PHOTO- AND THERMOCHROMIC MANNICH BASES.

1. MANNICH BASES FROM 3,5-DI-*tert*-BUTYL-4-HYDROXYBENZALDEHYDE AND 2-NAPHTHOLS

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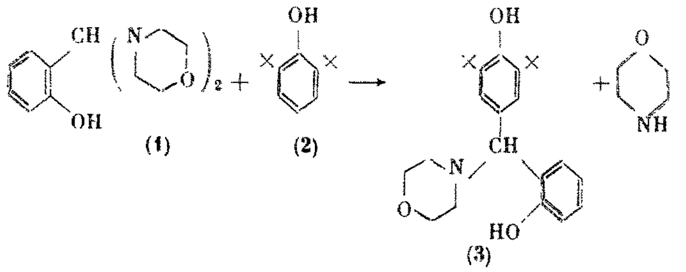
*Mannich bases exhibiting photo- and thermochromic properties in solutions were synthesized from 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde and 2-naphthols. An investigation of an acetyl derivative of methylenequinone, modeling a product of photo- and thermochromic transformations, proved that the color change of solutions of the Mannich bases is due to reversible dissociation into colored methylenequinones and morpholine. On the basis of data of x-ray diffraction analysis of one of the Mannich bases, characteristics of their molecular structure were determined, and reasons were stated for their effect on the dissociation mechanism.*

Keywords: *synthesis, crystal structure, UV spectra, 2,6-di-*tert*-butyl-4-[α-(2-hydroxy-1-naphthyl)methyl]phenol, 2,6-di-*tert*-butyl-4-[α-morpholino-α-(2-hydroxy-6-bromo-1-naphthyl)methyl]phenol, 2,6-di-*tert*-butyl-4-α-(2-hydroxy-1-naphthyl)-1,4-methylenequinone, 2,6-di-*tert*-butyl-4-α-(2-acetyloxy-1-naphthyl)-1,4-methylenequinone.*

Previously, we reported the synthesis of Mannich bases from aminals of aromatic aldehydes and 2,6-di-*tert*-butylphenol [1]. Among other compounds, we obtained 2,6-di-*tert*-butyl-4-[α-(2-hydroxyphenyl)-α-morpholinomethyl]phenol (**3**):



(1)

However, attempts to synthesize its naphthalene analog from 2-hydroxy-1-naphthaldehyde by this same method were unsuccessful.

We obtained such analogs from 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (**4**) by heating its solutions in morpholine with 2-naphthol or 6-bromo-2-naphthol in the presence of zinc chloride:

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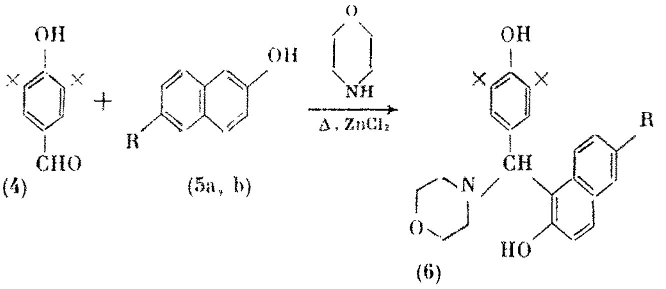
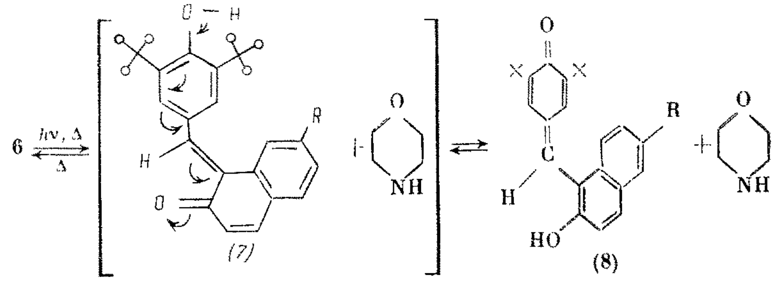


R = H (a), Br (b).

