Structure and photochromic properties of the crystalline 1,3-dimethyl-2-(3-phenylnorbornadienyl)benzimidazolium tetrafluoroborate

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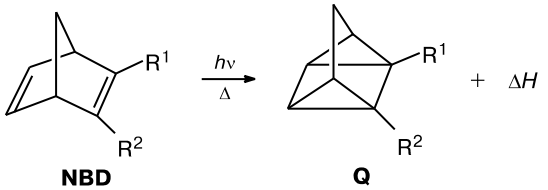
Molecular and crystal structures, as well as photochemistry in the solid state were studied for the norbornadiene, whose one double bond was modified by the simultaneous introduction of an electron-donating and electron-withdrawing substituents. Effects of the nature of substituents on the distance of the substituted C=C bond were analyzed by quantum chemical calculations.

Key words: norbornadiene, crystal structure, photochemistry.

The norbornadiene—quadricyclane photochromic system (Scheme 1) can display properties of the solar energy battery,[1,2] as well as optical systems for recording and storage of information.[3] The photoreaction process includes the valent isomerization of the norbornadiene (**NBD**) system to the metastable quadricyclane structure (**Q**) containing highly strained fragments: two cyclopropane and a cyclobutane rings. This results in the high thermal effect the reverse dark reaction $\Delta H = -89$ kJ mol^{-1}.[4] Because of high activation barrier, the reverse transformation **Q** → **NBD** requires catalytic or thermal initiation.

Scheme 1

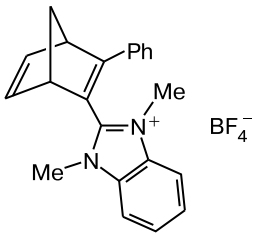


NBD **Q**

The disadvantage of this system is the short-wave absorption of **NBD** (below 300 nm) and a low quantum yield of the direct photoreaction (0.05). In this connection, there arises a necessity to modify the norbornadiene molecule. One of the approaches is to use various sensitizers of the **NBD** → **Q** valent isomerization including those chemically bound to the **NBD** molecule.[1]

Another approach consists in the structural modification of starting **NBD** by the simultaneous introduction of electron-donating and electron-withdrawing substituents to the same double bond. In this case, the double bond of norbornadiene is involved into the chain of conjugation between the substituents and, as it was shown by the X-ray diffraction studies of the structures of such compounds,[2] the multiple bond distance becomes longer by 0.01—0.05 Å. Variation of substituents allows one to shift the absorption border to the long-wave region to λ_b = 400 nm and to increase the quantum yield to $\varphi = 0.3$—0.6.[2]

1,3-Dimethyl-2-(3-phenylnorbornadien-2-yl)benzimidazolium tetrafluoroborate (**1**) synthesized by us earlier[5,6] can serve as an example of such systems.



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In solutions of norbornadiene **1**, the value λ_b reaches 350 nm, whereas the quantum yield of the photoreaction in propan-2-ol is 0.41. The reverse reaction takes place upon heating (343 K, acetonitrile) with the rate constant $k = 6 \cdot 10^{-4}$ s^{-1}. The cycle **NBD** ⇆ **Q** can be repeated many times without visible signs of destruction.

Possessing such properties, compound **1** with the cationic benzimidazolium substituent seems a promising intermediate product for the synthesis of polyfunctional materials combining photochromic and, for example, magnetic properties. Such photomagnets have been obtained by introduction of cations of photochromic compounds

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between the layers of the magnetic anionic net $[Mn^{II}Cr^{III}(ox)_3]_n^{n-}$ (ox = $C_2O_4^{2-}$).[7,8]

In the present work, we studied the structure of compound **1** by X-ray crystallography and its photochemistry in the solid state.

Experimental

Salt **1** was obtained according to the procedure described earlier.[5] Single crystals were grown by crystallization from acetonitrile.

