

Structures and Binding Energies of the (Dibenzoylmethanato)boron Difluoride Complexes with Aromatic Hydrocarbons in the Ground and Excited States. Density Functional Theory Calculations

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Abstract—Structures of the (dibenzoylmethanato)boron difluoride molecule (DBMBF2) and its complexes with a series of aromatic hydrocarbons (benzene; toluene; *o*-, *m*-, and *p*-xylenes, naphthalene; anthracene; and pyrene) in the ground and the first singlet excited states have been calculated. The calculations have been performed by the density functional theory (DFT) and time-dependent density functional theory (TDDFT) for the ground and excited states, respectively, with the empirical dispersion correction. It has been shown that the complexes in the ground and excited states have similar stacking structures and are characterized by short contacts between the F atom of DBMBF2 and H atoms of the hydrocarbon molecule, which decrease on transition from the ground to the excited state. The calculated binding energies in the complexes in the excited state are two to three times higher than those in the ground state. The charge transfer in the ground state of the complexes is insignificant and directed from DBMBF2 to the ligand, while in the excited state it is 0.6–0.8 e and directed from the ligand to DBMBF2.

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Boron difluoride β -diketonate dyes have been extensively studied owing to their application as laser dyes, IR light absorbers, and materials for organic light emitting diodes and nonlinear optics [1]. (Dibenzoylmethanato)boron difluoride (DBMBF2) is one of the most interesting representatives of the dyes of this class, in particular, because of its ability to form fluorescent exciplexes with benzene and its methyl derivatives [2–7]. The heats of formation (binding energies) of DBMBF2 exciplexes in solutions were measured in [3]. The DBMBF2 crystal structure is determined by the X-ray diffraction method [8].

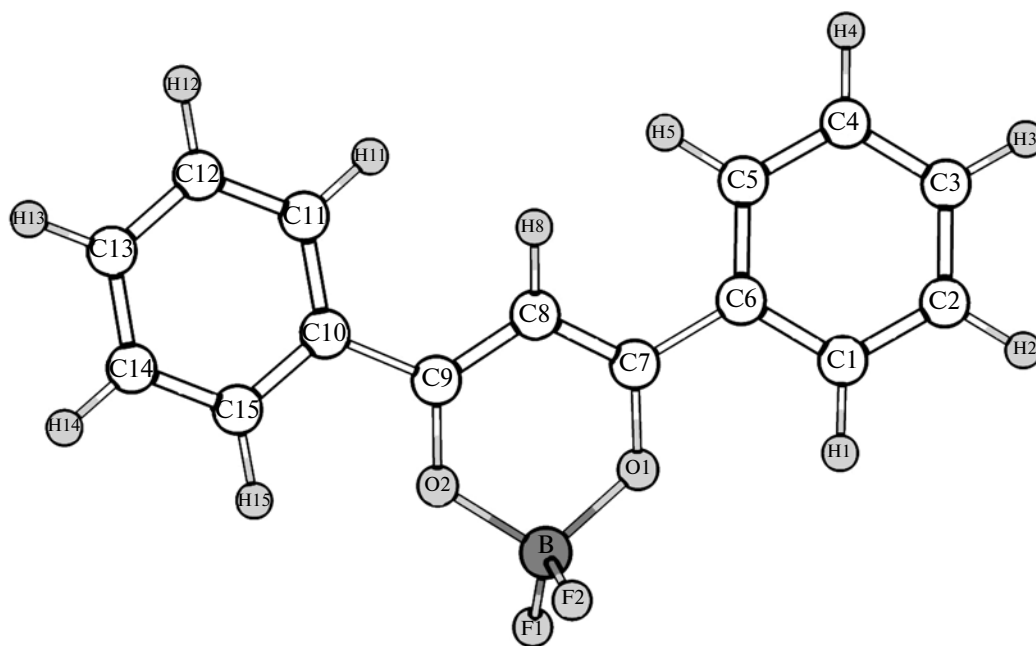
Quantum-chemical calculations of the structures and binding energies of the complexes of (dibenzoylmethanato)boron difluoride with aromatic hydrocarbons in the ground and first singlet excited states were performed in this work using density functional theory (for the ground state) and time-dependent density functional theory (for the excited state).