(2)

In solutions, Mannich bases **6** exhibited photo- and thermochromic properties due to their reversible dissociation into morpholine and compounds identified as methylenequinones **8**. The naphthol hydroxyl, having acidity much higher than that of sterically hindered hydroxyl [2], is located so that a six-membered cyclic transition state preceding abstraction of morpholine can be formed. This suggests that in the first stage **6** was converted to phenol **7** with an unstable *o*-methylenequinone substituent, which rapidly isomerized to stable sterically hindered *p*-methylenequinone **8**:



(3)

In organic solvents, solutions of **6**, colorless at first, gradually (20 min) became yellow as a result of the establishment of equilibrium **6** ⇄ **8**. Heating of the solutions or their photolysis resulted in deepening of the color (shift of the equilibrium to the right), but addition of morpholine decolorized the solutions (suppression of dissociation of **6**). The UV spectrum of solutions of **6** changed correspondingly. Heating or photolysis increased the intensity of the long-wave band at 415 nm, and addition of morpholine resulted in its disappearance (Fig. 1a).

The structure of Mannich base **6a** was reliably established from an x-ray diffraction experiment. The general form of the molecule of **6a** and its main bond lengths and valence angles are shown in Fig. 2.

Just as the spiro atoms in previously studied 2,6-di-*tert*-butyl-4-morpholino-4-(2-hydroxyphenyl)cyclohexa-2,5-dienone (**10**) [3] and 2,6-di-*tert*-butyl-4-(dimethylamino)-4-(2-hydroxyphenyl)cyclohexa-2,5-dienone (**11**) [4], the C^{15} atom had a tetrahedral configuration, the distortion of which is due to steric interactions of three bulky substituents bonded to that atom, i.e., morpholine, naphthol, and hydroxyphenyl.

As in the molecule of **10** [3], the morpholine ring has a chair conformation with folding angles of 50.7° and 49.5° along the $C^{27}...C^{28}$ and $C^{26}...C^{29}$ lines, respectively. From a comparison of the values of the emergence of the N atom from the base plane of the coordination pyramid (0.48, 0.43, and 0.46 Å) and the sum of the valence angles at the N atom (330.0°, 335.8°, and 335.6°) for **6a, 10,** and **11**, respectively, it is evident that the pyramidal nature of the N atom in the molecule of **6a** is greater than that of **10** and **11** [4].

The phenyl and naphthol rings are virtually planar. The dihedral angle between them is 74.7°. The deviations of the atoms from the root-mean-square planes drawn through them are in the range 0.001-0.024 Å.

In the benzene ring, because of the electron-donor effect of methyl and *tert*-Bu groups and the electron-acceptor effect of the hydroxyl group, the endocyclic angles at C^1, C^3, and C^5 atoms are decreased to 118.2°, 117.3°, and 117.7°, and those at C^4, C^2, and C^6 atoms are increased to 121.6°, 122.3°, and 122.5°, respectively. However, such a distribution of valence angles is probably due not only to the electronic properties of substituents, but also to steric strains appearing between *ortho* substituents which, as is known [5], causes additional contractions of angles at donor groups and an increase of angles at acceptor groups. The lengths of aromatic bonds in the ring have values of 1.380-1.413 Å, which are the usual ones for substituted benzenes.

The orientation of the *tert*-Bu groups with respect to the plane of the Ph ring is similar to that in **10**: the central carbon atom and one of the methyl carbon atoms are almost in the plane of the ring, and the other two deviate ≈ 1.3 Å in opposite directions, occupying the position most sterically favorable with respect to O^3. The elongation of the C^3-C^{11}, C^5-C^7, $C^{11}-C^{14}$,

