SYNTHESIS AND STRUCTURE OF 2,6-DI-TERT-BUTYL-1,4-BENZOQUINONE-4N-(8-TOSYLAMINO-1-NAPHTHYL)IMINE

S. M. Aldoshin, M. A. Novozhilova, L. O. Atovmyan,
V. N. Komissarov, L. Yu. Ukhin, and V. A. Kharlanov

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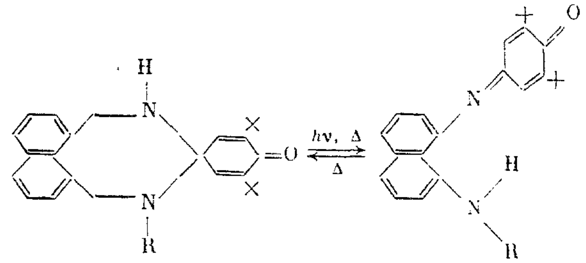
The structure of 2,6-di-tert-butyl-1,4-benzoquinone-4-N-(8-tosylamino-1-naphthyl)imine (IId) has been studied as a model for the open form of thermo- and photochromic compounds in the cyclohexadienoneperimidine series (I), in which rearrangement occurs due to C_{spiro}–N bond cleavage and N → N proton transfer upon thermal or photoexcitation. Introduction of a bulky, electron-withdrawing tosyl substituent to the nitrogen atom stabilizes the open quinoneimine form, both in the crystalline state and in solution. The cyclohexadienone fragment is nonplanar and exists in a "boat" configuration. The open quinoneimine structure is retained upon replacement of the tosyl substituent by a less bulky electron-withdrawing acetyl substituent, suggesting that electronic factors are decisive in formation of the open structure.

We have previously reported [1, 2] the synthesis and structure of spiran derivatives in the cyclohexadienoneperimidine series; these compounds are reactive with respect to both thermo- and photoinitiated reversible rearrangement



(I) (II)

(1)

$R = H$ (a); CH_3 (b); $CH_2CH(CH_3)_2$ (c).

The same type of properties have been observed earlier [2, 3] for 4H-naphthalenone-perimidine spiran derivatives. Conversion of the open form (II) to the spiran form (I) can be envisioned as resulting from intramolecular nucleophilic attack on the quinoneimine fragment by the unshared electron pair on the amine nitrogen atom, accompanied by N → N proton transfer.

It was anticipated that introduction of relatively strong electron-withdrawing functional group substituents to one of the nitrogen atoms should lead to a sharp reduction in the amine basicity, making it possible, in turn, to prepare or isolate model compounds for the open form (II) of thermochromic spirans (I). The same result should be produced by the presence of bulky substituents attached to the nitrogen atom; bulky substituents should lead to steric hindrance with respect to spiran ring closure.

Our goal in the present paper was to study the possible stabilization of quinoneimine structures via the introduction of electron-withdrawing substituents, and to further investigate the structural characteristics of these model compounds.

Two groups were examined as strong electron-withdrawing substituents for this purpose, the bulky tosyl functional group and the less bulky acetyl group. Compounds (IId-f) were

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Institute of Chemical Physics Branch, Academy of Sciences of the USSR, Chernogolovka. Scientific Research Institute of Physical and Organic Chemistry, Rostov State University, Rostov-on-Don. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1802-1808, August, 1991. Original article submitted May 30, 1990.

