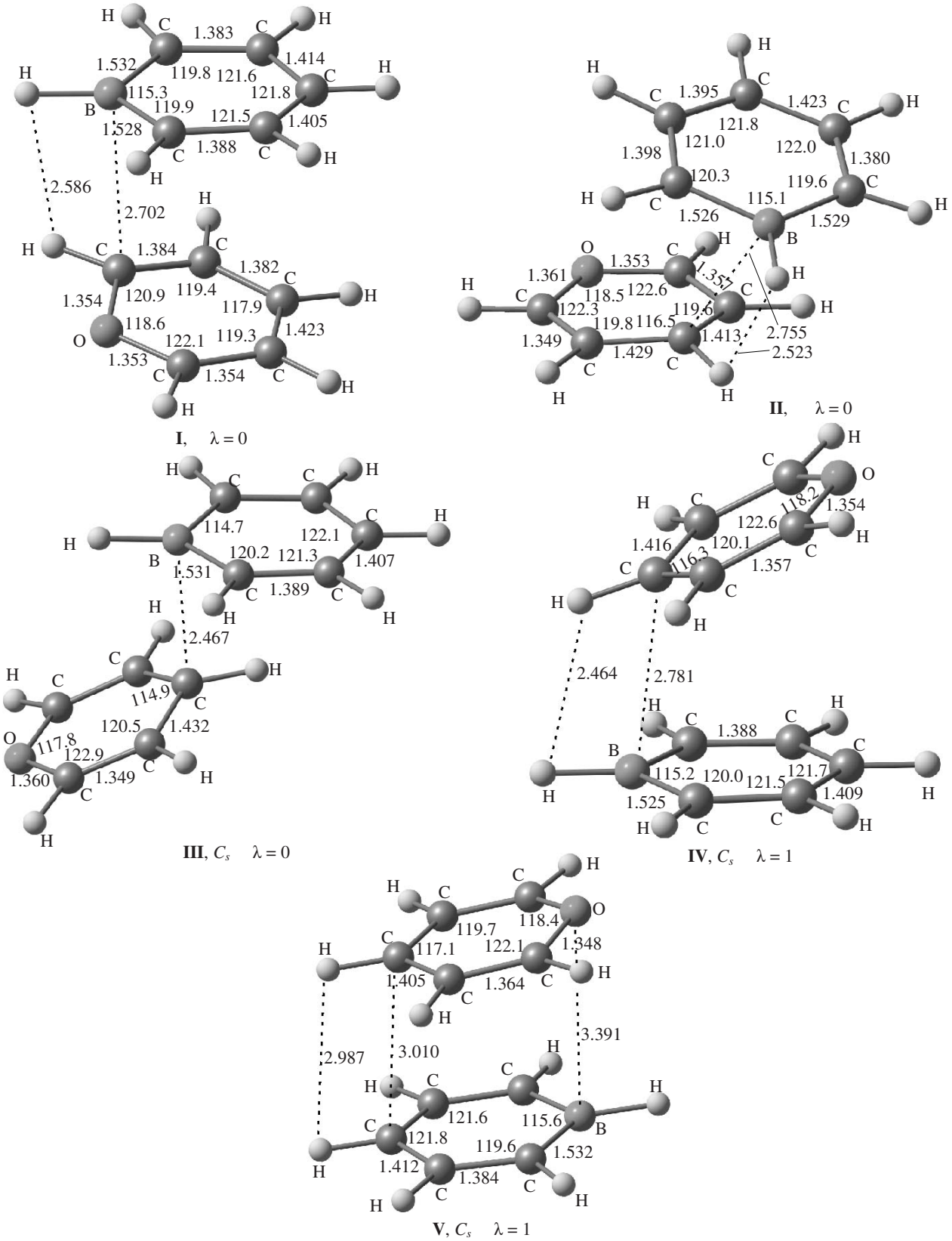


Fig. 1. Geometries of structures **I–V**, calculated by the DFT method. Interatomic distances are given in Å, and angles, in degrees; the same for Figs. 2 and 3.

