Donor-acceptor complexes of dipyrrolylmethenes with boron trifluoride as intermediates in the synthesis of Bodipy

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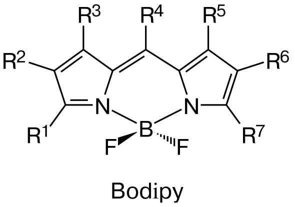
The formation of donor-acceptor complexes of dipyrrolylmethene and structurally similar biladiene-*a,c* with boron trifluoride was studied by electronic absorption, IR, and ^{1}H NMR spectroscopies as well as by quantum chemical calculations. It was shown that the formation of donor-acceptor complexes is the first step of the synthesis of the corresponding boron fluoride chelate complexes (Bodipy). The hydrogen bond N—H...F—B additionaly stabilizes the donor-acceptor complexes. The stability constants, geometric parameters, and energy characteristics of the donor-acceptor complexes were determined; the two-step mechanism of Bodipy synthesis was analyzed.

Key words: donor-acceptor complexes (DAC), dipyrrolylmethenes, boron trifluoride, Bodipy complexes, stability, mechanism of formation, electronic absorption spectroscopy, IR spectroscopy, ^{1}H NMR spectroscopy, semiempirical methods.

Dipyrrolylmethenes are promising chelating ligands. Under the action of a metal, a coordination center in metal complexes, their π-electron system becomes strongly polarized, which offers great prospects for practical use of these compounds as optical limiters,[1] photosensitizers,[2] chromophore and fluorescent markers, sensors,[3] *etc.* Coordination chemistry of dipyrrolylmethenes is extensively developed mainly due to their ability to form boron fluoride complexes whose spectral and photophysical parameters in many respects are better than the corresponding parameters of other chemical classes of dyes.[4] In the present, boron fluoride complexes of dipyrrolylmethenes and their numerous derivatives form a family of compounds called Bodipy.



Bodipy

There are two main synthetic routes to Bodipy and other dipyrrolylmethene complexes. One of them is the synthesis of complexes from monopyrroles *via* the formation of a dipyrrole ligand directly in the reaction mixture. In this case, isolation of an individual complex requires purification from the side products of dipyrrolylmethane formation and complexation. The other route is simpler and involves the synthesis from dipyrrolylmethenes or their salts with inorganic acids (in the latter case, preliminary deprotonation of the salt with a strong base is needed). The available methods allow one to synthesize Bodipy in 2—50% yields and involve a long-term refluxing of the reaction mixture.[5] Taking into account high practical value of Bodipy not only as individual substances used as limiters of hard radiation and photosynthesizers, but also as components of more complex molecular systems used to enchance the optical responses to various physicochemical factors (chromogenic and fluorophore markers for chemical and biological processes), attempts to intensify the synthesis of Bodipy are topical.

Information on the mechanisms of formation of dipyrrolylmethene complexes is unavailable. For complexes with d-elements, this is first of all due to high rates of establishing of equilibrium of complexation,[6] which makes direct kinetic studies of such reactions difficult. An analysis of published data also reveals little attention paid so far to the studies of intermediates of the synthesis of dipyrrolylmethene complexes including Bodipy.

Previously,[7] we found that the reactions of boron trifluoride etherate $BF_3 \cdot OEt_2$ with dipyrrolylmethenes in solutions result in stable donor-acceptor complexes (DAC) instead of expected boron fluoride complexes. Obviously, the structural and energy parameters of DAC are basic to the understanding of the mechanism of Bodipy formation.

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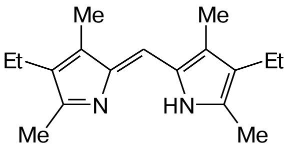
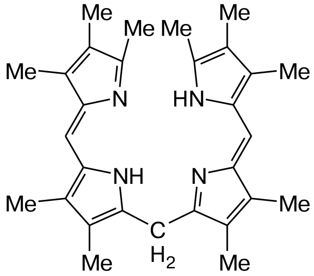
In a continuation of these investigations, we studied the possibilities for donor-acceptor interaction of dipyrrolylmethenes and biladiene-*a*,*c* [bis(dipyrrolylmethene)] with BF_3 to occur using spectroscopic methods and quantum chemical calculations. Analysis of experimental results was performed for alkyl-substituted dipyrrolylmethene (Hdpm) and biladiene-*a*,*c* (H_2bd).