X-ray diffraction analysis. Parameters of the crystal unit cell and three-dimensional set of intensities were obtained on a Bruker P-4 autodiffractometer (Mo-Kα radiation, graphite monochromator). Colorless clears crystals of **1** are monoclinic, $C_{22}H_{21}N_2F_4B$, M = 400.22, a = 11.927(1) Å, b = 13.198(1) Å, c = 12.969(2) Å, β = 103.47(1)°, V = 1985.3(4) Å^3, Z = 4, d_{calc} = 1.339 g cm^{-3}, μ(Mo-Kα) = 0.10 mm^{-1}, the space group is $P2_1/n$. Intensities of 3983 reflections were measured in the reverse space quadrant (2θ ≤ 50°) using the ω/2θ-scanning from the single crystal of 0.4×0.4×0.4 mm in size. After the systematically extinct reflections were excluded and intensity of equivalent reflections were averaged, the operating massif of measured F^2_{hkl} and σ(F^2) contained 3186 independent reflections (R_{int} = 0.023), from which 1923 were with $F^2 > 4\sigma(F^2)$. The structure was solved by the direct method using the SHELXTL program (see Ref. 9) and refined using the full-matrix least squares method (LSM) relatively to F^2 using the SHELXTL program in anisotropic approximation for nonhydrogen atoms. The H atoms were localized in the Fourier synthesis of the differential electron density, then the coordinates and isotropic thermal parameters of all the H atoms were calculated using the least squares method procedure on the riding model.[9]

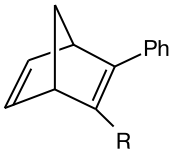
The final refinement parameters: R_1 = 0.062 on 1923 observed reflections with $I \geq 2\sigma(I)$ and R_2 = 0.1025 on all the measured reflections, GOF = 1.043. After the refinement was finished, the maximum and minimum values of the differential electron density were 0.517 and –0.245 e A^{-3}, respectively.

Quantum chemical calculations were performed using the GAUSSIAN-03 program (see Ref. 10) in the framework of the functional density theory by the B3LYP/6-31G* method with the full optimization of geometry.

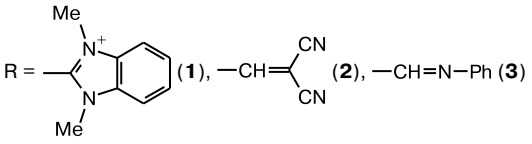
Photochemical studies of the salt **1** in the solid state were performed on the thin-layer samples prepared from the powder of fine crystals. A PL-S 9W gas-discharge low pressure mercury lamp producing the UV light in the range 340—390 nm with the maximum at 355 nm was used for the irradiation, whose internal surface was covered with a luminophore. Absorption spectra were recorded on a Shimadzu UV-3101PC spectrophotometer. Placement of the samples in the instrument was strictly fixed and the same in each measurement in order to exclude changes in the base line, which depends on the position of the sample with respect to the optical axis of the instrument.

Results and Discussion

Crystal structure of salt 1. For the discussion of the research results for the salt **1**, we compared them with the data obtained earlier[11] for compounds **2** and **3**.



1—3



The structure of salt **1** is shown in Fig. 1. In the **NBD**-fragment, the angle between the planes C(1′)—C(2′)—C(3′)—C(4′) and C(1′)—C(4′)—C(5′)—C(6′) is 112.7(2)°, the angles of the two indicated planes with the plane of the atoms C(1′)—C(7′)—C(4′) are equal to 122.1(2) and 125.1(2)°, respectively. The single bond distances of the **NBD**-fragment lie within the range 1.505—1.562 Å. The **NBD**-fragments in compounds **1**—**3** have the same structure, which is close to the structure of unsubstituted **NBD** ($R^1 = R^2$ = H).[12,13] Figure 2 shows the picture of three compared molecules superimposed on the plane of the atoms C(1′)—C(7′)—C(4′) (here and further, all the atoms are shown having the numeration of atoms in the studied compound **1**).

