

HeI photoelectron spectra and X-ray crystal structure of 2,2-difluoro-4-methyl-5,6-[2*H*-benzopyrano(3,4-*e*)-2-one]-1,3,2-dioxaborine

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Abstract

The HeI photoelectron spectra of 2,2-difluoro-4-methyl-5,6-[2*H*-benzopyrano(3,4-*e*)-2-one]-1,3,2-dioxaborine have been measured and compared with PES of 3-acetyl-4-hydroxycoumarin. The ionization bands in the spectra have been assigned on the basis of AM1 semi-empirical quantum chemical calculations. X-ray analysis of the boron chelate crystals has also been undertaken. Effective π -electron delocalization in the 1,3,2-dioxaborine ring of 2,2-difluoro-4-methyl-5,6-[2*H*-benzopyrano(3,4-*e*)-2-one]-1,3,2-dioxaborine both in gas phase and in solid state has been suggested.

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Keywords: 3-Acetyl-4-hydroxycoumarin; 2,2-Difluoro-4-methyl-5,6-[2*H*-benzopyrano(3,4-*e*)-2-one]-1,3,2-dioxaborine; Tautomerism; Photoelectron spectroscopy; X-ray crystal analysis; Electron structure

1. Introduction

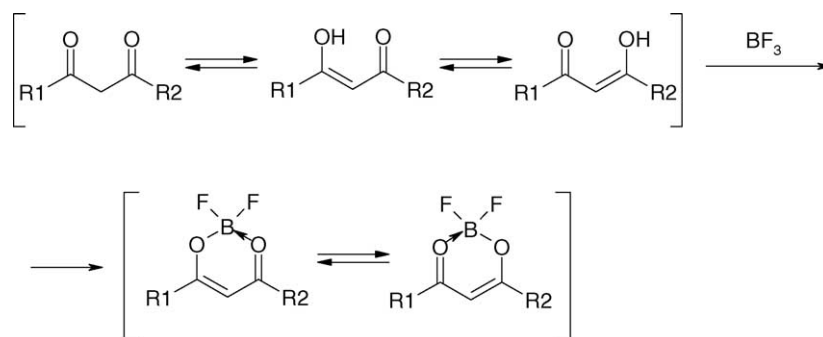
Complexes of β -diketones with acceptor boron compounds behave an increased reaction ability when compared with the uncomplexed substrates. For example complexes of β -diketones with boron trifluoride provide a high proton reactivity of an alkyl group joined the B-chelate ring [1–6]. The methyl group in boron complexes of substituted *o*-hydroxyacetophenones, benzoylacetones and acetylnaphthols has been shown to participate easily in condensation reactions with carbonyl compounds and their derivatives: aldehydes, formamides, *ortho*formates and tetraethoxypropane, derivatives of glutamic aldehyde [7–10].

We have also prepared earlier, a series of complexes of 3-acetyl-4-hydroxycoumarin (**1**) and 8-acetyl-7-

hydroxycoumarin with boron trifluoride and have studied condensation reactions of these complexes with carbonyl compounds. Polymethine dyes possessing a prominent fluorescence have been isolated as products of the reactions [11].

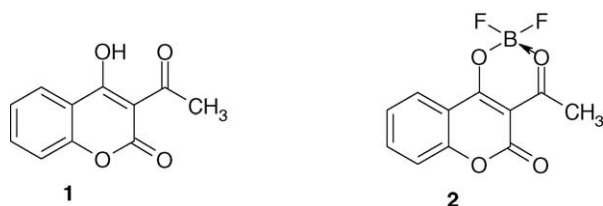
Due to their high reactivity, the steric and electronic structure of boron diketonates has been studied in much detail. These complexes have been shown to exist as non-ionized chelates. They are stable to hydrolysis and differ in this stability as compared with complexes of boron trifluoride with many other organic compounds. Based on the chemical shifts of C–H protons in the ^1H NMR spectra of complexes of BF_3 with acetylacetone and dibenzoylmethane, quasi-aromaticity of cyclic difluorodioxaborine has been proposed [4,12,13]. IR and NMR spectroscopy are also in accordance with the quasi-aromatic structure of boron diketonates [14]. They are planar molecules with six π -electrons, delocalized in the boronate cycle.

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Nevertheless, these boron β -diketonates have been found to have rather large values of dipole moments: 6.7 and 4.6 D, respectively [15,16]. These values are in accordance with a charge separation in the dioxaborine cycle.