CALCULATION METHODS

Reliable data on the structure and energy characteristics of molecular systems in the ground electronic

state can be obtained using calculations by the density functional theory (DFT). The known drawback of the DFT method ignoring van der Waals interactions, which are particularly important for the complexes of DBMBF2 with aromatic hydrocarbons considered in this work, can be eliminated by introducing an empirical dispersion correction (DFT-D method) [9–11]. The DFT-D method was validated for a large number of systems including van der Waals complexes for which accurate *ab initio* calculations are possible; close agreement of results obtained with the DFT-D method and the coupled cluster method CCSD(T) was observed [9–12].

Calculation for exciplexes is a complicated problem with any theoretical approach. The approach based on the TDDFT with the dispersion correction introduced was suggested in [13] for calculation of structures and binding energies of excimers and exciplexes. The empirical dispersion correction is parameterized for the ground rather than the excited state; however, Huenerbein and Grimme [13] indicate that this correction gives the lower bound of the van der Waals contribution to energy, since the molecular polarizability in the excited state is higher than in the



Structure of the DBMBF2 molecule in the ground electronic state.

ground state. Thus, in the case of excited states, introduction of the dispersion correction will provide more accurate results. To overcome another problem of TDDFT related to incorrect description of charge-transfer transitions, it was suggested to use a hybrid functional that includes a large portion of Hartree–Fock exchange, for example BHandHLYP, in which this portion makes 50%. The use of this approach made it possible to obtain the dissociation energies of the benzene and pyrene excimers, as well as styrene and trimethylamine exciplexes, consistent with experimental data [13].

In this work we mainly followed the calculation procedure presented in [13]. The DFT-D method was used for geometry optimization of the ground electronic state, and the TDDFT method with dispersion correction (TDDFT-D) was used for calculating the excited state with the hybrid functional BHandHLYP [14–16] and the SVP double-zeta basis set [17]. Energies at the optimized geometries were calculated by the same method using the TZVP triple-zeta basis set [18]. The computations were run by the Orca program [19]. The Mulliken charges on the atoms in the excited state were calculated using the GAMESS-US program [20].

RESULTS AND DISCUSSION

The calculated structures of the DBMBF2 molecule in the ground state are presented in the figure. The calculated bond lengths and bond angles of the DBMBF2 molecule in the ground and excited states and experimental values obtained from X-ray diffraction data for crystalline DBMBF2 [8] are collated in Table 1.

The calculated bond lengths and bond angles for DBMBF2 in the ground state are in good agreement with the experimental X-ray diffraction data; the deviations are less than 0.05 Å and 3.5°, respectively, and the mean deviations are 0.017 Å and 1°, respectively. The bond lengths and bond angles change insignificantly on transition to the excited state; the changes do not exceed 0.036 Å and 2.6°, respectively.

Table 2 presents the calculated structures of the DBMBF2 complexes with aromatic hydrocarbons (benzene; toluene; *o*-, *m*-, and *p*-xylenes; naphthalene; anthracene; and pyrene) in the ground and the first singlet excited state. These structures have a stacking arrangement and are characterized by short contacts between the F atom of the DBMBF2 molecule and H atoms of the hydrocarbon molecule. In the majority of cases (except the DBMBF2–benzene

