Photochemical properties and structures of substituted norbornadienes
1. Molecular and crystal structures of 3-phenylnorbornadiene-2-(*N*-phenyl)aldimine and 3-phenyl-2-(2,2-dicyanovinyl)norbornadiene

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The spectral and photochemical properties of 3-phenylnorbornadiene-2-(*N*-phenyl)aldimine and 3-phenyl-2-(2,2-dicyanovinyl)norbornadiene have been studied, and their structures have been established by X-ray analysis. It was found that the C(2)=C(3) bonds in these compounds are longer than those in unsubstituted norbornadienes. It was established that long-wave absorbtion boundaries and quantum yields of the photoisomerization of 2,3-disubstituted norbornadienes to give the corresponding quadricyclanes increase as the C(2)=C(3) bond length increases and as the bond order decreases.

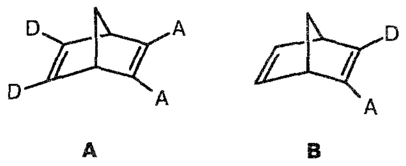
Key words: norbornadiene, photoisomerization, molecular structure.

Photoinduced isomerization of norbornadiene derivatives to the corresponding quadricyclanes is one of the most promising methods for developing abiotic systems accumulating solar energy.[1—4] However, unsubstituted norbornadiene exhibits no absorption in the spectral region of λ > 300 nm, while the quantum yield of photoisomerization is only 0.05.[5] To improve the photochemical characteristics of the norbornadiene—quadricyclane system, it is necessary to increase the long-wave absorption boundary (λ_{bound}) of norbornadiene and the quantum yield of photoisomerization.

Attempts have been made to substantiate the general structural approach to the optimization of the characteristics of diene cyclic systems containing electron-donating and electron-withdrawing substituents at different double bonds.[4] However, the chosen system **A** has a number of disadvantages, the most substantial of which is the complicated method for synthesizing the initial compounds (the corresponding substituted cyclopentadienes and acetylenes). We are now developing a simple method for designing photochromic norbornadienes (**B**, Scheme 1),[6—11] in which one of the two multiple bonds is involved in a conjugation chain with the electron-releasing and electron-withdrawing groups.

Owing to this fact, rather strong interaction between the above-mentioned groups can be achieved in compounds of type **B**, thus providing a substantial bathochromic shift of the long-wave absorption band compared to that in unsubstituted norbornadiene.

Scheme 1



In both **A** and **B** type compounds, the long-wave electronic transition is associated with a partial electron transfer to the π^* orbital of the double bond containing electron-withdrawing substituents, which should cause elongation of the double bond. It was of interest to study the character of the correlation between the molecular structure of 2,3-disubstituted norbornadienes in the ground electronic state and their photochemical properties. The information of this sort available in the literature is poor and conflicting.[3,12—20]

In this work, the spectral and photochemical properties of norbornadiene (**1a**), 3-phenylnorbornadiene-2-(*N*-phenyl)aldimine (**2a**), and 3-phenyl-2-(2,2-dicyanovinyl)norbornadiene (**3a**), as well as their molecular structures are compared based on the X-ray structural analysis of compounds **2a** and **3a** performed in this work and the data in the literature on the structures of norbornadiene **1a**[12] and 3-phenyl-(2,2-diphenylvinyl)norbornadiene-2-carboxylic acid **4a**.[20]

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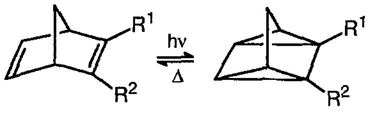
Scheme 2



1a—4a **1b—4b**

1: $R^1 = R^2 = H$
2: $R^1 = Ph$, $R^2 = -CH{=}NPh$
3: $R^1 = Ph$, $R^2 = -CH{=}C(CN)_2$
4: $R^1 = COOH$, $R^2 = -CH{=}CPh_2$

Table 1. Spectral characteristics of norbornadienes **1a—3a** and quantum yields of photoreactions

Compound	λ_{max}/nm ($\varepsilon \cdot 10^{-3}$)	λ_{bound}/nm	Quantum yield
1a	230(0.2)* sh	270	0.05
2a	343(16.6)**	425	0.15
3a	382(21.5)	480	0.74

* In ethanol.[5] ** In 2-propanol.