Hdpm



H_2bd

Quantum chemical calculations were carried out mainly for unsubstituted structures.

Experimental

2,4,8,10-Tetramethyl-3,9-diethyldipyrrolylmethene-5,7 (Hdpm), 1,2,3,7,8,12,13,17,18,19-decamethylbiladiene-*a*,*c* (H_2bd), and their salts with HBr were synthesized, purified, and identified by known procedures.[8,9] Boron trifluoride etherate (Aldrich, chemically pure grade) was additionally purified by distillation at a reduced pressure over calcium hydride following a previously described procedure.[10] Benzene and DMF (extra pure grade) used as organic solvents were purified by known procedures.[11]

Electronic absorption spectra were registered in the region λ = 350—800 nm using a SF-103 spectrophotometer (Akvilon, Russia) controlled by a personal computer with the Spectr 1.0 program package.

^1H NMR spectra of solutions of the compounds studied in $CDCl_3$ were recorded on a Bruker Avance spectrometer (Germany) (500 MHz).

IR spectra (in KBr pellets) were registered with an Avatar 360 FT-IR ESP spectrometer in the region 400—4000 cm^{-1}.

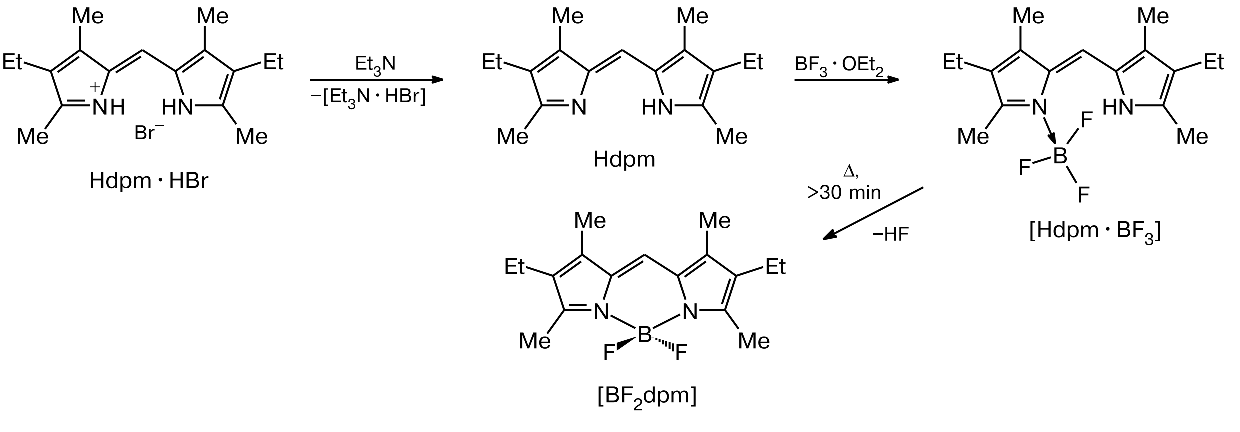
Quantum chemical calculations were performed using the Gaussian03W (see Ref. 12) and HyperChem 8.0.3 (see Ref. 13) program packages. Preliminary geometry optimization and construction of cross-sections of the potential energy surface (PES) were performed by the PM3 semiempirical method, which most correctly reproduces the X-ray data and the results of quantum chemical calculations of dipyrrolylmethenes, their complexes, and related compounds.[14—16] More exact geometric and energy parameters of molecules were obtained using the B3LYP/3-21G(d,p) density functional method.