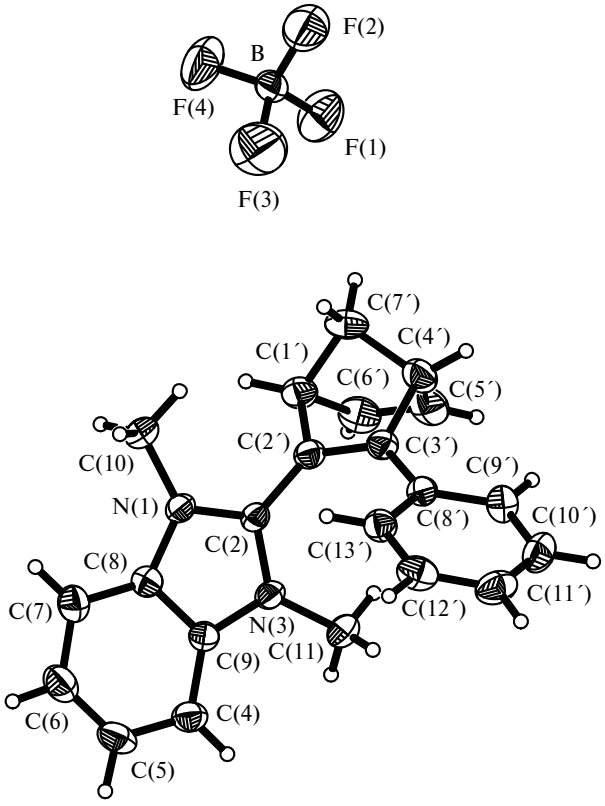


Fig. 1. The structure of salt **1**.

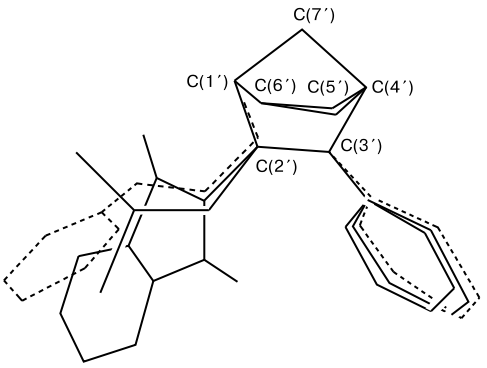


Fig. 2. The picture of molecules **1**, **2**, and **3** superimposed on the plane of the atoms C(1')—C(7')—C(4').

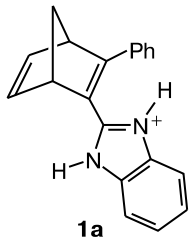
In the cation **1**, the positive charge is delocalized over the fragment N(1)—C(2)—N(3) (the bond distances C(2)—N(1) 1.350(4) and C(2)—N(3) 1.347(4) Å), the atoms come out of the plane of benzimidazolium fragment no more than by 0.013 Å.

The substituted (C(2′)=C(3′)) and unsubstituted (C(5′)=C(6′)) double bond distances differ and are equal to 1.350(4) and 1.299(5) Å, respectively, which coincide with the values in molecule **3** within the error limits (1.342(6) and 1.310(8) Å). In compound **2**, the C(2′)=C(3′) bond is elongated to 1.38(1) Å, though the C(5′)=C(6′) bond remains unchanged (1.29(2) Å). Note that in the molecule **2**, the C(2′)=C(3′) bond distance has the maximum value among the organic compounds in the Cambridge Structural Database, which satisfy the structural formula of **NBD** in Scheme 1. For the comparison, note that in the unsubstituted norbornadiene, the distances for these bonds are 1.333 Å.[12,13]

This difference in the double bond distances can be due to the differences in the electron-donating and -withdrawing properties of substituents, as well as to the efficiency of conjugation of the C(2′)=C(3′) π-bond with substituents R^1 and R^2. In compounds **1—3**, the phenyl rings at the C(3′) atom are turned from the plane of the double bond: the torsional angle C(2′)—C(3′)—C(8′)—C(13′) insignificantly increases in the series −33.0(3)°, 39.4(7)°, and −42(2)° for **1**, **3**, and **2**, respectively. Conversely, electron-withdrawing substituents in the compounds under study have different angles of the turn. The torsional angle N(1)—C(2)—C(2′)—C(3′) in the structure **1** is equal to 125.5(4)°, whereas analogous angles in **2** and **3** are equal to 178.0(5) and 178.6(5)°, respectively. It is obvious, that conjugation of the C(2′)=C(3′) double π-bond with the electron-withdrawing substituents in compounds **2** and **3** should be considerably more efficient than in cation **1**. Apparently, the elongation of this bond in the studied compound **1** is due to the electron-withdrawing inductive properties of the benzimidazolium substituent.