The calculated NICS indices for the pyrylium cation in complexes **I–III** are somewhat shifted toward nonaromatic values (vary from –3 to –5), whereas for the borabenzene anion the indices vary from –6 to –7 and are typical of aromatic compounds (for benzene, NICS(0) ~–8) [11].

Thiopyrylium complexes in the gas phase. As in the case of pyrylium, thiopyrylium cation forms π complexes with borabenzene anion. The structures formed remain the most energetically favorable in the corresponding area of the potential energy surface. The calculations revealed four structures **VI–IX** (Fig. 2) corresponding to the minima on the potential energy surface, of which structure **VII** is the most stable, but the difference from the other structures in the energy does not exceed 4 kcal mol^{-1}. It should be noted that the complexation energy decreases in going from pyrylium to thiopyrylium.

As in complexes **I–III**, in complexes **VI–IX** there is significant electron density transfer (~0.4–0.5 e), leading to distortion of the thiopyrylium ring plane by 7°–12°. The dipole moment of the system, however, remains high (~4–5 D).

Systems **X** and **XI** revealed in the course of the calculations correspond to the transition state of the stereoisomerization of structures **VI** and **VII**. The isomerization barrier does not exceed 3 kcal mol^{-1}.

The covalence factor χ for the C···B contacts in systems **VI–IX** varies in the same range as for the pyrylium complexes. This fact shows that the strength of the coordination interaction is virtually independent of the heteroatom in the aromatic cation. The nature of this contact (data of NBO analysis) is also preserved: one *p* orbital of each heteroring (in borabenzene anion, the *p* orbital of the boron atom) participates in the donor–acceptor interaction.

The NICS indices calculated for the thiopyrylium complexes show that the structure of the thiopyrylium ring is largely nonaromatic, whereas the borabenzene anion remains aromatic.

Pyrylium and thiopyrylium complexes in solution. The solvent effect was considered for the two most stable (for each cation) gas-phase structures in a polar aprotic solvent, DMSO (ε 46.7). The calculation results are given in Fig. 3 and Table 2.

Table 2. Results of calculations of structures **Ia, IIa, VIa**, and **VIIa** in DMSO

Structure	E_{tot}	ZPE	ω_1	ΔE	ΔE_{ZPE}
Ia	–487.817461	0.181880	14	5.21	4.47
IIa	–487.816195	0.181883	25	4.42	3.67
VIa	–810.795829	0.178106	11	2.17	1.57
VIIa	–810.796057	0.178159	25	2.31	1.68

In going to the polar solvent, all the complexes revealed for the gas phase preserve their geometric structures (**Ia, IIa, VIa, VIIa**), but the coordination interaction between the components in solution is considerably weaker. This is manifested in an increase in the intermolecular distance by no less than 0.2 Å, in considerably (by a factor of ~2) weaker transfer of the electron density from the donor ring to the acceptor ring (0.2–0.3 e), and in the lower complexation energy. At the same time, the pyrylium and thiopyrylium rings in the complexes in solution are appreciably less distorted (4°–8°), and the dipole moment of the complexes is no less than 12–14 D. The nature of the interaction is preserved, and variation of the NICS index reflects an increase in the aromaticity of the pyrylium and thiopyrylium cations.

Thus, the calculations show that pyrylium and thiopyrylium cations form with borabenzene anion stable π complexes with a significant charge transfer, leading to deformation of the aromatic ring and partial loss of aromatic properties. The complexes have a large dipole moment, and the complexation is provided by overlap of only two *p* orbitals, one of which is necessarily localized on the boron atom. Presumably, using the C–B contact as axis, it may be possible to construct treelike structures consisting of a large number of ion pairs of cations and anions. These structures may exhibit unusual physicochemical properties.