Results and Discussion

The formation of a stable intermediate in the synthesis of Bodipy starting from alkylated dipyrrolylmethene was indicated for the first time by the analysis of the reaction mixture followed by chromatographic separation. The synthesis from dipyrrolylmethene hydrobromide (Hdpm • HBr) was performed in methanol in accordance with Scheme 1.

The free ligand L (L = Hdpm) was obtained by deprotonation of the initial salt Hdpm • HBr with triethylamine as a base. Then, an excess $BF_3 \cdot OEt_2$ was added and the reaction mixture was refluxed for 30 min. Spectrophotometric monitoring of the reaction revealed that, initially, a chromophore compound characterized by an intensive maximum at λ ~482 nm and a weak band in the near-UV region predominates in the solution (Fig. 1). This spectrum is very similar to the electron absorption spectrum of the protonated form of dipyrrolylmethene.[5] Subsequent prolonged heating of the reaction mixture resulted in

Scheme 1



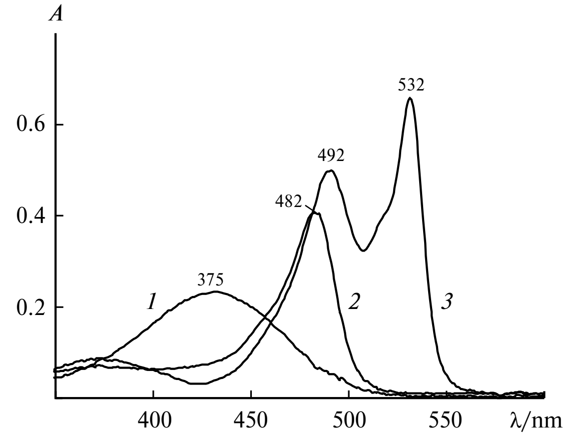


Fig. 1. Changes in electronic absorption spectra during formation of Hdpm complexes with BF_3: spectrum of free Hdpm ligand (*1*); spectrum of solution after addition of BF_3 to solid Hdpm (*2*); spectrum of reaction mixture after heating at ~60 °C (*3*).

a boron fluoride chelate [BF_2dpm] with an absorption maximum at $\lambda = 532$ nm.

Separation of the reaction mass in the initial stage by column chromatography (SiO_2, acetone—chloroform as eluent) suggested the presence of two fractions corresponding to the intermediate and to the boron fluoride complex. Then, the intermediate and the complex were isolated as individual compounds and characterized by electronic absorption, IR, and ^{1}H NMR spectroscopies.

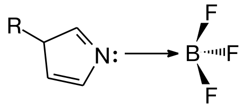
Along with the isolation of the intermediate from the reaction mixture, we studied the reactions between dipyrrolylmethenes (Hdpm and H_2bd) in the crystalline state with $BF_3 \cdot OEt_2$ twice distilled at a reduced pressure over calcium hydride. It was found that the electron adsorption spectrum of the product is identical to the spectrum observed during its formation in the reaction mixture in the synthesis of Bodipy. A similar result was obtained when solutions of free ligands Hdpm and H_2bd were mixed with $BF_3 \cdot OEt_2$ solution in benzene and DMF. Subsequent heating of the reaction mixtures and the solutions of the DAC synthesized in solution or from solid compounds led to boron fluoride complexes, which was indicated by changes in the electronic adsorption spectra, *viz.*, by the appearance of a strong maximum at $\lambda = 531$—533 nm (see Fig. 1).

Thus, our initial assumption that similarity of absorption spectra can suggest the formation of protonated forms of compounds was rejected. Would mixing of solutions of the ligands studied with $BF_3 \cdot OEt_2$ result in the protonated forms of compounds, their transformation to boron fluoride complexes should be impossible.

