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.

LITERATURE CITED

1. V. N. Komissarov, V. A. Kharlanov, L. Yu. Ukhin, and V. I. Minkin, Dokl. Akad. Nauk SSSR, 301, No. 4, 902 (1988).
2. S. M. Aldoshin, M. A. Novozhilova, L. O. Atovmyan, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 702 (1991).
3. V. I. Komissarov, V. A. Kharlanov, L. Yu. Ukhin, and Z. S. Morkovnik, Zh. Org. Khim., 26, No. 5, 1106 (1990).
4. G. G. Aleksandrov, Yu. T. Struchkov, R. I. Kalinin, and M. G. Neigauz, Zh. Strukt. Khim., 14, No. 5, 852 (1973).
5. E. Bayer and G. Hafelinger, Chem. Ber., 99, 1689 (1966).
6. J. Trotter, Acta Crystallogr., 13, No. 2, 86 (1960).
7. E. E. Cox, D. W. J. Cruickshank, and J. A. S. Smith, Proc. R. Soc., 247A, 1 (1958).
8. T. V. Timofeeva, N. D. Chernikova, and P. M. Zorkii, Usp. Khim., 69, No. 6, 966 (1980).

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

UDC 542.91:548.737:
547.567.3+547.562

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

---

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.

Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1808-1813, August, 1991. Original article submitted May 30, 1990.

0568-5230/91/4008-1600$12.50

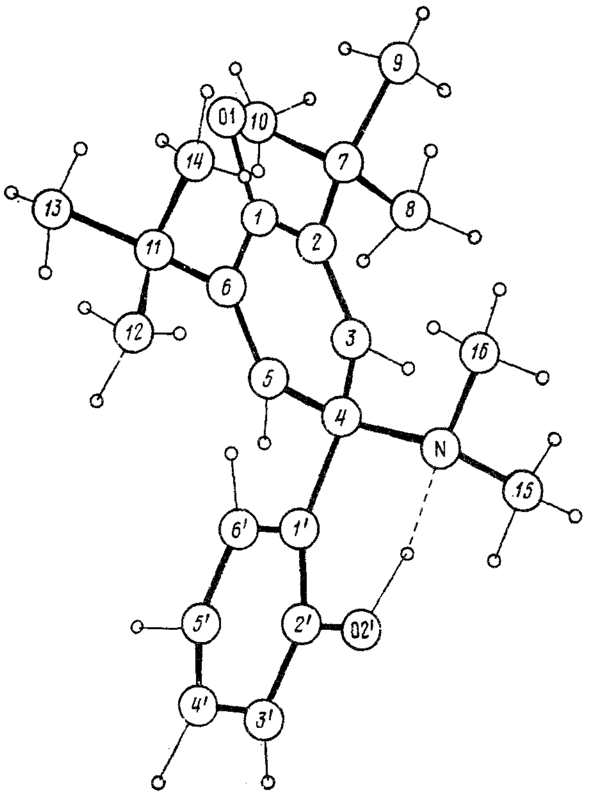
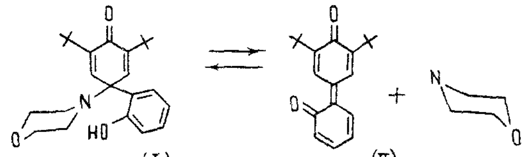
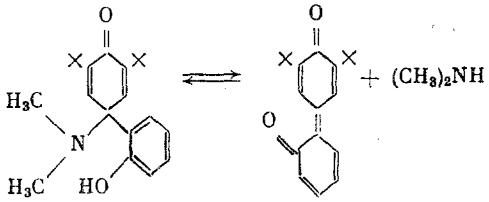


Fig. 1. General view of III with thermal vibration ellipsoids (50% probability).