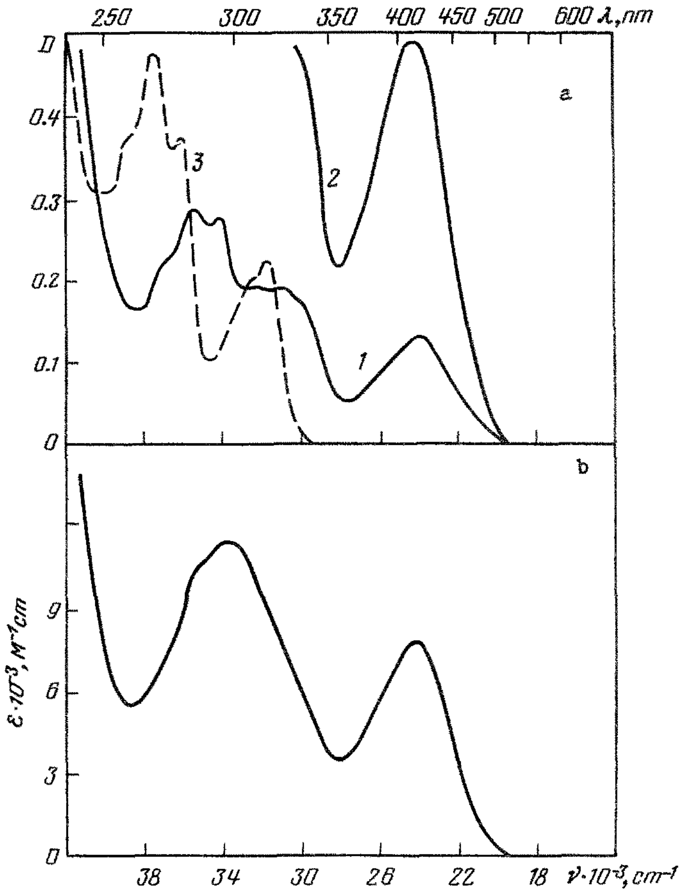


Fig. 1. Absorption spectra (ethanol, 293 K) of compound **6a** (a) ($c = 3.59 \cdot 10^{-4}$ mole/liter and cuvette thickness 0.199 cm) before irradiation (1) and after irradiation (2) (λ 313 nm and $\tau = 400$ sec), and after morpholine addition (3) and of compound **8a** (b) ($c = 3.37 \cdot 10^{-4}$ mole/liter and cuvette thickness 0.201 cm).

and C^7-C^8 bonds in the *tert*-Bu substituents to 1.560-1.573 Å in comparison with the value 1.540 Å, which is normal for $C_{sp^3}-C_{sp^3}$ bonds, can be explained by the great anisotropy of thermal vibrations of the atoms in these groups.

The tetrahedral coordination of the C^{15} atom governed the rigid fixation of the positions of the C^1, C^{21}, and N atoms with respect to each other. During rotation of the morpholine ring by 56.0° about the $C^{15}-N$ bond, an arrangement of the C^{27} and C^{28} atoms was attained where their repulsions from the C^1 and C^{21} atoms were found to be minimal, i.e., in the considered molecule of **6a**, just as in **10** and **11**, the most sterically favorable skewed conformation was attained. A Newman projection along the $N-C^{15}$ bond is shown in Fig. 3. The elongation of the cleaved $C^{15}-N$ bond, even in the ground state, to 1.492 Å in comparison with the values 1.47-1.48 Å, which are the usual ones for the $C_{sp^3}-N_{sp^3}$ bond [6], is probably due to the above-mentioned steric repulsions of atoms [3, 4], because, even with favorable conformation, the $C^1 \ldots C^{27}$ and $C^{21} \ldots C^{28}$ interatomic distances (2.93 and 2.90 Å, respectively) are shortened.

In the molecule of **6a**, intramolecular hydrogen bonding of the same type as in the molecules of **10** and **11** occurs between the hydrogen atom of the hydroxy group and the N atom of the morpholine ring. The resulting intramolecular hydrogen-bonded six-membered $O^1H^1NC^{15}C^{21}C^{16}$ ring is significantly nonplanar, and the deviations of the atoms from the root-mean-square plane drawn through it are in the range 0.10-0.31 Å. The values of the NH^1O^1 and H^1NC^{15} angles are 119° and 102.5°, respectively. The given $O-H \ldots N$ intramolecular hydrogen bond has unfavorable geometry, i.e., the unshared electron pair of the nitrogen atom deviates significantly from the $H^1 \ldots N$ direction if the $O^1 \ldots N$ and $H^1 \ldots N$ contacts (2.654 and 1.98 Å, respectively) are