Photoelectron spectroscopy has never been used for structural studies of boron β -diketonates including 2,2-difluoro-4-methyl-5,6-[2*H*-benzopyrano(3,4-*e*)-2-one]-1,3,2-dioxaborine (**2**). While studying preparative schemes based on the boron β -diketonates reactivity, we have measured photoelectron spectra of 3-acetyl-4-hydroxycoumarin–boron trifluoride complex and have undertaken its X-ray crystal analysis.



2. Experimental

3-Acetyl-4-hydroxycoumarin (**1**) has been prepared by known procedure, melting point 137–139 °C [17].

2,2-Difluoro-4-methyl-5,6-[2*H*-benzopyrano(3,4-*e*)-2-one]-1,3,2-dioxaborine (**2**). BF_3 -etherate (9.8 g, 0.18 mol) has been added carefully to the boiled solution of 3-acetyl-4-hydroxycoumarin (14 g, 0.17 mol) in benzene (50 ml). The mixture has been boiled then for 1 h. The precipitate was filtered off, washed by benzene and dried. The compound **2** was obtained as colorless crystals, m.p. 199–200 °C (benzene), yield 72%.

HeI photoelectron spectra were measured on a Perkin-Elmer PS-18 spectrometer under pressure of 2×10^{-5} Torr. Xenon ionization bands at 12.130 and 13.436 eV corresponding to the ionizations $\text{Xe}^+(^2\text{P}_{3/2}) \leftarrow \text{Xe}(^1\text{S}_0)$ and $\text{Xe}^+(^2\text{P}_{1/2}) \leftarrow \text{Xe}(^1\text{S}_0)$, respectively, have been used as the calibrant bands. Experimental resolution was 0.06 eV and the accuracy of vertical ionization energies (VIEs) measurements ± 0.03 eV. Assignments of the experimental values of VIEs for the compounds **1** and **2** based on the Koopmans' theorem [18] and applied to the results of AM1 calculations are presented in Tables 1–3.

Table 1

Relative energies (kcal/mol) of tautomers **1a–1f** of 3-acetyl-4-hydroxycoumarin calculated by different methods

Method of calculation	1a	1b	1c	1d	1e	1f
AM1	0.75	0.00	6.58	8.89	15.63	20.46
PM3	0.26	0.00	3.86	6.02	18.00	25.03
3-21G	0.00	0.07	5.14	19.61	29.92	33.01
6-31G*	0.00	0.94	4.91	8.59	30.97	37.71
6-31G**	0.00	0.93	4.78	12.04	27.81	34.45

Table 2

Calculated MO-energies of tautomers of 3-acetyl-4-hydroxycoumarin **1a** and **1b**

Tautomer	Method of calculation	
	AM1 ⁶	6-31G**
1a	−9.17 (π_8)	−9.18
	−9.49 (π_7)	−9.65
	−10.42 n_0	−11.07
	−10.59 (π_6)	−11.68
1b	−9.04 (π_8)	−9.22
	−9.62 (π_7)	−9.69
	−9.86 (π_6)	−10.29
	−10.58 n_0	−11.80

Table 3

Experimental vertical ionization energies of 3-acetyl-4-hydroxycoumarin and their AM1 assignment

IP _i (eV)	MO
9.10	9.17 π_8
9.50	9.49 π_7
10.20	10.43 n_0
10.60	10.70 π_6

X-ray measurements have been carried out on a diffractometer Siemens P3 (Mo $\text{K}\alpha$ ($\lambda = 0.71073$ Å), graphite monochromator).

The semi-empirical quantum chemical calculations by the AM1 method were performed using the MOPAC program package [19]. Preliminary geometry optimization was carried out with use of the MM+ molecular mechanics method.