(I) (II)

The present work reports on the x-ray structure of another representative of this class of compounds, 2,6-di-tert-butyl-4-dimethylamino-4-(2-hydroxyphenyl)cyclohexadien-2,5-one (III), which has analogous thermochromic properties



(III)

The structure of III is shown in Fig. 1. The di-tert-butyl-substituted benzoquinone and hydroxyphenyl fragments in I and III have the same distribution of bond lengths and angles and conformational features.

The cyclohexadiene fragment is slightly deformed to the boat conformation along the $C^2...C^6$ and $C^3...C^5$ vectors (4.8 and 3.2°). The sp^2-hybridization of C^1, C^2, and C^6 is preserved by deviation of O^1, C^7, and C^{11} from the $C^2C^3C^5C^6$ plane by 0.20, 0.03, and 0.04 Å, respectively. The vibrations of the terminal C atoms of the tert-butyl groups (Fig. 1) and O^1 are anomalously large in I and III.

The tert-butyl groups occupy the sterically most favorable position relative to O^1. Atoms C^8, C^{12}, C^{11}, and C^7 are situated almost in the average plane of the cyclohexadiene

TABLE 1. Coordinates of Nonhydrogen Atoms ($\times10^4$) and H Atoms ($\times10^3$) and Their Standard Deviations in III

Atom	x	y	z
O^1	4299(3)	882(2)	7047(4)
$O^{2'}$	−1189(2)	1730(2)	8425(3)
N	875(2)	2341(1)	7714(3)
C^1	3303(3)	1076(2)	6978(4)
C^2	2995(3)	1530(2)	5838(3)
C^3	1940(3)	1779(2)	5878(3)
C^4	1054(3)	1657(2)	6999(3)
C^5	1422(3)	1158(2)	8061(3)
C^6	2434(3)	867(2)	8069(3)
$C^{1'}$	−157(3)	1333(2)	6462(3)
$C^{2'}$	−1199(3)	1375(2)	7209(4)
$C^{3'}$	−2285(4)	1047(2)	6751(5)
$C^{4'}$	−2314(4)	665(2)	5553(6)
$C^{5'}$	−1303(4)	597(2)	4826(4)
$C^{6'}$	−228(3)	939(2)	5269(4)
C^7	3889(3)	1713(2)	4699(4)
C^8	3389(5)	2151(4)	3600(6)
C^9	4978(5)	2167(3)	5287(7)
C^{10}	4311(4)	1065(2)	4011(5)
C^{11}	2753(3)	366(2)	9205(4)
C^{12}	1712(5)	190(4)	10162(7)
C^{13}	3153(5)	−328(2)	8527(6)
C^{14}	3804(4)	694(2)	10022(4)
C^{15}	483(3)	2878(2)	6778(4)
C^{16}	1925(3)	2635(2)	8472(4)
$H^{2'}$	−23(3)	204(2)	834(3)
H^3	168(3)	205(2)	515(3)
$H^{3'}$	−300(4)	114(2)	738(5)
$H^{4'}$	−309(3)	36(2)	521(3)
H^5	84(2)	106(1)	879(3)
$H^{5'}$	−127(3)	32(2)	395(4)
$H^{6'}$	59(3)	86(2)	481(3)
H^8	278(4)	182(2)	338(5)
$H^{8'}$	275(6)	260(4)	363(7)
$H^{8''}$	386(5)	218(3)	284(6)
H^9	556(4)	229(3)	466(5)
$H^{9'}$	469(4)	257(3)	586(2)
$H^{9''}$	512(3)	169(3)	559(6)
H^{10}	340(6)	77(3)	391(7)
$H^{10'}$	469(4)	76(2)	468(5)
$H^{10''}$	487(4)	133(2)	500(5)
H^{12}	94(4)	−4(3)	968(6)
$H^{12'}$	198(4)	−15(3)	1073(6)
$H^{12''}$	182(3)	52(2)	1058(5)
H^{13}	232(3)	−43(2)	862(3)
$H^{13'}$	341(4)	−59(2)	924(5)
$H^{13''}$	261(4)	−67(3)	781(5)
H^{14}	361(3)	116(2)	1047(4)
$H^{14'}$	402(3)	42(2)	1085(3)
$H^{14''}$	459(4)	79(2)	939(5)
H^{15}	27(3)	328(2)	734(3)
$H^{15'}$	−30(3)	265(2)	620(3)
$H^{15''}$	111(3)	307(2)	612(4)
H^{16}	263(3)	273(2)	786(4)
$H^{16'}$	221(2)	231(2)	911(3)
$H^{16''}$	168(3)	308(2)	894(4)