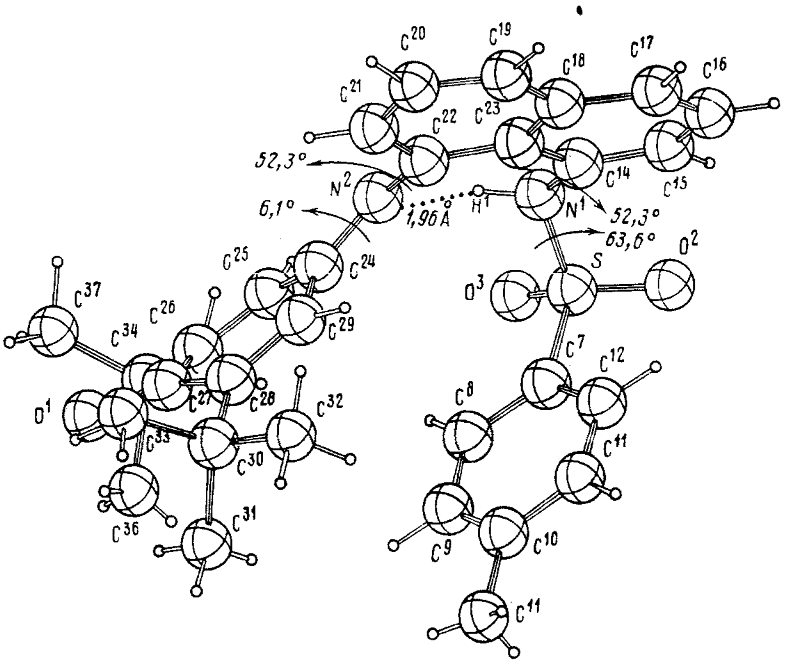
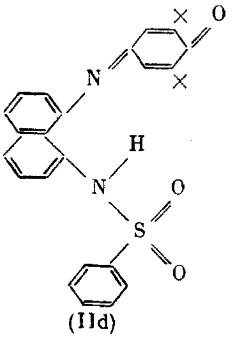
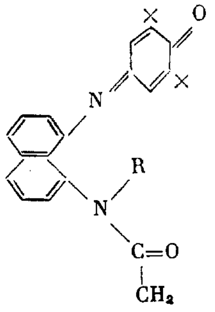


Fig. 1. Molecular projection of compound (IId).

prepared and their spectral characteristics corresponded to the open quinoneimine structure



(IId)



(II)

R = H (IIe), CH_3(IIf).

X-ray structural analysis of compound (IId) revealed that this compound did in fact exist in the quinoneimine structure. A molecular projection of this compound is illustrated in Fig. 1. The molecule is essentially nonplanar due to rotation about the C^{22}—N^2, C^{14}—N^1, N^2—C^{24}, and N^1—S bonds by 52.3°, 52.3°, 6.1°, and 63.6°, respectively.

Despite the presence of a bulky tosyl substituent attached to the N^1 atom in this molecule there are no unusually short intramolecular distances in its structure. The separation between the atoms in the tert-butyl-substituted cyclohexadienone ring and the tosyl fragment is greater than 3.6 Å.

The N^1 atom adopts a pyramidal configuration. Its deviation from the $C^{14}SH^1$ coordination plane is 0.24 Å, while the sum of the bond angles around the N^1 atom is equal to 346.9° The pyramidal nature of the N^1 atom may be due to deviation of the H^1 atom away from the $C^{14}N^1S$ plane in the direction of the N^2 atom accompanying intramolecular hydrogen bond (IHB) formation: $H^1 \ldots N^2$ 1.96(3) Å ($N^1 \ldots N^2$ 2.671(3) Å). However, this IHB does not appear to be very strong, despite the relatively short N...H and N...N distances, because of the unfavorable orientation of the unshared electron pair (UEP) on the N^2 atom vis-a-vis the direction of the $H \ldots N^2$ bond. The angle between these directions is 50.8°, which is not even close to 0°, the most advantageous angle for IHB formation. In addition, the six-membered ring $N^2C^{22}C^{23}C^{14}N^1H^1$ is also essentially nonplanar. The H^1 atom deviates from the $C^{22}N^2C^{24}$ plane by 1.1 Å. The intramolecular $N^2 \ldots H^1$—N^1 hydrogen bond is thus not linear; the $N^1H^1N^2$, $H^1N^2C^{22}$, and $H^1N^2C^{24}$ angles are equal to 133(3), 101.1(9), and 126.9(9)°, respectively.