Experimental

Compounds **2a** and **3a** were synthesized according to the procedures reported in Refs. 6 and 11. The electronic absorption spectra were recorded on a Specord M-40 spectrophotometer. Solutions of norbornadienes **2a** and **3a** in 2-propanol were irradiated with a DRSh-250 mercury lamp equipped with a set of interchangeable filters. Spectral characteristics of compounds **1a—3a** and quantum yields of photoreactions are given in Table 1. Aberchrom 540 was used as the actinometer.[21]

Crystals of compounds **2a** and **3a** suitable for X-ray analysis were obtained by crystallization from 2-propanol. The compounds under study form yellow needle-like crystals belonging to the monoclinic (**2a**) and tetragonal (**3a**) systems.

The principal crystallographic data are as follows: **2a**, $C_{20}H_{17}N$, a = 19.332(6), b = 13.864(5), c = 5.823(6) Å, γ = 74.18°, V = 1502 Å^3, Z = 4, d = 1.207 g/cm^3, the space group is $P\ 2_1/b$; **3a**, $C_{17}H_{12}N_2$, a = 8.767(7), b = 8.767(7) c = 35.989(1) Å, V = 2766.0 Å^3, Z = 8, d = 1.18 g/cm^3, the space group is $P\ 4_12_12$. Intensities of 2776 (**2a**) and 2127 (**3a**) independent reflections with $I \geq 2\sigma(I)$ were measured on an automated KM-4 diffractometer (Mo Kα radiation, absorption was ignored). The structures were solved by the direct method using the SHELXS-86 program package[22] and refined anisotropically by the full-matrix least-squares method (SHELXTL-76). Coordinates for all of the hydrogen atoms, except the H(4) atom in the structure of **3a**, were located from the difference Fourier syntheses; only the positional parameters were refined for these atoms. The final R factors are R = 0.044 (**2a**) and R = 0.065 (**3a**); atomic coordinates corresponding to these R factors are given in Tables 2 and 3. The overall views of the molecules are shown in Figs. 1 and 2.

Nortricyclane 5 (R = CH_3) is a colorless powder, m.p. 97—98 °C. Found (%): C, 78.45; H, 5.85; N, 10.25. $C_{18}H_{16}N_2O$. Calculated (%): C, 78.23; H, 5.84; N, 10.14. ^1H NMR (δ): 1.80 (m, 2 H, H(5), H(7)); 2.08 (d, 1 H, H(6));

Table 2. Coordinates for nonhydrogen atoms (×10^4) and hydrogen atoms (×10^3) in the structure of **2a**

Atom	x	y	z
N	9655(2)	2819(3)	63(6)
C(1)	10380(3)	957(4)	2529(7)
C(2)	10733(2)	1710(3)	1446(7)
C(3)	11442(2)	1370(3)	1837(6)
C(4)	11549(2)	394(4)	3211(7)
C(5)	11182(3)	697(4)	5507(7)
C(6)	10490(3)	1035(4)	5124(8)
C(7)	10971(3)	−13(4)	2083(7)
C(8)	12044(2)	1777(3)	1277(7)
C(9)	12614(3)	1677(4)	2797(7)
C(10)	13188(3)	2054(4)	2339(8)
C(11)	13220(3)	2527(4)	264(8)
C(12)	12672(3)	2618(4)	−1280(7)
C(13)	12089(3)	2255(4)	−807(7)
C(14)	10334(3)	2617(4)	336(7)
C(15)	9298(2)	3692(4)	−1163(7)
C(16)	8631(3)	4260(4)	−394(8)
C(17)	8257(3)	5093(4)	−1610(9)
C(18)	8528(4)	5349(5)	−3615(9)
C(19)	9167(3)	4763(4)	−4438(9)
C(20)	9554(3)	3950(4)	−3236(8)
H(1)	991(1)	103(1)	208(1)
H(4)	1207(1)	−5(1)	326(1)
H(5)	1151(1)	64(1)	750(1)
H(6)	1005(1)	138(1)	605(1)
H(7.1)	1089(1)	−63(1)	281(1)
H(7.2)	1105(1)	−19(1)	47(1)
H(9)	1260(1)	123(1)	404(1)
H(10)	1364(1)	196(1)	344(1)
H(11)	1365(1)	282(1)	−7(1)
H(12)	1263(1)	304(1)	−249(1)
H(13)	1164(1)	242(1)	−170(1)
H(16)	842(1)	397(1)	89(1)
H(17)	781(1)	556(1)	−96(1)
H(18)	826(1)	598(1)	−429(1)
H(19)	932(1)	515(1)	−605(1)
H(20)	999(1)	360(1)	−371(1)

Table 3. Coordinates for nonhydrogen atoms (×10^4) and hydrogen atoms (×10^3) in the structure of **3a**