The large angle of turning of the benzimidazolium fragment can be explained, first, by the intramolecular steric hindrance and partially by the effects of crystal packing. To evaluate effects of these factors, we performed quantum chemical calculations for the cation with full optimization of the cation geometry. The optimization results in the increase of the angle N(1)—C(2)—C(2′)—C(3′) by 6.4° (Table 1). However, with such geometry the π-orbitals of the double bond and benzimidazolium fragment have an unfavorable orientation for the interaction to occur.

Effect of the steric factor in the first place is due to the methyl groups at the C(10) and C(11) atoms in the benzimidazolium fragment. We suggested that their replacement with the hydrogen atoms in the modified cation **1a** will allow the positively charged fragment to rotate more freely.



1a

In fact, with the full optimization of the geometry of molecule **1a**, the torsional angle N(1)—C(2)—C(2′)—C(3′) was increased to −174.4° (see Table 1). But even with the favorable planar geometry, the double (C(2′)=C(3′)) and single (C(3′)—C(8′) and C(2)—C(2′)) bond distances were changed little; no conjugation with the phenyl ring occurred, and the C(3′)—C(8′) bond distance remained unchanged. The largest changes, caused by the arisen conjugation between the benzimidazolium and **NBD**-fragments, are observed for the C(2)—C(2′) bond, it became shorter by 0.02 Å. Elongation of the C(2′)=C(3′) bond is less pronounced (see Table 1). Apparently, such a low lability of the bond is due to the high rigidity of the **NBD**-fragment, which does not permit more strong distortions. Thus, according to our calculations even in norbornadiene **4** with $R^1 = NH_2$ and $R^2 = NO_2$ the C(2′)=C(3′) bond distance is 1.376 Å.

Note that the character of R^1 and R^2 affects not only photochemical parameters of norbornadiene, but also the difference in the energies between the **NBD**- and **Q**-forms in considerable extent.[14] Thus, our calculations for unsubstituted **NBD** and **Q** ($R^1 = R^2 = H$) gave ΔE =

Table 1. Selected bond distances and torsional angles in cations **1** and **1a** according to the experimental and calculated data

Parameter	Experiment (X-ray), **1**	DFT/B3LYP calculations	
		1	**1a**
Bond distance/Å			
C(2′)=C(3′)	1.350(4)	1.364	1.370
C(3′)—C(8′)	1.462(4)	1.463	1.464
C(2)—C(2′)	1.441(4)	1.446	1.427
Torsional angle/deg			
C(2′)—C(3′)—C(8′)—C(13′)	−33.0(3)	−30.2	−46.5
C(3′)—C(2′)—C(2)—N(1)	+125.5(4)	+131.9	−174.4

= 20.4 kcal mol^{-1}, which is close enough to the experimental value 21.3 kcal mol^{-1}.[4] When R^1 and R^2 were respectively replaced with an electron-donating and electron-withdrawing substituents, the ΔE value increased and became equal to 25.7 kcal mol^{-1} in cation **1** and reached 40.2 kcal mol^{-1} in the earlier analyzed norbornadiene **4** with $R^1 = NH_2$, $R^2 = NO_2$.[14]

Photochemical studies of salt 1. The absorption spectrum of a solution of salt **1** is shown in Fig. 3 (line *1*). The spectrum exhibits three absorption bands with the maxima at λ/nm (ε/L mol^{-1} cm^{-1}) 207 ($31.7 \cdot 10^3$), 218 (sh), 274 ($15.4 \cdot 10^3$), and 320 ($11.2 \cdot 10^3$). Thus, due to the donor-acceptor substituents the spectrum is bathochromically shifted as compared to the spectrum of unsubstituted **NBD**,[15] the shift reaches 100 nm for the long-wave absorption band. When a solution of salt **1** was irradiated with the UV light (354 nm), it isomerizes to the quadricyclane **Q**-form, the intensities of both long-wave bands decrease and a new band with λ_{max} = 278 nm (ε = $12.7 \cdot 10^3$ L mol^{-1} cm^{-1}) and a shoulder at 287 nm appear instead (see Fig. 3, line *2*). The extinction coefficient for the **Q**-isomer was determined because this form does not absorb in the region 340—370 nm. The quantum yield in ethanol was 0.23.