fragment whereas C^9, C^{10}, C^{13}, and C^{14} deviate from this plane and are maximally removed from O^1 by 2.94, 3.03, 2.94, and 3.00 Å, respectively.

Like in I, the very large geometric distortions of the cyclohexadiene ring are caused by the strictly tetrahedral coordination of $C_{spiro}{}^4$. The endocyclic angle $C^3C^4C^5$ decreases to 112.4° whereas angles $C^2C^3C^4$ and $C^4C^5C^6$ increase to 125.7 and 125.5°.

Molecule III contains an intramolecular H-bond (IHB) between $H^{2'}$ of the hydroxy group and N of the dimethylamine. This bond has features identical to those of the IHB of I. The contacts $H^{2'}$...N and $O^{2'}$...N are rather short (1.46, 2.596 Å), characteristic of a strong IHB. The orientation of the hydroxy group and the unshared electron pair (UEP) of the trigonal pyramidal N are unfavorable for formation of an IHB. The angle between the direction N...$O^{2'}$ and the plane of the pyramid base $C^4C^{15}C^{16}$ can serve as a criterion of the favorability. In the optimal case, this angle is close to 90°. However, in the molecule examined,

TABLE 2. Bond Lengths in III

Bond	d, Å	Bond	d, Å
O^1-C^1	1,225(5)	$N-C^{15}$	1,474(4)
C^1-C^2	1,473(5)	$N-C^{16}$	1,462(4)
C^1-C^6	1,475(4)	$C^{11}-C^{12}$	1,514(6)
C^2-C^3	1,332(4)	$C^{11}-C^{13}$	1,587(6)
C^2-C^7	1,519(4)	$C^{11}-C^{14}$	1,512(5)
C^3-C^4	1,485(4)	$C^{1'}-C^{2'}$	1,396(4)
C^4-C^5	1,495(4)	$C^{1'}-C^{6'}$	1,382(4)
C^4-N	1,512(4)	$C^{2'}-O^{2'}$	1,365(5)
$C^4-C^{1'}$	1,538(4)	$C^{2'}-C^{3'}$	1,394(5)
C^5-C^6	1,325(4)	$O^{2'}-H^{2'}$	1,19(3)
C^6-C^{11}	1,532(4)		1,45(3)