Table 1. Bond lengths (Å) and bond angles (degree) in the DBMBF2 molecule

Bond	Experiment [8]	Calculation	
		ground state	excited state
F(1)–B	1.362	1.345	1.346
F(2)–B	1.348	1.355	1.364
O(1)–B	1.486	1.499	1.497
O(2)–B	1.478	1.499	1.497
C(1)–C(2)	1.399	1.385	1.376
C(2)–C(3)	1.343	1.389	1.398
C(3)–C(4)	1.339	1.389	1.393
C(5)–C(4)	1.376	1.384	1.378
C(6)–C(1)	1.383	1.396	1.416
C(6)–C(5)	1.371	1.397	1.419
C(6)–C(7)	1.469	1.469	1.433
C(7)–C(8)	1.377	1.392	1.424
C(9)–C(8)	1.382	1.392	1.424
O(1)–C(7)	1.298	1.275	1.290
O(2)–C(9)	1.290	1.275	1.290
C(9)–C(10)	1.457	1.469	1.433
C(10)–C(11)	1.388	1.397	1.419
C(11)–C(12)	1.372	1.384	1.378
C(12)–C(13)	1.359	1.389	1.393
C(15)–C(14)	1.379	1.385	1.385
Angle			
F(2)–B–F(1)	111.9	115.0	115.2
F(1)–B–O(2)	108.7	109.0	108.9
F(1)–B–O(1)	108.9	108.0	108.9
F(2)–B–O(2)	108.5	108.0	107.8
F(2)–B–O(1)	107.8	108.0	107.8
O(2)–B–O(1)	111.0	107.4	107.6
C(3)–C(2)–C(1)	119.1	120.0	120.4
C(3)–C(4)–C(5)	120.4	120.0	120.3
C(4)–C(3)–C(2)	121.7	120.1	119.8
C(5)–C(6)–C(1)	118.8	119.3	118.2
C(6)–C(5)–C(4)	120.1	120.2	120.5
C(6)–C(1)–C(2)	119.9	120.2	120.5
C(1)–C(6)–C(7)	119.8	118.8	118.9
C(5)–C(6)–C(7)	121.4	121.7	122.8
O(1)–C(7)–C(6)	115.6	115.8	118.4
O(1)–C(7)–C(8)	119.6	121.1	118.8
C(7)–O(1)–B	122.1	122.9	120.6
C(8)–C(7)–C(6)	124.7	122.9	122.6
C(8)–C(9)–C(10)	124.0	122.9	122.6
O(2)–C(9)–C(10)	116.3	115.8	118.4
C(9)–O(2)–B	122.5	122.9	120.6
O(2)–C(9)–C(8)	119.7	121.2	118.8
C(7)–C(8)–C(9)	121.9	118.5	119.8
C(11)–C(10)–C(9)	121.9	121.7	122.8
C(15)–C(10)–C(9)	120.0	118.8	118.9
C(10)–C(15)–C(14)	120.8	120.2	120.5
C(13)–C(14)–C(15)	119.4	120.0	120.4
C(12)–C(11)–C(10)	121.0	120.2	120.5
C(13)–C(12)–C(11)	119.2	119.9	120.3
C(14)–C(13)–C(12)	121.4	120.1	119.8
C(15)–C(10)–C(11)	118.2	119.3	118.2

complex), these contacts in the excited state are shorter by 0.1–0.2 Å than in the ground state.

The binding energies of complexes in the ground and excited states were calculated as the difference of the total energy of the complex in the corresponding state and the total energies of the isolated components: DBMBF2 in the ground or excited state, respectively, and the hydrocarbon molecule in the ground state. The charge transfer in the complexes was estimated as the sum of Mulliken charges of all the atoms of the hydrocarbon molecule.

The calculated formation energies of the DBMBF2 complexes in the ground and excited states and the values of charge transfer are presented in Table 3. The binding energies of complexes in the excited state are two to three times higher than those in the ground state, thereby indicating the formation of exciplexes. The charge transfer in the ground state of the complexes is insignificant and directed from the ligand to DBMBF2, whereas in the excited state it is directed from DBMBF2 to the ligand and is as large as 0.6 – 0.8 e. The latter is also characteristic of exciplexes.

The calculated binding energies in exciplexes cannot be directly compared with the available experimental estimates of the free energy of the exciplex formation in solutions because of the difficulty of evaluating the solvation energy change during the complex formation in the solution.