An analysis of the IR spectra of the DAC studied showed that the stretching and deformation vibrations of the N—H bond are less pronounced and blue shifted relative to the spectrum of free ligand by $\Delta\nu_{NH} = \nu_{NH}{}^{Hdpm} - \nu_{NH}{}^{[Hdpm \cdot BF_3]} = 15.2$ cm^{-1} and $\Delta\delta_{NH} = \delta_{NH}{}^{Hdpm} - \delta_{NH}{}^{[Hdpm \cdot BF_3]} = 16.8$ cm^{-1}, respectively. This suggests the involvement of the hydrogen atom of NH group in the formation of a hydrogen bond.[17] Thus, we obtained the first evidence of the existence of hydrogen bond between the hydrogen atom of the NH group in Hdpm and a fluorine atom of BF_3. In addition, the IR spectra unambiguously indicate that the intermediate of the reaction of Hdpm with BF_3 is the donor-acceptor complex rather than the protonated form. Similar results were obtained for the DAC formed by biladiene-*a*,*c*.

The existence of the DAC revealed was additionally substantiated by the ^{1}H NMR spectra. Indeed, the signals of NH proton in the spectrum of the complex [Hdpm$\cdot BF_3$] are shifted upfield (δ_{NH} 9.01) compared to spectrum of the free ligand (δ_{NH} 11.98) due to the increased shielding of the hydrogen atom. This in turn suggests a rather strong interaction [N—H...F—B] between the starting compounds and an additional stabilization of the complex [Hdpm$\cdot BF_3$] by the hydrogen bond.

Therefore, the electronic absorption, IR and ^{1}H NMR spectroscopy data confirm the existence of a stable product of the reaction of dipirrolylmethene with BF_3, formed due to the donor-acceptor interaction of the lone electron pair of the pyrrolenine nitrogen atom of ligands with the vacant orbital of the boron atom in BF_3.



A strong donor-acceptor interaction in the DAC studied is suggested by their electronic absorption spectra containing a charge transfer band in the near UV-region (Fig. 2, *a*; see Fig. 1). Similarity between the electronic spectra of the complexes and the protonated forms of ligands suggests an approximately equal degree of polarization of the π-electron system of dipyrrolylmethene by H^+ and BF_3. Thus, the donor-acceptor bond formed by insertion of the lone electron pair of the N atom of the pyrrolenine cycle of the ligand into the vacant orbital of the B atom is due to quite a strong interaction. This fact is very important for coordination chemistry of linear olygopyrroles because it allows one to refine the complexation mechanisms of this group of chelating ligands. Obviously, the formation of the DAC detected and synthesized in the present work is the first step of coordination of linear olygopyrroles not only with BF_3, but also with d- and f-element compounds.

We determined the stabilities of the complexes [Hdpm$\cdot BF_3$] and [H_2bd$\cdot(BF_3)_2$] in DMF and benzene by the mole fraction method. At a constant concentration of Hdpm or H_2bd, changes in the electronic absorption spectra and the corresponding mole fraction curves (see Fig. 2, *a*, *b*) suggest the interactions of the ligands L with