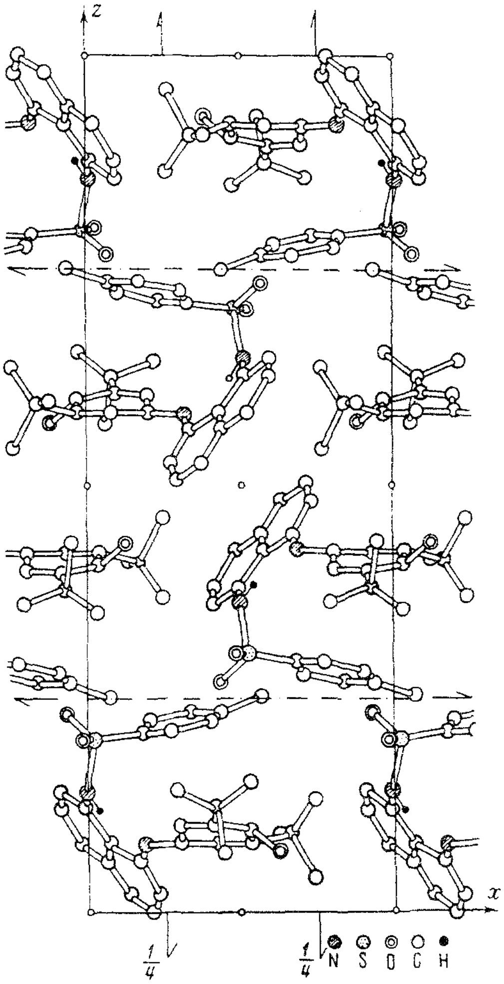


Fig. 2. Structural projection of (IId) along the [010] plane.

The N^1–C^{14} bond length of 1.415(4) Å is elongated relative to analogous bonds in cyclohexadienoneperimidine and 4H-naphthalenoneperimidine spirans (1.382-1.398 Å [2]). This bond stretching can be attributed, apparently, to weakening of the conjugation interaction between the UEP on the N^1 atom and the π-system in the naphthyl fragment, due to two factors: first of all, due to the large rotation angle (52.3°) relative to the C^{14}–N^1 bond; and secondly, because of the strong electron-withdrawing effect of the tosyl substituent.

Contraction of the N^1–C^{22} bond length to 1.405(4) Å may be associated with the existence of conjugation interaction between the UEP on the N^2 atom and the π-system in the naphthalene ring; the right angle between these is 37.6°, the result of torsional rotation about the C^{22}–N^2 bond by 52.3°. The bond length and bond angle distribution pattern in the cyclohexadiene fragment is consistent with the analogous distribution pattern observed for 2,6-di-tert-butyl-1,4-benzoquinone [4].

Elongation of the N^2=C^{24} double bond length to 1.313(3) Å, compared to a normal or standard value of 1.255 Å [5], and contraction of the C^{24}–C^{29} and C^{24}–C^{25} bond lengths to 1.447(4) and 1.443(4) Å, compared to the analogous bond lengths of 1.477 Å in 1,4-benzoquinone [6], are indicative of the existence of $\pi_{C=N}$ and $\pi_{C=C}$ conjugation.

The C^{22}–C^{21} 1.376(5) Å, C^{20}–C^{19} 1.348(5) Å, C^{16}–C^{17} 1.352(6) Å, and C^{14}–C^{15} 1.358(4) Å bond lengths are shorter than all of the other C–C bond lengths, which is characteristic of naphthalene ring structures.

The bond length distribution in the benzene ring is consistent within experimental error with the normal C–C bond length value 1.392(4) Å [7].

In analogy with the previously studied spirocyclic structures in the cyclohexadienoneperimidine and 4H-napthalenoneperimidine series [2], the cyclohexadienone fragment is nonplanar and adopts a "boat" configuration. The sum of the endocyclic angles in the ring

TABLE 1. Nonhydrogen Atom ($\times 10^4$) and Hydrogen Atom ($\times 10^3$) Coordinates in the Molecular Structure of (IId)