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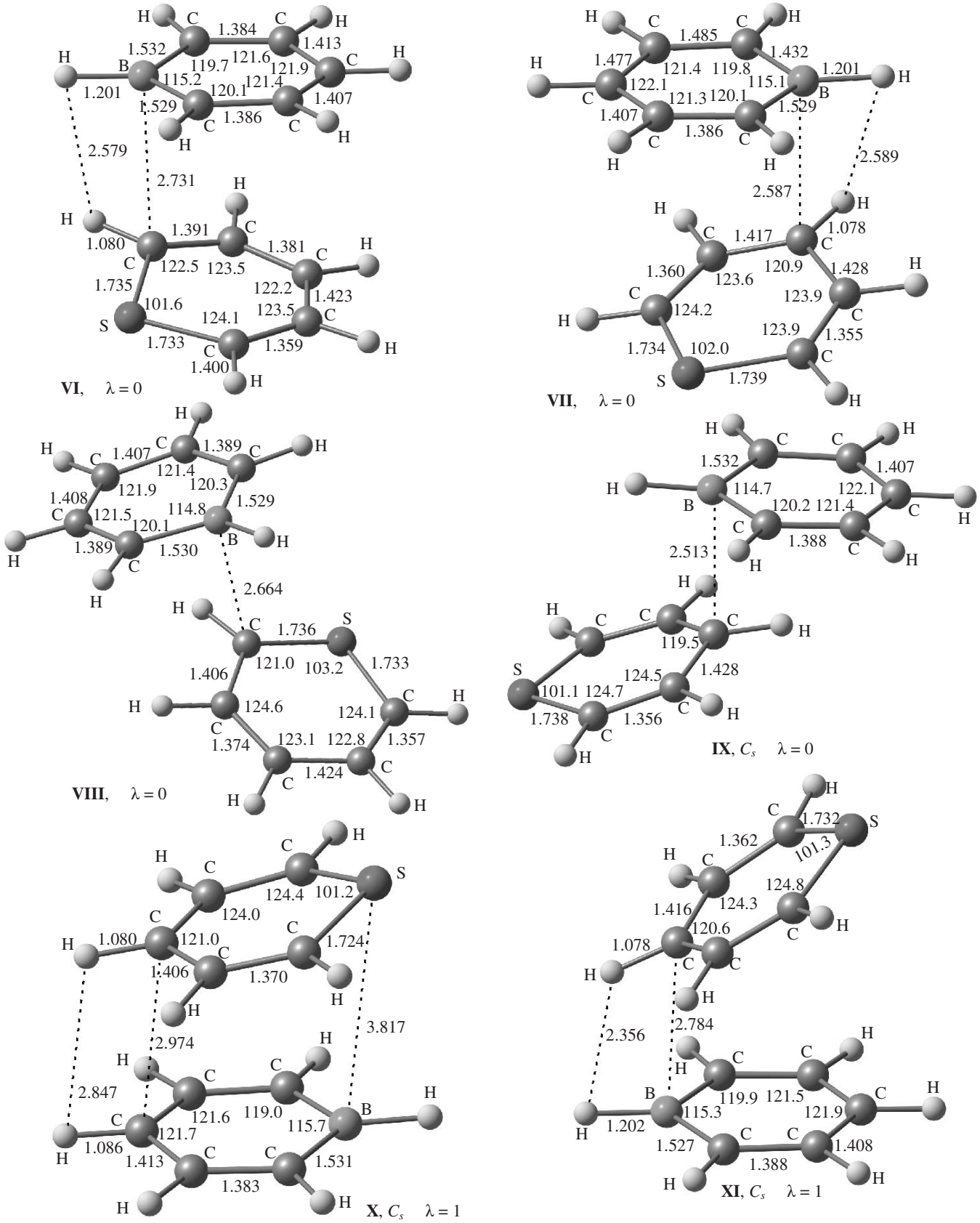

Fig. 2. Geometries of structures **VI–XI**, calculated by the DFT method.