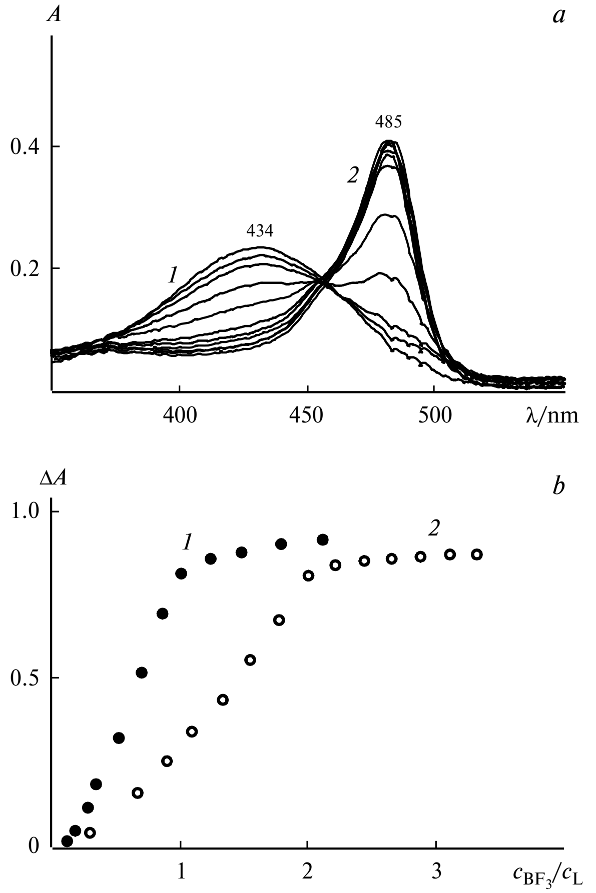


Fig. 2. Changes in electronic absorption spectra (*a*) in the reaction of H_2bd ($c_{H_2bd} = 6.6 \cdot 10^{-6}$ mol L^{-1}) with BF_3 in DMF (c_{BF_3}/mol L^{-1} = 0 (*1*), $2.69 \cdot 10^{-5}$ (*2*)) and molar ratio diagram (*b*) for systems L—BF_3 (λ = 489 nm) at constant ligand concentration in benzene (L = Hdpm (*1*), H_2bd (*2*)).

BF_3 in a 1 : 1 (L = Hdpm) and 1 : 2 ratio (L = H_2bd) in accordance with the following schemes:

$$\mathrm{Hdpm} + BF_3 \rightleftharpoons [\mathrm{Hdpm} \cdot BF_3],$$
$$H_2\mathrm{bd} + 2\,BF_3 \rightleftharpoons [H_2\mathrm{bd} \cdot (BF_3)_2].$$

The logarithms of the stability constants of the complexes [Hdpm•BF_3] and [H_2bd•$(BF_3)_2$] in DMF are 5.22±0.13 and 10.62±0.16, in benzene — 6.43±0.10 and 11.24±0.18, respectively. This suggests that the DAC can be treated as quite stable compounds. The differences in stability of the DAC in DMF and in benzene are probably due to the different solvation of the initial ligands and BF_3. The presence of quite stable complexes of BF_3 with electron donor DMF molecules in solution[18] prevents their replacement by di- or tetrapyrrole ligands, whereas BF_3 in benzene is solvated considerably weaker.

Then we performed quantum chemical calculations of geometruc and energy characteristics of the DAC, initial reactants, and products of the synthesis of Bodipy in the gas phase. The molecular models for [Hdpm•BF_3] and [H_2bd•$(BF_3)_2$] obtained from calculations are shown in Fig. 3. The calculated interatomic distances and bond angles (Table 1) suggest a tetrahedral environment of boron atom in the complexes [Hdpm•BF_3] and [BF_2dpm]. Analysis of geometric parameters of the molecules studied indicates considerable changes in the geometry of the initial ligands upon the addition of BF_3. For instance, the Hdpm ligand has a planar structure; in complex [Hdpm•BF_3], the dihedral angle between the pyrrole rings is 8.1°, whereas the dipyrrole ligand in complex [BF_2dpm] remains planar.

The calculated N→B bond length (1.606 Å) in complex [Hdpm•BF_3] is close to the known values for other BF_3 complexes with compounds containing donor N atoms (see Ref. 19). The nearest value (1.610 Å) was found for the donor-acceptor bond in complex [C_5H_5N•BF_3]. From the standpoint of the donor and acceptor orbitals the DAC under study belong to the nv-type.[20] The formation of [Hdpm•BF_3] causes the residual positive charge on the boron atom to decrease by ~0.2 (Table 2).

The results of calculations confirm the previously made suggestions about the formation of a hydrogen bond between the hydrogen atom of NH group of the ligand and the nearest fluorine atom (F''') in the BF_3 molecule. The distance between the interacting atoms is 0.175 nm, the N—H...F angle in the DAC of unsubstituted dipyrrolylmethene is 162.2°, *i.e.*, close to 180°, which allows this type of interaction to be attributed to hydrogen bonding based on the geometric criterion.[21] Such a bonding promotes further elimination of HF in the last step of the synthesis of Bodipy.