3. Results and discussion

Since 2,2-difluoro-4-methyl-5,6-[2*H*-benzopyrano(3,4-*e*)-2-one]-1,3,2-dioxaborine consists of 3-acetyl-4-

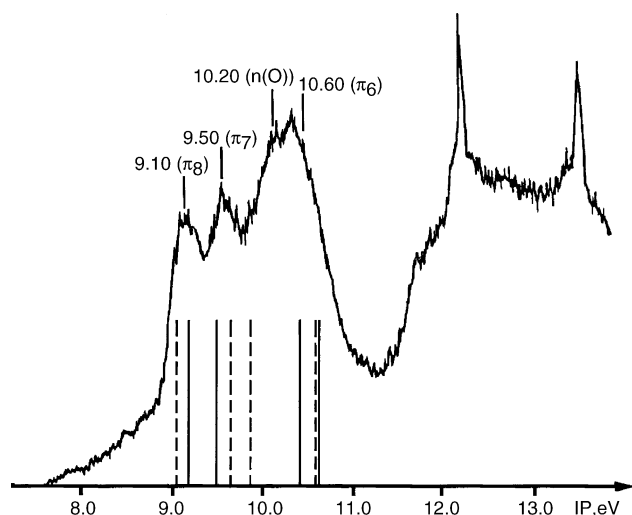
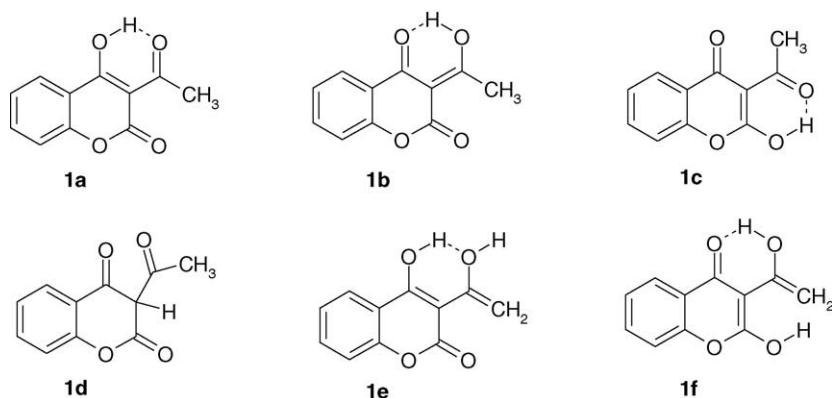


Fig. 1. HeI photoelectron spectrum of 3-acetyl-4-hydroxycoumarin (**1**).

hydroxycoumarin and BF_3 fragments, it is reasonable to discuss, first of all, structural characteristics of these initial compounds.

HeI photoelectron spectrum of the compound **1** is shown on Fig. 1. 3-Acetyl-4-hydroxycoumarin represents an enol form of the coumarin derivative that has three carbonyl functions. Therefore, it can exist in several tautomeric structures. Some of them (**1a–1f**) are shown below.

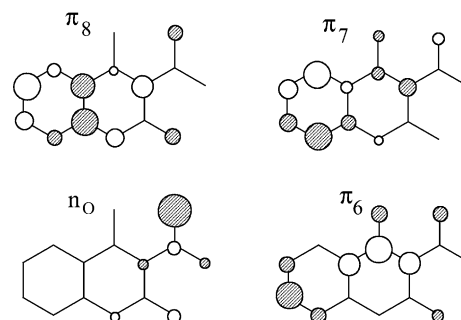


Since these tautomeric forms are rather different in energy, equilibrium between two forms, **1a** and **1b** seem to be the predominant ones in the structural transformations of the compound **1**. We have made this conclusion while studying electronic structure of 3-acetyl-4-hydroxycoumarin with use of both semi-empirical and non-empirical quantum chemical calculations [20,21]. The relative energies of the tautomers **1a–1f** are compared in Table 1 [21]. All the calculation procedures show the forms **1a** and **1b** to have maximal stabilities.

We have also calculated energies of occupied molecular orbitals of the tautomeric forms **1a** and **1b** both by the AM1 method and by ab initio method with a 6-31G** basis set. These values are compared in Table 2. Both methods of calculations agree in the assignment of the σ/π symmetry to the occupied molecular orbitals. However, the AM1

calculated values seem better to fit to the experimental data. Therefore, the following analysis is based on the AM1 calculations.

PES-study of the compound **1** confirms a predominance of the tautomeric form **1a**. As one can see from comparison of calculated values, tautomeric forms **1a** and **1b** differ in sequence of the third and the fourth occupied molecular orbitals: ionization of the n_{O} -orbital of acetyl function should be seen as the third band in the spectrum of the tautomeric form **1a** and as the fourth band in the spectrum of the tautomeric form **1b**.