Atom	X	Y	Z	Atom	X	Y	Z
S	168(1)	7517(1)	2004(0)	C^{37}	7393(4)	9199(4)	394(2)
O^2	110(2)	8898(2)	2024(1)	H^1	32(3)	781(3)	123(1)
O^3	−691(2)	6555(3)	2293(1)	H^8	248(3)	943(3)	210(1)
O^1	6250(2)	11509(2)	732(1)	H^9	460(3)	924(3)	227(1)
N^1	−89(2)	7116(2)	1419(1)	H^{12}	361(3)	511(3)	237(1)
N^2	1814(2)	8034(2)	778(1)	$H^{11.1}$	588(3)	622(3)	238(1)
C^7	1755(3)	7367(3)	2138(1)	$H^{11.2}$	609(3)	774(3)	243(1)
C^8	2738(4)	8512(3)	2147(1)	$H^{11.3}$	568(3)	685(3)	273(1)
C^9	3969(4)	8384(3)	2253(2)	H^{13}	137(3)	532(3)	222(1)
C^{10}	4279(4)	7148(4)	2347(1)	H^{15}	−147(3)	489(3)	173(1)
C^{11}	5625(4)	7003(4)	2479(2)	H^{16}	−154(3)	265(3)	139(1)
C^{12}	3297(4)	6020(4)	2330(2)	H^{17}	−20(3)	229(3)	69(1)
C^{13}	2041(4)	6128(3)	2220(2)	H^{19}	116(3)	320(3)	7(1)
C^{14}	−70(3)	5812(3)	1238(1)	H^{20}	258(3)	506(3)	−36(1)
C^{15}	−908(3)	4731(4)	1427(2)	H^{21}	286(3)	720(3)	3(1)
C^{16}	−949(4)	3424(4)	1245(2)	H^{25}	411(3)	735(3)	81(1)
C^{17}	−232(4)	3232(3)	847(2)	H^{29}	213(3)	1042(3)	106(1)
C^{18}	612(3)	4344(3)	621(1)	$H^{31.1}$	526(3)	1388(3)	163(1)
C^{19}	1305(4)	4138(3)	190(2)	$H^{31.2}$	584(3)	1282(3)	136(1)
C^{20}	2108(3)	5176(4)	−27(1)	$H^{31.3}$	526(3)	1271(3)	178(1)
C^{21}	2288(3)	6452(3)	172(1)	$H^{32.1}$	302(3)	1379(3)	150(1)
C^{22}	1667(3)	6716(3)	597(1)	$H^{32.2}$	276(3)	1211(3)	167(1)
C^{23}	738(3)	5651(3)	817(1)	$H^{32.3}$	219(3)	1246(3)	121(1)
C^{24}	2963(3)	8795(3)	851(1)	$H^{33.1}$	523(3)	1338(3)	44(1)
C^{25}	4173(3)	8345(3)	829(1)	$H^{33.2}$	372(3)	1318(3)	50(1)
C^{26}	5319(3)	9209(3)	852(1)	$H^{33.3}$	435(3)	1426(3)	74(1)
C^{27}	5299(3)	10670(3)	859(1)	$H^{35.1}$	733(3)	705(3)	97(1)
C^{28}	4104(3)	11107(3)	1012(1)	$H^{35.2}$	599(3)	699(3)	126(1)
C^{29}	3005(3)	10178(3)	991(1)	$H^{35.3}$	590(3)	683(3)	67(1)
C^{30}	4161(3)	12569(3)	1158(1)	$H^{36.1}$	697(3)	928(3)	157(1)
C^{31}	5266(4)	12996(4)	1547(2)	$H^{36.2}$	827(3)	916(3)	135(1)
C^{32}	2937(4)	12755(4)	1403(2)	$H^{36.3}$	736(3)	1056(3)	133(1)
C^{33}	4397(4)	13443(3)	703(2)	$H^{37.1}$	809(3)	888(3)	46(1)
C^{34}	6617(3)	8785(3)	880(1)	$H^{37.2}$	759(3)	1032(3)	48(1)
C^{35}	6444(4)	7270(4)	927(2)	$H^{37.3}$	715(3)	902(3)	16(1)
C^{36}	7364(4)	9453(4)	1320(2)				

is equal to 715.3°. The C^{24} and C^{27} atoms deviate from the $C^{25}C^{26}C^{28}C^{29}$ plane by 0.13 and 0.23 Å. The folds or bends along the $C^{25}...C^{29}$ and $C^{26}...C^{28}$ lines are 9.9 and 18.2°. However, the sum of the bond angles around all the carbon atoms in the ring is equal to 359.9-360.0°, which indicates that the sp^2-hybridization of these bonds is retained. This planar coordination is maintained by the deviations of the O^1, N^2, C^{30}, and C^{34} atoms from the C^{25}-$C^{26}C^{28}C^{29}$ plane by 0.64, 0.29, 0.13, and 0.27 Å, respectively.

The orientation of the tert-butyl groups relative to the carbonyl oxygen atom O^1 is the most sterically favorable one. The C^{30}, C^{34}, C^{31}, and C^{36} carbon atoms are found on one side of the $C^{25}C^{26}C^{28}C^{29}$ plane, the O^1, C^{33}, and C^{37} atoms on the other side. This results in maximum separation between the carbon atoms and the carbonyl oxygen. The intramolecular $O^1...C^{30}$, $O^1...C^{34}$, $O^1...C^{31}$, $O^1...C^{36}$, $O^1...C^{33}$, and $O^1...C^{37}$ distances are equal to 2.884(3), 2.900(3), 2.976(3), 3.044(3), and 2.994(3) Å.