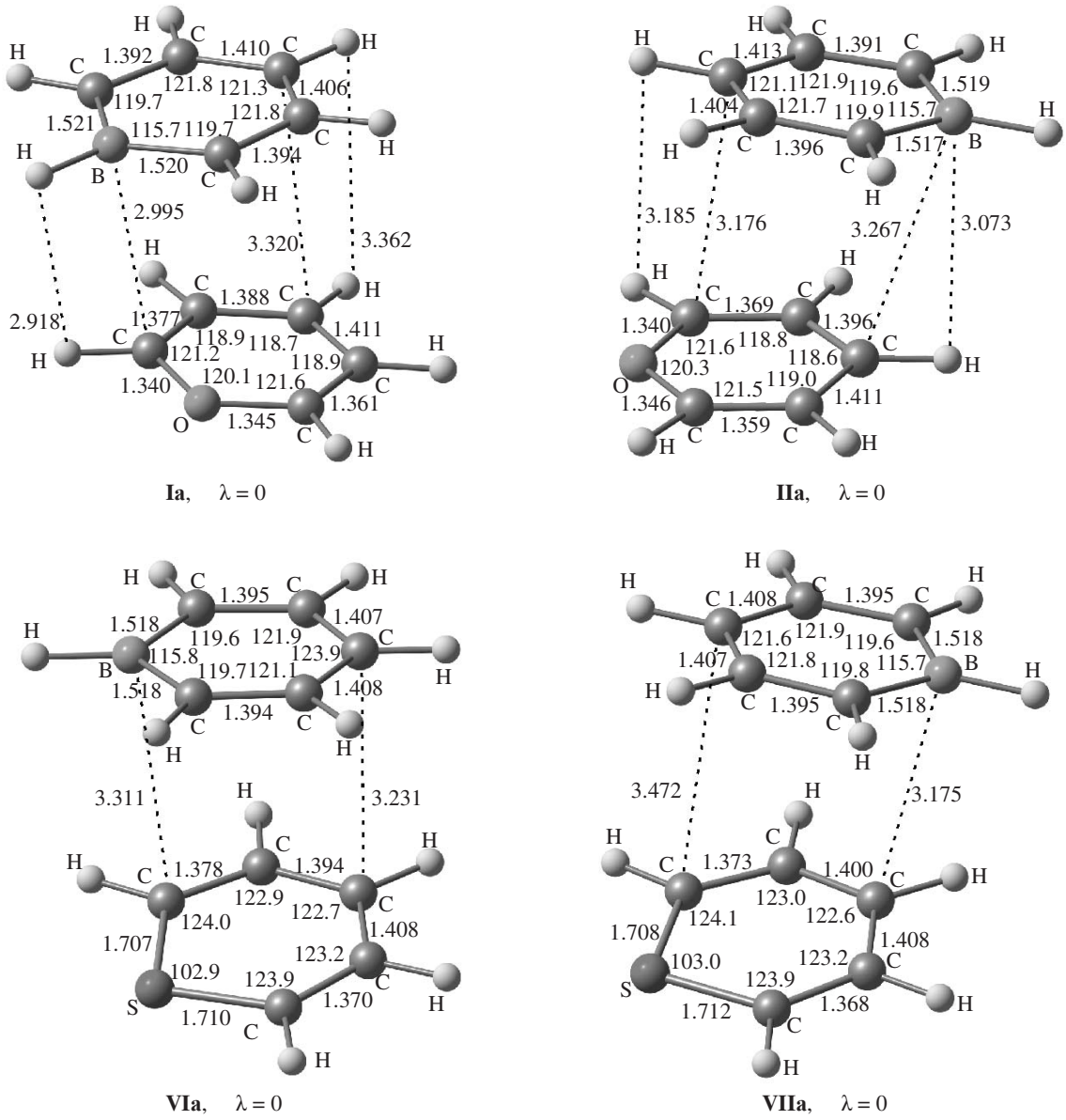

Fig. 3. Geometries of structures **Ia, IIa, VIa**, and **VIIa**, corresponding to the minima on the potential energy surface (DFT calculations taking into account the effect of a polar solvent, DMSO)

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