CONCLUSIONS

Structures of the (dibenzoylmethanato)boron difluoride complexes with benzene; toluene; *o*-, *m*-, and *p*-xylenes; naphthalene; anthracene; and pyrene in the ground and the first singlet-excited states were calculated using the DFT-D and TDDFT-D methods. It was found that the complexes in the ground and excited states have a similar stacking structure and are characterized by short contacts between the F atom of the DBMBF2 molecule and the H atoms of the hydrocarbon molecule. These distances decrease upon transition from the ground to the excited state. The calculated binding energies in the excited-state complexes (exciplexes) are two to three times higher than in the ground state. The charge transfer in the ground state of the complexes is insignificant and directed from DBMBF2 to the ligand, whereas in the excited state it is in the range of 0.6–0.8 e and directed from the ligand to DBMBF2.

Table 2. Structures of the DBMBF2 complexes with benzene; toluene; *o*-, *m*-, and *p*-xylenes; naphthalene; anthracene; and pyrene molecules in the ground and the first singlet excited state, and lengths of short intermolecular contacts (Å)

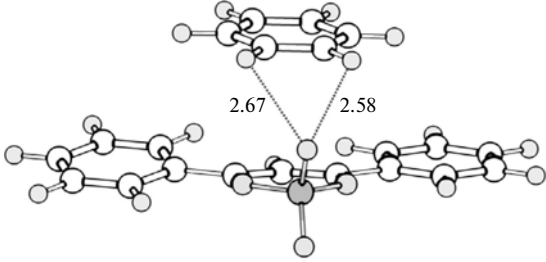
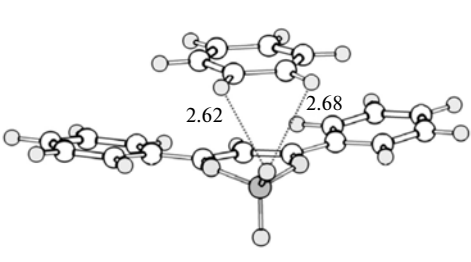
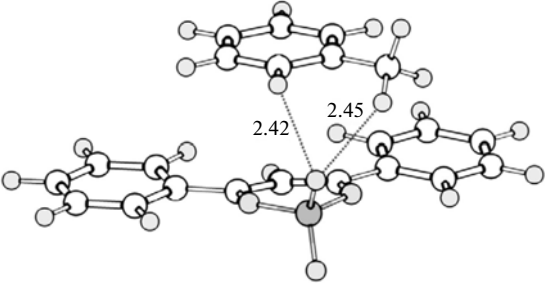
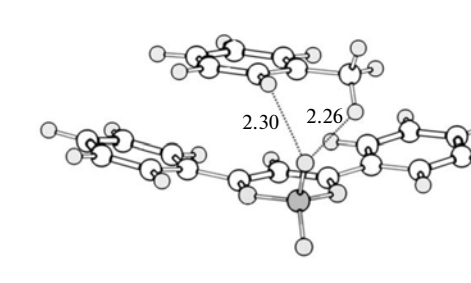
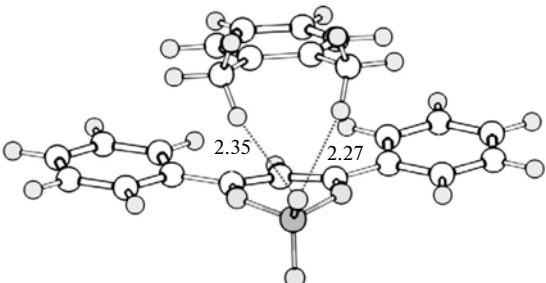
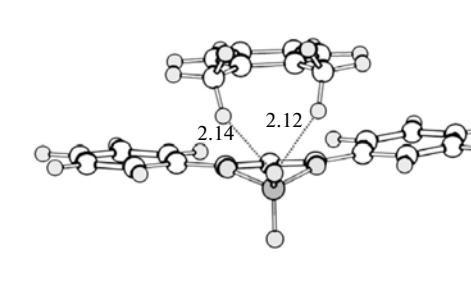
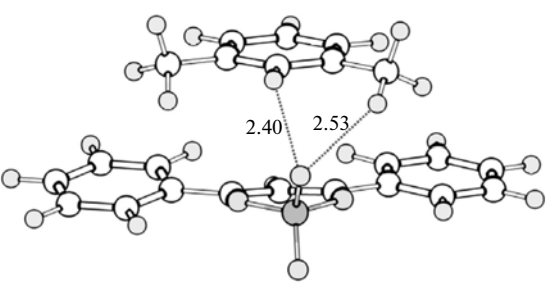
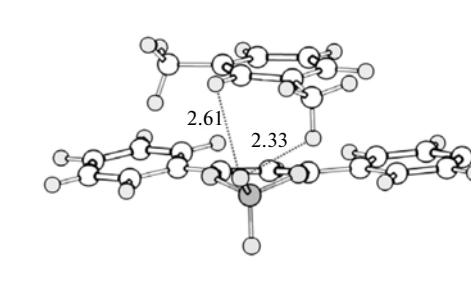
Molecule	Ground state	Excited state
Benzene		
Toluene		
<i>o</i> -Xylene		
<i>m</i> -Xylene		