Atom	x	y	z
N(1)	4950(10)	6280(10)	1805(3)
N(2)	490(10)	8220(10)	1712(3)
C(1)	2800(10)	4170(10)	982(3)
C(2)	4200(10)	3290(20)	1124(3)
C(3)	3610(10)	1720(20)	1255(3)
C(4)	3160	1010(10)	961(3)
C(5)	3430(10)	2010(10)	618(3)
C(6)	2350(10)	3360(10)	670(3)
C(7)	4910(10)	2790(20)	750(4)
C(8)	990(10)	3640(10)	442(3)
C(9)	160(20)	3250(10)	317(3)
C(10)	−1160(10)	2560(20)	110(3)
C(11)	−1630(20)	4010(20)	30(3)
C(12)	−840(20)	5230(20)	123(4)
C(13)	500(20)	5090(10)	342(3)
C(14)	2010(10)	5380(10)	1146(3)
C(15)	2390(10)	6250(10)	1443(2)
C(16)	3830(20)	6220(10)	1638(3)
C(17)	1330(20)	7360(10)	1589(3)
H(2)	490(10)	360(10)	126(2)
H(3)	350(10)	150(10)	160(2)
H(4)	287(9)	−30(10)	92(2)
H(7.1)	585(9)	187(9)	83(2)
H(7.2)	520(10)	360(10)	55(2)
H(9)	70(10)	140(10)	41(3)
H(10)	−180(10)	160(1)	2(2)
H(11)	−260(10)	410(10)	−15(3)
H(12)	−80(10)	630(10)	8(2)
H(13)	100(10)	600(10)	40(2)
H(14)	80(10)	550(10)	107(2)

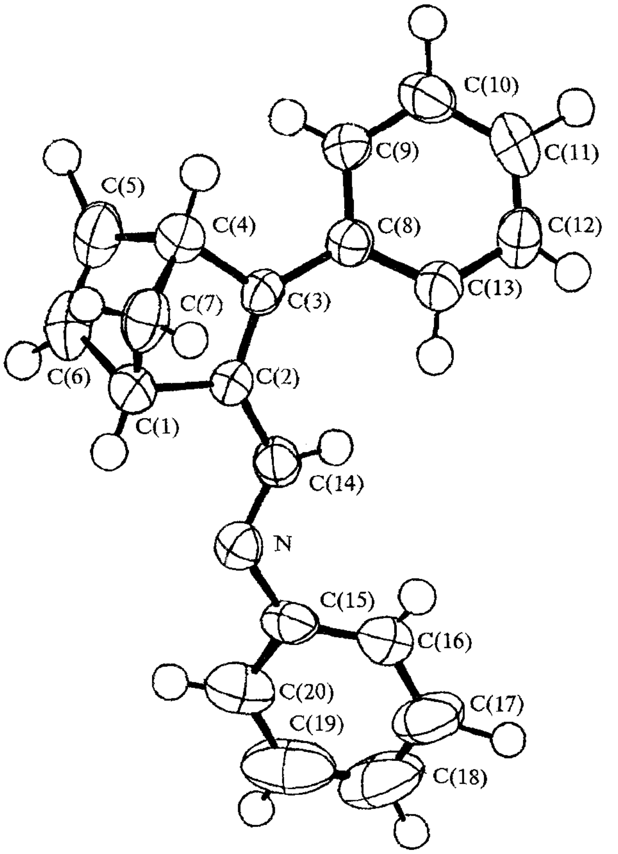


Fig. 1. The overall view of molecule **2a** with thermal ellipsoids drawn at the 50% probability level.

2.19 (d, 1 H, H(7')); 2.46 (s, 1 H, H(5)); 3.32 (m, 1 H, H(1)); 3.37 (s, 3 H, OCH_3); 3.88 (s, 1 H, H(4)); 7.04—7.35 (m, 6 H, C_6H_5, CH=C(CN)$_2$).