The molecular crystal packing arrangement for (II) is shown in Fig. 2. Intermolecular interaction energy (IMIE) calculations reveal that the largest (conjugate) paired IMIE values occur between molecules located centrosymmetrically about the two system center sites: (1/200) and (000) (−10.84 and −7.71 kcal/mole, respectively). The next largest paired IMIE values are −8.29 and −6.69 kcal/mole, which correspond to the interaction energies between molecules associated via the sliding reflection and translation plane b, and via translation-identical molecules (along b), respectively. However, the intermolecular distances are shorter than the sum of the corresponding van der Waals radii, which may suggest the effect of undetected molecules on the structure.

The PMR spectra of compounds (IIe, f, and d) indicate that the tert-butyl groups in them are not equivalent, which is characteristic of quinoneimine structures.

The absorption spectrum of (IId) in methanol (λ_{max}^a = 504 nm) is essentially identical to that measured in octane solution; in contrast, in alcohol solutions of compounds (Ia-c) the equilibrium is shifted completely in favor of their spiran structures, and the spectra in alcohol solution differ from their spectra in nonpolar solvents, in which equilibrium reaction (1) is observed [1]. Varying the temperature and photolysis of solutions of (IId) do not alter its absorption spectrum. The absorption spectra of compounds (IIe, f) in hexane solution also suggest the existence or presence of only the open quinoneimine structures.

The spectral data lead us to conclude, therefore, that strong electron-withdrawing substituents attached to the nitrogen atom stabilize the quinoneimine structure in compounds (IId-f) and make them unreactive with respect to tautomeric conversion to their spirocyclic analogs (I).

EXPERIMENTAL

UV spectra were measured on a Specord M-40 spectrophotometer using a 0.2 cm cuvette. Temperature measurements were made in a thermostatted cell in the spectrophotometer using a 1.00 cm path length cuvette; the temperature was regulated in the 293-365 K range. Solution photolysis experiments were carried out via irradiation with a mercury DRSh-250 lamp; individual lines in the spectrum were separated using standard filters. IR spectra were recorded on a Specord IR-75 spectrophotometer using vaseline mulls. PMR spectra were obtained on a Tesla BS 567 A (100 MHz) spectrometer using solutions in $CDCl_3$ versus HMDS as internal standard.

X-ray structural analysis was performed using red, prismatic crystals, 0.1 × 0.15 × 1.0 mm in size. The principal crystallographic data for compound (IId) are as follows: $C_{31}H_{34}N_2O_3S$, $M = 514.70$, $a = 10.554(2)$, $b = 10.159(3)$, $c = 27.045(9)$ Å, $\gamma = 101.82(5)°$, $Z = 4$, $V = 2838.2$ Å^3, $d_{calc} = 1.210$ g/cm^3, space group $P2_1/n$. The intensities of 2643 independent reflections with $I > 3\sigma(I)$ of the type hk0-hk27 were measured on a DAR-UM automated diffractometer (λCu Kα, $3.1° \leq \theta \leq 33.6°$). Absorption (corrections) were not taken into account. The structure was solved by direct methods using the Roentgen-75 system of programs and was refined by full matrix least squares using anisotropic approximations (for the nonhydrogen atoms). The hydrogen atoms, with the exception of four which were not included in the calculations, were localized by direct observation from a difference Fourier synthesis. Only the positional parameters were refined for the nonhydrogen atoms. The atomic coordinates are listed in Table 1.

Intermolecular interaction energy (IMIE) calculations were carried out within the framework of atom—atomic approximations using 6-exp-potentials, without taking into account their electrostatic component terms [8].

2,6-Di-tert-butyl-1,4-benzoquinone-4-N-(8-tosylamino-1-naphthyl)imine (IId). A solution of 1.08 g (3 mmoles) 2,3-dihydro-2-spiro-(4-2,6-di-tert-butylcyclohexadien-2,5-one)-perimidine (Ia) and 0.67 g (3.5 mmoles) tosyl chloride in 7 ml pyridine was refluxed for 15 min. The mixture was cooled, 30 ml water was added, and the precipitate was removed by filtration and washed with water. The product was dissolved in chloroform and passed through an alumina column to remove resin by-product. After solvent evaporation the yield of dark red crystals was 1.2 g (78%), mp 172-173°C (from propanol). IR spectrum, cm^{-1}: νNH = 3367; νCO = 1627. UV spectrum (methanol), nm (log ε): 229 (4.59), 299 (4.31), 504 (3.75). Found, %: C 72.40; H 6.53; N 5.27; S 6.57. $C_{31}H_{34}N_2O_3S$. Calculated, %: C 72.35; H 6.66; N 5.44; S 6.23.