Table 2. (Contd.)

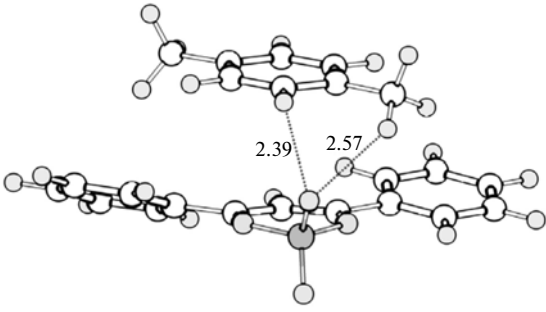
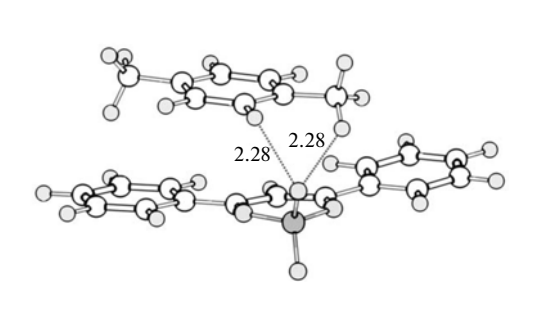
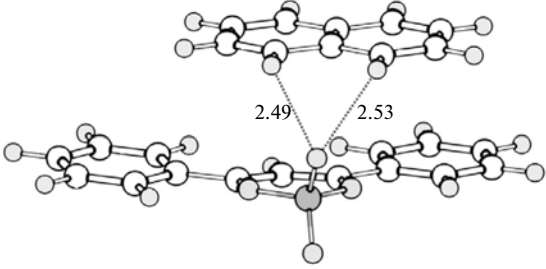
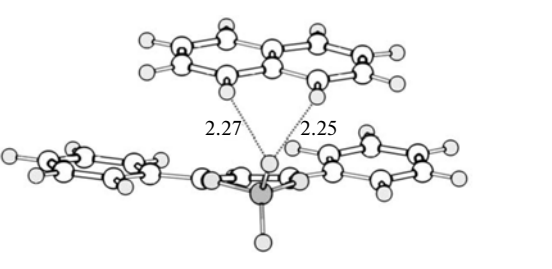
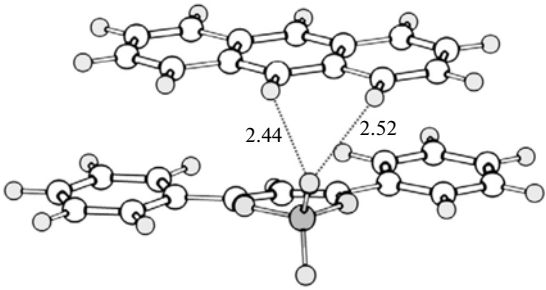
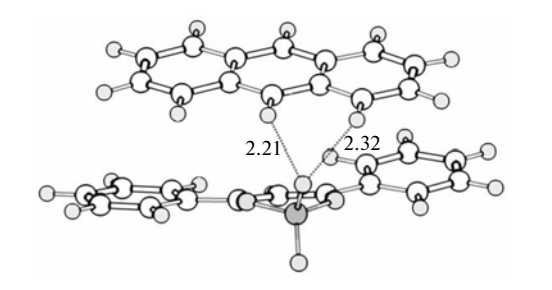
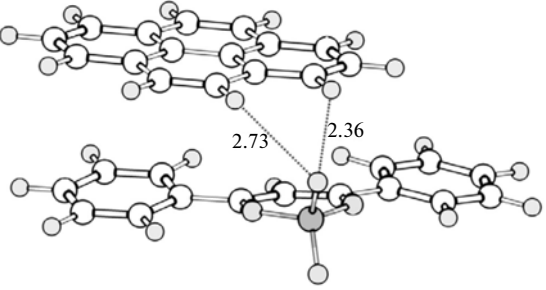
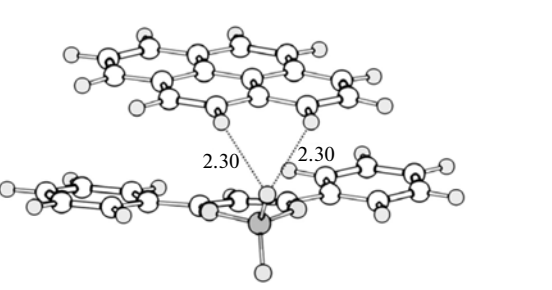
Molecule	Ground state	Excited state
<i>p</i> -Xylene	 <p>Diagram showing the ground state structure of <i>p</i>-Xylene. The molecule consists of two benzene rings connected by a para-substituted methylene group. The structure is shown in a perspective view. Two dashed lines indicate distances: 2.39 Å and 2.57 Å.</p>	 <p>Diagram showing the excited state structure of <i>p</i>-Xylene. The structure is shown in a perspective view. Two dashed lines indicate distances: 2.28 Å and 2.28 Å.</p>
Naphthalene	 <p>Diagram showing the ground state structure of Naphthalene. The molecule consists of two fused benzene rings. The structure is shown in a perspective view. Two dashed lines indicate distances: 2.49 Å and 2.53 Å.</p>	 <p>Diagram showing the excited state structure of Naphthalene. The structure is shown in a perspective view. Two dashed lines indicate distances: 2.27 Å and 2.25 Å.</p>