Experimental values of VIEs of compound **1** are given on Fig. 1. The calculated values for the form **1a** and of the form **1b** are also shown there by bold and dotted vertical lines. The data, calculated for the form **1a**, seem to be in better agreement with the experimental IP-values. The first

and the second bands in the spectrum are due to ionization of the π -orbitals delocalized through the whole molecule. The third band appears to be a complex one and is caused by overlapping of ionization of two occupied molecular orbitals. According to the AM1 calculated data, these orbitals are n_{O} (acetyl)-orbital of σ -symmetry and π_6 -orbital, delocalized through the whole molecule. Assignment of the experimental IP-values of the compound **1** is summarized in Table 3.

This assignment is in a good agreement with the analysis of the photoelectron spectrum of compound **2**. The photoelectron spectrum of 2,2-difluoro-4-methyl-5,6-[2H-benzopyrano(3,4-e)-2-one]-1,3,2-dioxaborine is shown on Fig. 2. Experimental VIEs are given by numbers near the bands and calculated MO energies are shown by vertical bold lines below the bands. In whole, formation of the

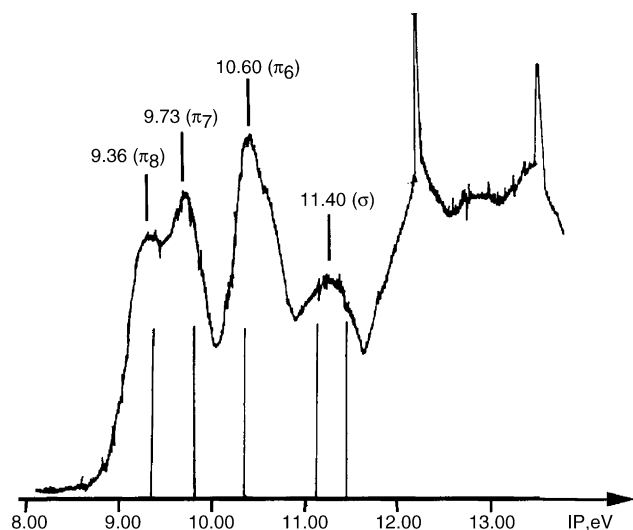
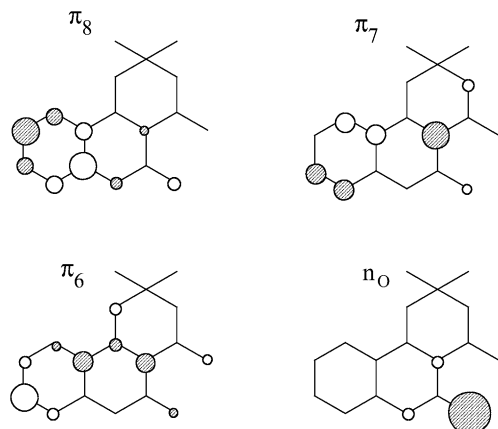


Fig. 2. HeI photoelectron spectrum of 2,2-difluoro-4-methyl-5,6-[2H-benzopyrano(3,4-e)-2-one]-1,3,2-dioxaborine (2).

boron-complex changes the electronic structure of 3-acetyl-4-hydroxycoumarin in a certain extent. Due to the acceptor properties of the boron atom, VIE_1 and VIE_2 are shifted to the higher values. The first overlapped band of the spectrum is due to ionization of the π_8 - and π_7 -molecular orbitals.



Their experimental VIE-values (9.36 and 9.73 eV) are in a good agreement with the calculated values: 9.45 and 9.84 eV, respectively. The second band is also due to ionization of a π -orbital (π_6 -orbital) delocalized through out the 3-acetyl-4-hydroxycoumarin fragment. The third broad band at 11.4 eV in the spectrum is due to ionization of at least two σ -orbitals, which have calculated VIE-values equal to 11.17 and 11.58 eV.

As can be seen from the comparison of photoelectron spectra and structures of occupied molecular orbitals of the compounds **1** and **2**, the lack of ionization from a n_O (acetyl)-orbital of σ -symmetry is a specific property of the spectrum of 2,2-difluoro-4-methyl-5,6-[2H-benzopyrano(3,4-e)-2-one]-1,3,2-dioxaborine. Absence of a n_O -orbital ionization in this part of the spectrum is due to its participation in the formation of a boron–oxygen σ -bond and transformation of

Table 4

Experimental vertical ionization energies of 2,2-difluoro-4-methyl-5,6-[2H-benzopyrano(3,4-e)-2-one]-1,3,2-dioxaborine and their AM1 assignment

IP _i (eV)	MO
9.36	9.45 π_8
9.73	9.84 π_7
10.56	10.56 π_6
~11.4	11.17, 11.58 σ

the boron atom to the tetrahedral state. As a result, the second band in the photoelectron spectrum of compound **2** is not an overlapped one. It has a narrow shape, since it is due to ionization of π -orbital. Assignment of the experimental VIEs of the compound **2** is summarized in Table 4.