2,6-Di-tert-butyl-1,4-benzoquinone-4-N-(8-acetylamino-1-naphthyl)imine (IIe). A solution of 1.08 g (3 mmoles) 2,3-dihydro-2-spiro-(4-2,6-di-tert-butylcyclohexadien-2,5-one)-perimidine (Ia) in 7 ml acetic anhydride was refluxed for 5 min, cooled to 0°C, and the resulting precipitate removed by filtration. Yield 1.1 g (92%). Dark claret crystals, mp 204-206°C (from heptane). IR spectrum, cm^{-1}: νNH = 3367; νCO = 1690, 1615. UV spectrum (hexane), nm (log ε): 230 (5.12); 309 (4.93); 536 (4.33). PMR spectrum ($CDCl_3$, δ, ppm): 1.14 s (9H, t-C_4H_9), 1.32 s (9H, t-C_4H_9), 2.19 s (3H, CH_3—CO); 6.60-7.75 m (8H, aromatic and quinoid protons); 8.59 d.d (1H, NH). Found, %: C 77.56; H 7.40; N 7.12. $C_{26}H_{29}N_2O_2$. Calculated, %: C 77.78; H 7.30; N 6.97.

2,6-Di-tert-butyl-1,4-benzoquinone-4-N-[8-(N-methyl-N-acetyl)amino-1-naphthyl]imine (IIf). A solution of 0.37 g (1 mmole) 1-methyl-2,3-dihydro-2-spiro-(4-2,6-di-tert-butylcyclohexadien-2,5-one)perimidine (Ib) in 1 ml acetic anhydride was refluxed for 10 min, evaporated under vacuum (2-3 mm Hg) to dryness, and the residue was recrystallized from methanol. Red crystals, mp 178-179°C. Yield 0.34 g (80%). IR spectrum, cm^{-1}: νCO = 1665,

1640. UV spectrum (hexane), nm (log ε): 268 (4.81); 325 (4.80); 470 (4.04). PMR spectrum ($CDCl_3$, δ, ppm): 1.08 s (9H, t-C_4H_9), 1.39 s (9H, t-C_4H_9), 1.70 s (3H, CH_3CO), 2.95 s (3H, CH_3—N), 6.65-7.78 m (10H, aromatic and quinoid protons). Found, %: C 77.93; H 7.58; N 6.42. $C_{27}H_{32}N_2O_2$. Calculated, %: C 77.85; H 7.75; N 6.72.

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SYNTHESIS AND CRYSTAL STRUCTURE OF THERMOCHROIC 2,6-DI-TERT-BUTYL-4-DIMETHYLAMINO-4-(2-HYDROXYPHENYL)CYCLOHEXADIEN-2,5-ONE

S. M. Aldoshin, O. S. Filipenko, M. A. Novozhilova,
L. O. Atovmyan, V. N. Komissarov, and L. Yu. Ukhin

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The compound 2,6-di-tert-butyl-4-dimethylamino-4-(2-hydroxyphenyl)cyclohexadien-2,5-one is synthesized and its structure is studied. The thermochromism of the compound is due to cleavage on excitation of the C_{spiro}—N bond, which is lengthened to 1.512 Å under normal conditions, and O → N proton transfer. A deeply colored diphenoquinone and dimethylamine are formed. The C_{spiro}—N bond is lengthened due to mutual steric repulsion of the atoms bound to C^4 and N.

The anomalous bond lengthening in molecular fragments is predictive in a number of cases of their possible cleavage under the influence of temperature, photoexcitation, or the medium. Thus, the photochemical properties of photochromic systems based on spiropyrans with reversible photoinitiated opening of the rings are mainly determined by the fact that the cleaving C_{spiro}—O bond is already lengthed in the ground state [1].

A dependence between the lengthening of the C—O bond in the ground state and the rate of the heterolytic reaction in solution has been demonstrated in a number of acetyl systems [2, 3].

An unusual lengthening of the C_{spiro}—N bond to 1.510(2) Å compared with the standard value 1.472 Å [4] was observed by us in a crystal of the first representative of new thermochromic sterically hindered cyclohexadienones (I) [5] that dissociates in organic solvents into an intensely colored diphenoquinone (II) and morpholine

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N. N. Semenov Branch, Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka. Scientific Research Institute of Physical and Organic Chemistry, Rostov State University, Rostov-on-Don.

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