The calculated values of the enthalpies of formation of the [Hdpm•BF_3] complexes under study from the initial reactants are ~33 kcal mol^{-1}, which is in good agreement with the published data. In particular, the enthalpy of

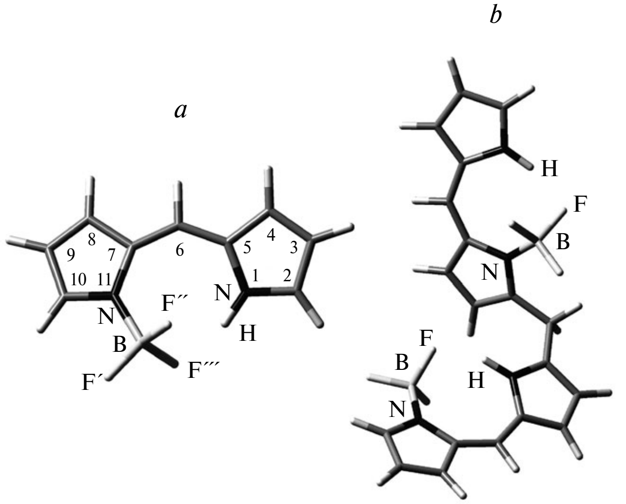


Fig. 3. Molecular structures of [Hdpm•BF_3] (*a*) and [H_2bd•$(BF_3)_2$] (*b*) according to quantum chemical calculations.

Table 1. Bond lengths (*d*) and bond angles (ω) in Hdpm ligand and [Hdpm • BF_3], [BF_2dpm] complexes calculated by the B3LYP/3-21G method

Bond	*d*/Å		
	Hdpm	[Hdpm • BF_3]	[BF_2dpm]
C(2)—C(3)	1.399	1.382	1.404
C(3)—C(4)	1.410	1.392	1.376
C(4)—C(5)	1.410	1.393	1.405
C(5)—C(6)	1.417	1.413	1.382
C(6)—C(7)	1.373	1.367	1.382
C(7)—C(8)	1.452	1.432	1.405
C(8)—C(9)	1.372	1.356	1.376
C(9)—C(10)	1.451	1.417	1.404
C(2)—N(1)	1.362	1.330	1.316
C(5)—N(1)	1.393	1.371	1.383
C(7)—N(11)	1.427	1.401	1.383
C(10)—N(11)	1.329	1.305	1.316
N(1)—H	1.020	0.998	—
N(11)—H	2.008	3.116	—
N(1)—N(11)	2.759	3.579	2.494
B—N(11)	—	1.606	1.507
B—F	—	1.366	1.367
F—H	—	1.813	—

Angle	ω/deg		
	Hdpm	[Hdpm • BF_3]	[BF_2dpm]
H—N(1)—C(2)	126.1	125.2	—
H—N(1)—C(5)	125.0	125.2	—
B—N(1)—C(2)	—	—	126.4
B—N(1)—C(5)	—	—	125.8
C(5)—C(6)—C(7)	127.4	138.5	121.8
C(7)—N(11)—C(10)	106.5	107.5	107.8
C(7)—N(11)—B	—	131.2	125.8
C(10)—N(11)—B	—	121.0	126.4
N(11)—B—F′	—	106.5	110.1
N(11)—B—F″	—	107.4	110.1
N(11)—B—F‴	—	107.6	—
F′—B—F″	—	113.6	111.1
F′—B—F‴	—	111.5	—
F″—B—F‴	—	109.9	—

formation of complex [$C_5H_5N \cdot BF_3$] is 24.9 kcal mol^{-1} (see Ref. 22).