We have also undertaken the X-ray crystal analysis of 2,2-difluoro-4-methyl-5,6-[2H-benzopyrano(3,4-e)-2-one]-1,3,2-dioxaborine. Bond lengths and angles are given in Table 5 (Fig. 3). Compound **2** was found to possess a planar molecule. Deviation of any atom in the dioxaborine cycle from planarity does not exceed 0.38 Å. As a result, the planar structure of this complex provides a good condition for effective delocalization of bonding electrons. Bond lengths in the dioxaborine fragment are in accordance with this proposition. For example bond lengths

Table 5

Bond lengths (r , Å) and valence angles (ω , °) 2,2-difluoro-4-methyl-5,6-[2H-benzopyrano(3,4-e)-2-one]-1,3,2-dioxaborine^a (X-ray crystal analysis)

Parameters	r (Å)	Parameters	ω (°)
C ¹ —C ²	1.376(3)	C ¹ C ² C ³	119.8(2)
C ² —C ³	1.391(3)	C ⁴ C ³ C ²	121.3(2)
C ³ —C ⁴	1.380(3)	C ³ C ⁴ C ⁵	118.7(2)
C ⁴ —C ⁵	1.389(3)	C ² C ¹ C ⁶	120.0(2)
C ⁵ —C ⁶	1.388(2)	C ⁴ C ⁵ C ⁶	121.2(2)
C ⁶ —C ¹	1.402(2)	C ⁵ C ⁶ C ¹	119.0(2)
C ⁵ —O ¹	1.371(1)	O ¹ C ⁵ C ⁴	116.7(2)
C ⁶ —C ⁷	1.439(2)	O ¹ C ⁵ C ⁶	122.0(1)
C ⁷ —C ⁸	1.395(2)	C ⁵ C ⁶ C ⁷	117.9(1)
O ⁴ —C ⁷	1.296(2)	C ¹ C ⁶ C ⁷	123.1(2)
C ⁸ —C ⁹	1.453(2)	C ⁸ C ⁷ C ⁶	119.7(1)
O ¹ —C ⁹	1.376(2)	O ⁴ C ⁷ C ⁶	117.9(1)
C ¹⁰ —C ⁸	1.413(2)	O ⁴ C ⁷ C ⁸	122.4(1)
C ¹¹ —C ¹⁰	1.476(3)	C ⁵ O ¹ C ⁹	122.3(1)
C ⁹ —O ²	1.203(2)	C ⁷ C ⁸ C ⁹	120.4(1)
O ³ —C ¹⁰	1.285(2)	O ¹ C ⁹ C ⁸	117.3(1)
F ¹ —B ¹	1.353(2)	C ⁷ C ⁸ C ¹⁰	118.3(1)
F ² —B ¹	1.359(2)	C ⁹ C ⁸ C ¹⁰	121.1(1)
O ³ —B ¹	1.503(3)	C ⁸ C ¹⁰ C ¹¹	124.7(2)
O ⁴ —B ¹	1.484(2)	O ² C ⁹ O ¹	116.0(1)
		O ² C ⁹ C ⁸	126.6(2)
		O ³ C ¹⁰ C ⁸	119.6(2)
		O ³ C ¹⁰ C ¹¹	115.7(2)
		C ¹⁰ O ³ B ¹	123.0(1)
		C ⁷ O ⁴ B ¹	120.5(1)
		F ¹ B ¹ F ²	113.2(2)
		F ¹ B ¹ O ⁴	109.6(2)
		F ² B ¹ O ⁴	108.9(2)
		F ¹ B ¹ O ³	108.0(2)
		F ² B ¹ O ³	107.8(2)
		O ⁴ B ¹ O ³	109.2(1)

^a All torsion angles are equal to 0° or 180°, respectively.