Results and Discussion

Unsubstituted norbornadiene **1a** exhibits low-intensity absorption (Table 1) in the 270 nm region, and isomerizes to quadricyclane **1b** in a low quantum yield (0.05) when irradiated at this maximum.[5] Aldimine **2a**, in which conjugation between the electron-releasing (R^1 = Ph) and electron-withdrawing (R^2 = CH=NPh) substituents occurs, exhibits absorption at substantially longer wavelengths, and the quantum yield of photoisomerization to the corresponding quadricyclane **2b** increases three times (see Table 1). The photoreaction was monitored by electron absorption spectroscopy; formation of quadricyclane **2b** was established by ^1H NMR spectroscopy.* The presence of a stronger electron-withdrawing substituent (R^2 = CH=C(CN)$_2$) compared to that in aldimine **2a** causes a substantial bathochromic shift of the long-wave absorption band and shifts the long-wave absorption bound to 480 nm with a high quantum yield (0.74). However, the dicyanovinyl group strongly activates the adjacent cyclopropane fragment of the molecule of quadricyclane **3b** with respect to nucleophilic reagents. Hence, when traces of water are present in a solvent or when photoisomerization is performed in alcohols, the final product is the corresponding nortricyclane **5**. Similar results were obtained previously.[8,23]

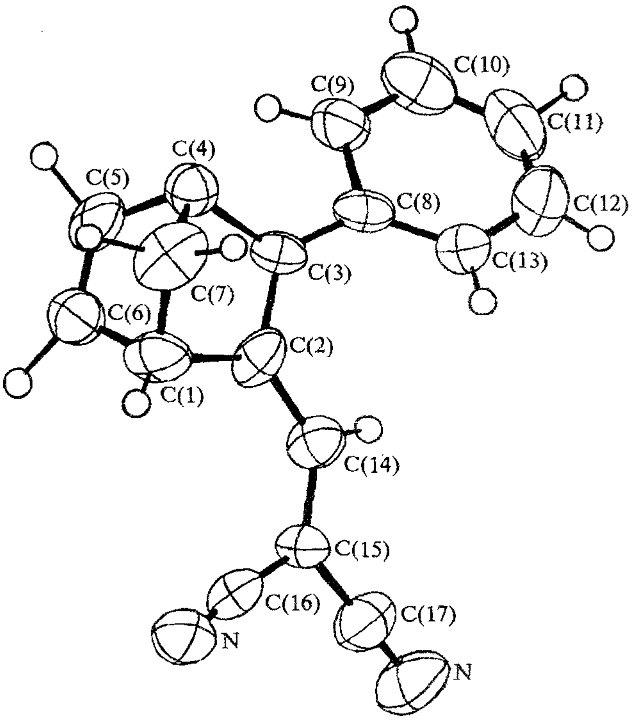
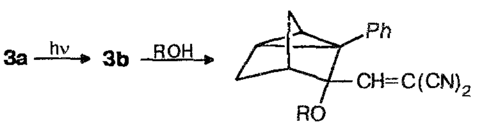


Fig. 2. The overall view of molecule **3a** with thermal ellipsoids drawn at the 50% probability level.

X-ray analysis of compounds **2a** and **3a** demonstrated that the structural characteristics of their norbornadiene fragments are close to the corresponding characteristics of unsubstituted norbornadiene **1a**[3,12,13] and its derivatives.[16—20] However, there are a number of features related to the effect of a substituent.

All single bonds of the norbornadiene fragment of compound **2a** have normal values (the average value is 1.57±0.01 Å), however, the C(2)=C(3) (1.342(6) Å)

Scheme 3



5: R = H, CH_3

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* Irradiation of a solution of aldimine **2a** in deuteromethanol (0.037 mol/L) leads to substantial changes in the ^1H NMR spectrum: the intensities of the signals of the olefin protons (δ 7.32) and the signals of H(1), H(4), and H(7) (δ 4.50, 4.10, and 2.32, respectively) decrease, a complex multiplet of protons of quadricyclane **4b** appears in the region 1.22—3.28 ppm, and the signals of the phenyl moieties also change their shape.

and C(5)=C(6) (1.310 Å) bond lengths differ substantially from those in norbornadiene **1a** (1.333 Å).[3,12] The 3-phenyl substituent is twisted relative to the C(1)C(2)C(3)C(4) plane by 37.0°. The C=N bond of the 2-phenylazomethine substituent is almost parallel to the C(2)=C(3) bond; its length (1.275(7) Å) is typical of conjugated C=N bonds.[24] The *N*-phenyl substituent is twisted relative to the C(2)C(14)N plane by 34.7°. The structure of molecule **2a** is indicative of conjugation of the C(2)=C(3) bond of the norbornadiene fragment with the azomethine bond and, apparently, with phenyl substituents, which leads to its elongation with simultaneous shortening of the C(5)=C(6) bond. The intramolecular distance between diene bonds remains nearly unchanged: C(2)...C(6), 2.434 Å; C(3)...C(5), 2.439 Å. The folding angle of the diene cycle between the C(1)C(2)C(3)C(4) and C(1)C(4)C(5)C(6) planes is 112.7°.