TABLE 3. Bond Angles (ω, deg) in III

Angle	ω°	Angle	ω°	Angle	ω°
$O^1C^1C^2$	120,1(3)	$C^2C^7C^8$	111,5(3)	$C^4C^{1'}C^{6'}$	120,3(3)
$O^1C^1C^6$	119,2(4)	$C^2C^7C^9$	109,4(3)	$C^4C^{1'}C^{2'}$	121,6(3)
$C^2C^1C^6$	120,7(3)	$C^8C^7C^9$	106,2(4)	$C^{2'}C^{1'}C^{6'}$	118,0(3)
$C^1C^2C^3$	117,6(3)	$C^8C^7C^{10}$	107,8(4)	$C^{1'}C^{2'}O^{2'}$	121,2(3)
$C^1C^2C^7$	119,6(3)	$C^9C^7C^{10}$	108,6(3)	$C^{1'}C^{2'}C^{3'}$	121,2(4)
$C^3C^2C^7$	122,8(3)	$C^2C^7C^{10}$	113,1(3)	$O^{2'}C^{2'}C^{3'}$	117,6(3)
$C^2C^3C^4$	125,7(3)	$C^2C^7C^9$	109,4(3)	$C^{2'}C^{3'}C^{4'}$	118,8(4)
$C^3C^4C^5$	112,4(3)	$C^8C^7C^{10}$	107,8(4)	$C^{3'}C^{4'}C^{5'}$	121,2(4)
C^3C^4N	110,7(2)	$C^6C^{11}C^{12}$	110,8(3)	$C^{4'}C^{5'}C^{6'}$	119,8(4)
$C^5C^4C^{1'}$	106,0(2)	$C^6C^{11}C^{13}$	109,0(3)	$C^{1'}C^{6'}C^{5'}$	121,0(3)
$NC^4C^{1'}$	108,1(2)	$C^{12}C^{11}C^{13}$	110,8(4)	$C^{12}C^{11}C^{14}$	109,2(4)
$C^4C^5C^6$	125,5(3)	$C^{12}C^{11}C^{14}$	109,2(4)	C^4NC^{15}	113,1(3)
$C^1C^5C^6$	117,7(3)	$C^{13}C^{11}C^{14}$	106,5(3)	C^4NC^{16}	112,8(3)
$C^1C^6C^{11}$	119,7(3)	$C^6C^{11}C^{14}$	110,4(3)	$C^{15}NC^{16}$	109,8(2)
$C^5C^6C^{11}$	122,5(3)	$C^6C^{11}C^{13}$	109,0(3)	C^4NC^{15}	113,1(3)

it is 61.9°. The IHB is nonlinear (angle $O^{2'}H^{2'}N = 158.6°$). The six-membered ring $NC^4C^{1'}$-$C^{2'}O^{2'}H^{2'}$ formed by the IHB is distinctly nonplanar. The deviations of the atoms from the mean-square plane of the ring are 0.1-0.3 Å.

It has been demonstrated [5] that such a geometry for the IHB is caused by steric repulsions of the substituents on N and C^4. As a result, the staggered conformation is most favorable for them. However, even with such a conformation the nonbonding interatomic distances $C^5...C^{16}$, $C^3...C^{16}$, $C^3...C^{15}$, and $C^3...C^{6'}$ of 2.846, 3.012, 2.935, and 2.850 Å are shortened.

It is proposed that namely these steric repulsions cause the lengthening of the C^4–N bond to 1.512(4) Å compared with the usual C_{sp^3}–N_{sp^3} length of 1.472 Å [4].

The strong IHB in the molecules examined can be formed by contracting the ring $NC^4C^{1'}$-$C^{2'}O^{2'}H^{2'}$, simultaneously creating a sterically very strained eclipsed conformation. This conformation probably exists at elevated temperature due to an increase of twisting vibrations around the single bonds. For this the IHB should be strongest and the C^4–N bond weakest. This largely determines the thermochromic properties of I and III due to $O^2 \rightarrow N$ proton transfer and cleavage of the C^4–N bond.

The packing of III is characterized by van der Waals contacts, in contrast to that of I, in which an intermolecular H-bond O–H...O exists between the hydroxy groups with distances $O^{2'}...O^{2'} = 2.87$, $O^{2'}...H^{2'} = 2.50$, $O^{2'}$–$H^{2'} = 0.98$ Å; and angle $O^{2'}...H^{2'}$–$O^{2'} = 102°$. Apparently this weakens the N...H–O IHB and is reflected in the distances N...O and N...H, which are shorter in III than in I by 0.07 and 0.42 Å, respectively.

EXPERIMENTAL

The compound was obtained as follows. Solutions of 2,4'-dihydroxy-3',5'-di-tert-butyldiphenyl (1.49 g, 5 mmoles) [6] in benzene (30 ml) and $K_3Fe(CN)_6$ (5 g) and KOH (2 g) in water (30 ml) were shaken for 2-3 min. The dark red benzene layer was separated. A stream of gaseous dimethylamine was passed through it. The dark red color quickly changed to yellow. After drying over anhydrous Na_2SO_4 and evaporation of solvent, an oil that crystallized on grinding with methanol was obtained. For the yellow crystals obtained (mp 113-114°C) (from CH_3OH), found, %: C 77.57, H 9.30, N 4.17. $C_{22}H_{31}NO_2$. Calculated, %: C 77.38; H 9.15; N 4.10.