It is important that this compound proved to be photochromic not only in solutions, but also in the solid state. The changes in the transmission spectra of the finely crystalline powder of **1** upon irradiation with the UV light are shown in Fig. 4. The long-wave region of the spectrum of the starting form shows the presence of two bands with the maxima at 280 and 340 nm, the latter is bathochromically shifted by ~20 nm as compared to the solution in ethanol. Like in solutions, the irradiation leads to a decrease in the intensity of this band accompanied by appearance of a new band in the region 250—310 nm, that indicates the formation of a quadricyclane structure. The rate constant of the reaction is 0.020(2) s^{-1} (see Fig. 4). Like in solutions, this form possesses high stability: the storage in the dark for 1 month produces no changes in the spectrum.

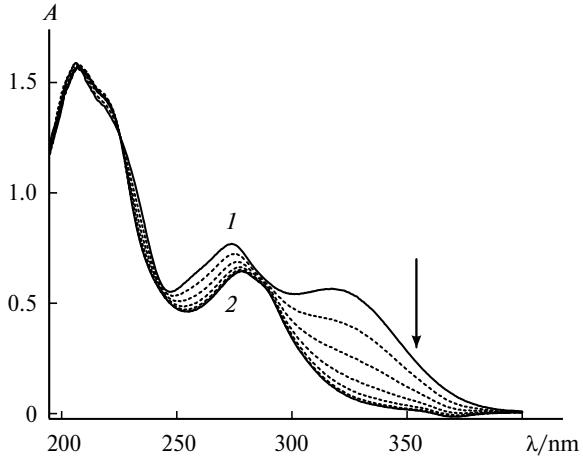


Fig. 3. Absorption spectra of compound **1** in ethanol ($c = 5.0 \cdot 10^{-5}$ mol L^{-1}) before (*1*) and after (*2*) irradiation with the UV light for 2.5 min.

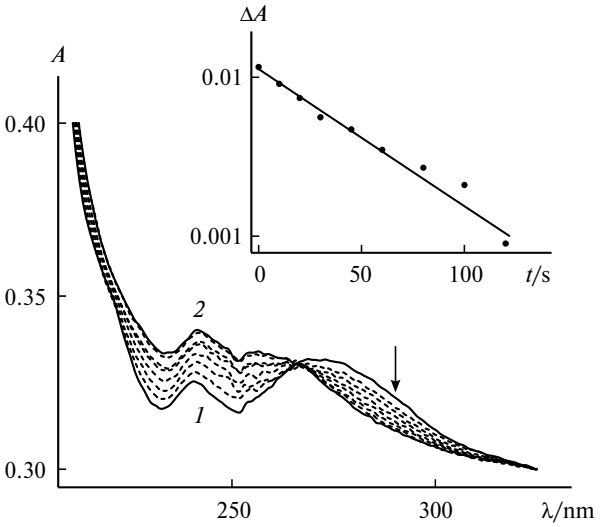


Fig. 4. Absorption spectra of polycrystals of compound **1** before (*1*) and after (*2*) irradiation with the UV light for 2 min. The insertion shows the changes in the optical density at 354 nm (the logarithmic scale), the dots show the experimental data, the solid line shows the approximation of the exponential function $A(t) = A_0[1 - \exp(-kt)]$.

In conclusion, introduction of electron-withdrawing and electron-donating substituents at one of the C=C bonds in norbornadiene leads to a considerable redistribution of the bond distances in the R^1—C=C—R^2 chain and appearance of conjugation between the substituents. This causes a bathchromic shift of the absorption bands in the optical spectra of **NBD**. At the same time, the use of even stronger donors/acceptors in the compounds under study does not allow one to make the C=C bond distance longer than 1.38 Å, which is due to the high rigidity of the **NBD** framework. A specific feature of this compound is its photochemical transformations in the solid phase, which allows one to use it for the creation not only solar energy batteries, but also optical systems for recording and storage of information, as well as polyfunctional materials.

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