The crystal packing of molecules **2a** is characterized by normal van der Waals contacts. No specific intermolecular interactions are observed, which is also true for the crystal structure of **3a**.

Compound **3a**, with the stronger electron-withdrawing dicyanovinyl substituent, has a similar overall structure. The phenyl substituent is twisted relative to the C(1)C(2)C(3)C(4) plane by 38.7° and the dicyanovinyl substituent is almost coplanar with this plane. The angle between the planes of the vinyl and C(2)=C(3) bonds is 4.1°. The distribution of bond lengths in the norbornadiene fragment is similar to that found in compound **2a**. The substituted C(2)=C(3) bond is substantially elongated (to 1.38(1) Å), while the C(5)=C(6) bond is substantially shortened (to 1.29(2) Å). Similar to **2a**, these changes in diene bond lengths compared to the unsubstituted norbornadiene are caused by participation of the C(2)=C(3) bond in conjugation with the strong electron-withdrawing dicyanovinyl substituent; this conjugation probably involves the 3-phenyl substituent.

The substantial changes in the diene bond lengths in molecule **3a** result in a change in their mutual arrangement. The bonds remain parallel to each other (the angle between these bonds is 2.1°), whereas the distances between the atoms forming the bonds in the corresponding quadricyclane are substantially different: C(2)...C(6), 2.47 Å; C(3)...C(5), 2.42 Å, which sets up the conditions for charge transfer interaction between the atoms even in the ground state.

We performed estimating MNDO[25] calculations of the charge distribution over the atoms in compounds **1a** and **3a**; these calculations demonstrated that the presence of substituents of different natures at one of the double bonds results in its polarization, *i.e.*, in the appearance of a weak positive charge on the C(3) atom with the stronger donating substituent (Fig. 3). This suggests that dipolar structure **6** should contribute significantly to the excited state of donor-acceptor norbornadienes.[3]

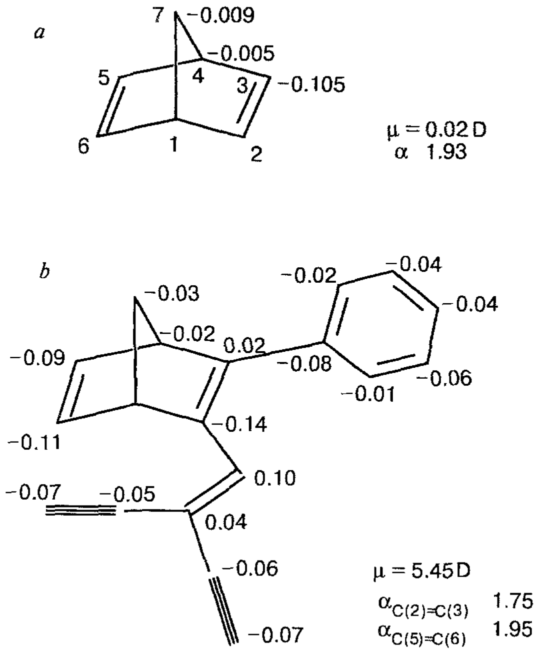
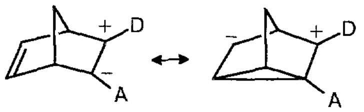


Fig. 3. The charge distribution at nonhydrogen atoms in compounds **1a** (*a*) and **3a** (*b*) according to the MNDO calculations, the values of dipole moments of the molecules (μ) and the orders of the diene bonds (α).

Scheme 4



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The estimate of the change in the orders of the double bonds on passing from norbornadiene **1a** to compound **3a** demonstrated that the order of the unsubstituted C(5)=C(6) bond is virtually unchanged (1.93 in **1a** and 1.95 in **3a**), while the order for the substituted C(2)=C(3) bond decreases significantly (to 1.75) on passing to **3a**. The similar character of a change in double bond lengths in norbornadiene, when one of these bonds has substituents of different nature, is also observed in compound **4a** studied previously,[20] in which the substituted C(2)=C(3) bond lengthens to 1.353(4) Å owing to conjugation with the π systems of the substituents, and the C(5)=C(6) bond shortens to 1.271(4) Å.

Therefore, based on an analysis of the structures of norbornadienes **1a**—**4a**, we established that the involvement of a norbornadiene double bond in a conjugation chain is accompanied by its elongation and an enchancement of electron-withdrawing properties of the R^2 substituent, which causes an increase in the long-wave absorption boundary and in the quantum yield of photopolymerization to the corresponding quadricyclanes.

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