The x-ray data were collected on a DAR-UM three-circle automatic diffractometer (Cu Kα radiation).

Crystals of III are monoclinic: a = 11.327(5), b = 19.083(10), c = 9.750(5) Å, γ = 95.97(3)°, V = 2096.1 Å^3, M = 341.3, d_{calc} = 1.09 g/cm^3, Z = 4, space group $P2_1/b$.

The structure was solved by direct methods using X-ray-75 programs and 1974 reflections with $I \geq 2\sigma(I)$. The model was refined by anisotropic least squares for all nonhydrogen atoms and isotropic for H atoms to R = 0.060. Absorption corrections were not made. The atomic coordinates are listed in Table 1. Principle bond lengths and angles of III are given in Tables 2 and 3.

LITERATURE CITED

1. S. M. Aldoshin and L. O. Atovmyan, Crystal Chemical Problems [in Russian], Nauka, Moscow (1984), p. 110.
2. M. R. Edwards, P. G. Jones, and A. J. Kirby, J. Am. Chem. Soc., 108, 7067 (1986).
3. A. J. Kirby, J. K. Parker, and P. R. Raithby, Acta Crystallogr. Sec. C: Cryst. Struct. Commun., 45, 224 (1989).
4. F. H. Allen, O. Kennard, and D. G. Watson, et al., J. Chem. Soc., Perkin Trans. 2, No. 12, S1 (1987).
5. V. N. Komissarov, L. Yu. Ukhin, V. A. Kharlanov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1121 (1991).
6. V. N. Komissarov and L. Yu. Ukhin, Zh. Org. Khim., 25, No. 12, 2594 (1989).

CRYSTAL STRUCTURE OF N-(β-ACETOXYETHYL)-4-METHYLPYRIDINIUM BROMIDE

I. A. Litvinov, O. N. Kataeva, G. I. Kovylyaeva,
and V. E. Kataev

UDC 548.737:547.82

In continuation of previous studies [1] on structures of compounds differing from acetylcholine and choline by having a pyridine ring instead of the quaternary N atom, the x-ray structure of N-(β-acetoxyethyl)-4-methylpyridinium bromide, which has cholinergic activity [2], is solved.

In conformation of the molecular cation N-(β-acetoxyethyl)-4-methylpyridinium (I) is described by four torsion angles $C^6NC^7C^8$ (φ_0), $NC^7C^8O^1$ (φ_1), $C^7C^8O^1C^9$ (φ_2), and $C^8O^1C^9C^{10}$ (φ_3). It seemed interesting to compare the φ values and the bond lengths and angles for a series of compounds including besides I the chloride (II), bromide (III), iodide (IV), and picrate (V) of acetylcholine and N-(β-hydroxyethyl)pyridinium bromide (VI) [1, 3-5].

The bond lengths found for the C—C—O—C(O)—C fragment of I (Fig. 1) agree with those known for II-VI. The C^7—C^8 bond length 1.484(9) Å of I is ~0.02 Å less than the corresponding values in III-VI but greater than the 1.47 Å obtained for acetylcholine chloride II [3]. Good agreement is also seen for the bond angles of this fragment in the series of compounds under discussion: $\angle NC^7C^8$ = 111.5(5)°, $\angle C^7C^8O^1$ = 110.8(5)°, $\angle C^8O^1C^9$ = 116.8(5)°, $\angle O^1C^9C^{10}$ = 112.4(6)°. The geometry of the pyridinium ring in I is practically the same as that in VI and N-n-butylpyridinium chloride (VII) [6]. The length of the exocyclic bond N—C^7, 1.479(6) Å,

---

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Scientific Center, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1813-1816, August, 1991. Original article submitted April 18, 1990.

0568-5230/91/4008-1604$12.50