We calculated the PES profile for two steps of the synthesis of [BF_2dpm] (Fig. 4):

$$\text{Hdpm} + BF_3 \longrightarrow [\text{Hdpm} \cdot BF_3],$$
$$[\text{Hdpm} \cdot BF_3] \longrightarrow [BF_2\text{dpm}] + \text{HF}.$$

The distance between the pyrrolenine N atom of the ligand and the B atom (B—N) was taken as reaction coordinate in the first step. The PES profile suggests a barrierless process; the decrease in the B—N distance leads to changes in the geometry of the BF_3 molecule from planar to tetrahedral. The energy gain in the formation of [Hdpm • BF_3] is ~34 kcal mol^{-1}. Analysis of the energy profile in the step of HF elimination was performed using the changes in the N—H and B—N distances as reaction coordinates. The calculated energy barrier was ~67 kcal mol^{-1}. Complex [BF_2dpm] is less stable than the donor-acceptor complex [Hdpm • BF_3]; the endothermic effect of the reaction is 26.2 kcal mol^{-1}.

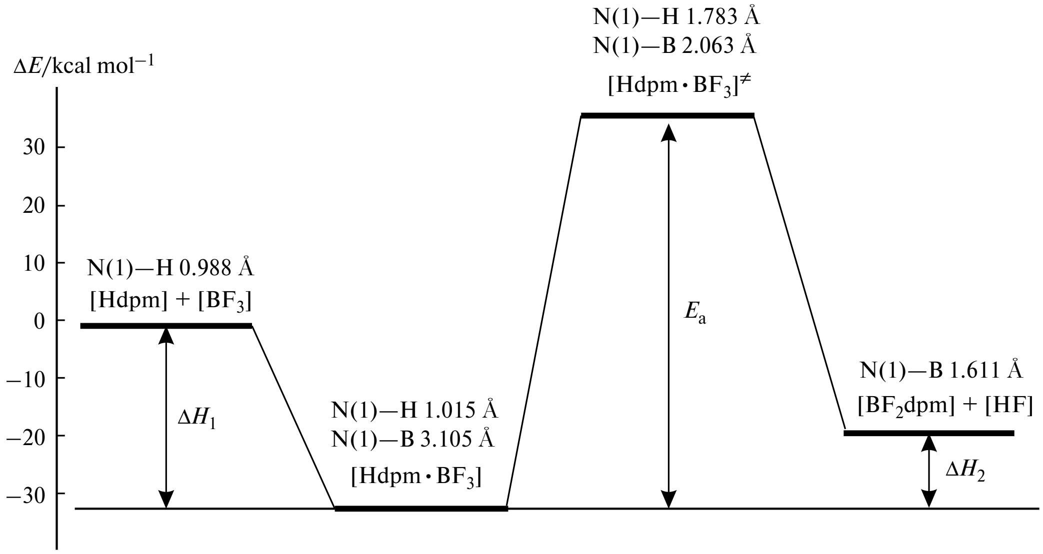


Fig. 4. Energy diagram of the reaction of BF_3 addition to unsubstituted dipyrrolylmethene molecule and subsequent elimination of HF (by PM3 method). The interatomic distances (*d*) are shown.

Table 2. Charges on the atoms of [$Hdpm \cdot BF_3$], [BF_2dpm] complexes and on the atoms of the starting compounds obtained by the PM3 method

Atom	Hdpm	BF_3	[$Hdpm \cdot BF_3$]	[BF_2dpm]
N(1)	0.439	—	0.440	0.308
N(11)	−0.129	—	0.315	0.308
B	—	0.331	0.094	0.060
F′	—	−0.110	−0.213	−0.210
F″	—	−0.110	−0.226	−0.209
F‴	—	−0.110	−0.229	—

Thus, analysis of the reaction route to Bodipy suggests high energy consumption to overcome the energy barrier to the transition [$Hdpm \cdot BF_3$] → [BF_2dpm]. This is in agreement with the severe temperature conditions used to increase the yield of boron fluoride complexes in the corresponding reactions.[5] The introduction of electron-donor solvents with good solvating ability toward HF into the molecular system should favour a decrease in the energy barrier.

In conclusion, the features of the synthesis of boron fluoride complexes of dipyrrolylmethenes studied in this work including the formation of the donor-acceptor bond between two starting reactants represent a remarkable example of the use of donor-acceptor complexes in substrate activation.[23]

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