Anthracene	 <p>Diagram showing the ground state structure of Anthracene. The molecule consists of three fused benzene rings. The structure is shown in a perspective view. Two dashed lines indicate distances: 2.44 Å and 2.52 Å.</p>	 <p>Diagram showing the excited state structure of Anthracene. The structure is shown in a perspective view. Two dashed lines indicate distances: 2.21 Å and 2.32 Å.</p>
Pyrene	 <p>Diagram showing the ground state structure of Pyrene. The molecule consists of four fused benzene rings. The structure is shown in a perspective view. Two dashed lines indicate distances: 2.73 Å and 2.36 Å.</p>	 <p>Diagram showing the excited state structure of Pyrene. The structure is shown in a perspective view. Two dashed lines indicate distances: 2.30 Å and 2.30 Å.</p>

Table 3. Binding energies ΔE (kcal/mol) and charge transfer (Q) in complexes of DBMBF2 with aromatic hydrocarbon molecules in the ground and excited states

Molecule	State			
	ground		excited	
	$-\Delta E$	Q	$-\Delta E$	Q
Benzene	9.2	-0.03	18.5	0.57
Toluene	11.4	-0.03	24.7	0.62
<i>o</i> -Xylene	13.2	-0.03	29.7	0.80
<i>m</i> -Xylene	13.6	-0.04	28.9	0.72
<i>p</i> -Xylene	12.6	-0.01	30.2	0.81
Naphthalene	12.4	-0.04	35.8	0.84
Anthracene	15.2	-0.04	50.5	0.82
Pyrene	15.8	-0.04	47.1	0.84

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