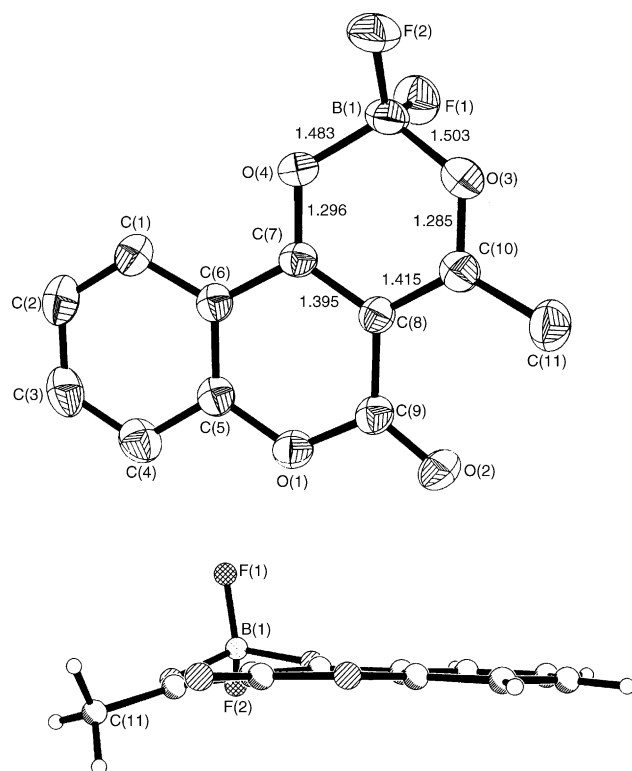


Fig. 3. X-ray structure of 2,2-difluoro-4-methyl-5,6-[2*H*-benzopyrano(3,4-*e*)-2-one]-1,3,2-dioxaborine (2).

B^1-O^3 and B^1-O^4 are equal to 1.503(1) and 1.483(1) Å, respectively. Bond lengths $C^{10}-O^3$ and C^7-O^4 are also rather close by value: 1.285(2) and 1.296(2) Å. The same is true for the C^8-C^{10} - and C^7-C^8 -bonds: 1.413(2) and 1.395(2) Å, respectively. We can compare these values with $C^{10}-O^3$ -, C^7-O^4 -, C^8-C^{10} - and C^7-C^8 -bond lengths that we have found in the 3-acetyl-4-hydroxycoumarin by X-ray crystal analysis: 1.254(2), 1.303(2), 1.454(2) and 1.392(2) Å, respectively[22]. We can conclude, delocalization of bonding electrons in the 1,3,2-dioxaborine fragment of 2,2-difluoro-4-methyl-5,6-[2*H*-benzopyrano(3,4-*e*)-2-one]-1,3,2-dioxaborine molecule is much more effective than electron delocalization in the H-bonding fragment of the 3-acetyl-4-hydroxycoumarin molecule.

4. Conclusions

For the first time photoelectron spectroscopy has been used for an analysis of electronic structure of boron diketonate. HeI photoelectron spectra of 3-acetyl-4-hydroxycoumarin and 2,2-difluoro-4-methyl-5,6-[2*H*-benzopyrano(3,4-*e*)-2-one]-1,3,2-dioxaborine have been recorded and their vertical ionization energies were assigned on the basis of the AM1 quantum chemical calculations. Although 3-acetyl-4-hydroxycoumarin can exist in several tautomeric forms, this particular form seems to be a predominant one according to the assignment of the exper-

imental VIE-values. The 3-acetyl-4-hydroxycoumarin tautomeric form transforms in a certain extent under complex formation with BF_3 . This conclusion agrees with the X-ray crystal analysis of the dioxaborine. The BF_2 -fragment looks to be connected by two equivalent $\sigma(B-O)$ -bonds with the fragment of 3-acetyl-4-hydroxycoumarin in the 2,2-difluoro-4-methyl-5,6-[2*H*-benzopyrano(3,4-*e*)-2-one]-1,3,2-dioxaborine molecule. Two B–O-bonds in the dioxaborine fragment are similar by length. The same is true for two C–O-bonds and two C–C-bonds in this fragment as well. We suggest an effective π -electron delocalization in the 1,3,2-dioxaborine ring of 2,2-difluoro-4-methyl-5,6-[2*H*-benzopyrano(3,4-*e*)-2-one]-1,3,2-dioxaborine both in gas phase and in solid state. This delocalization seems to lead to the mentioned above a high proton reactivity of an alkyl group joined the B-chelate ring.

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