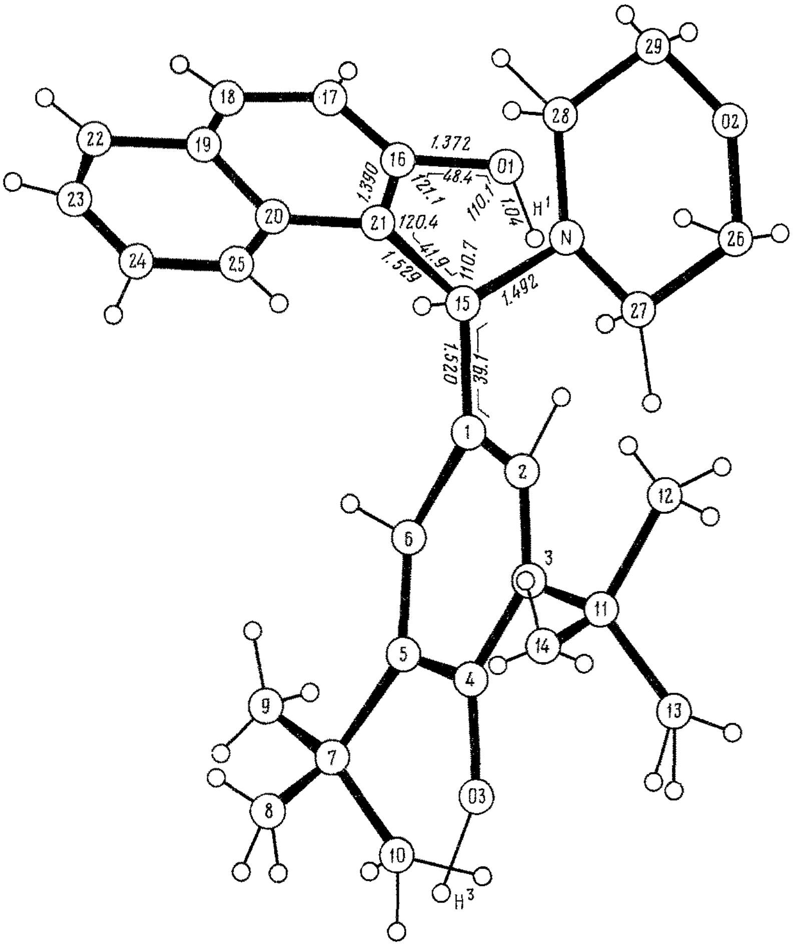
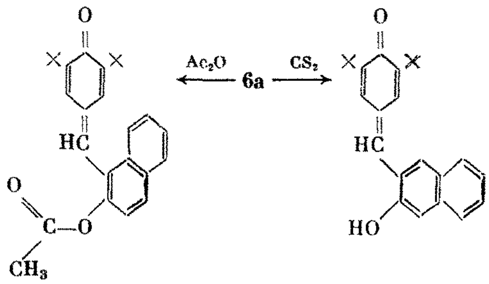


Fig. 2. General form of molecule of **6a** with some bond lengths and valence and torsion angles.

sufficiently short. A quantitative measure of such deviation is the angle ψ between a straight line (H^1N) and the unshared electron pair of the N atom directed approximately perpendicularly to the base plane of the $C^{15}C^{27}C^{28}$ pyramid. Angle ψ is equal to 28.5° in the molecule of **6a** and 13.5° in the molecule of **10** and, in the case optimal for strong intramolecular hydrogen bonding, the value of ψ should be close to 0°. We can assume that, just as in [3, 4], during heating, because of an increase of twisting vibrations about ordinary $C^{15}-N$, $C^{15}-C^{21}$, and $C^{16}-O^1$ bonds, a sterically strained shielded conformation occurred in the molecule, which resulted in further weakening and cleavage of the $C_{sp^3}-N$ bond, and favorable conditions were simultaneously provided for proton transfer along the O...N coordinate (ψ tended to 0°) and dissociation of the molecule.

For confirmation of the proposed mechanism of dissociative rearrangement of **6** in solutions (3), **6a** was completely converted to methylenequinone **8a** by the action of carbon disulfide, bonding morpholine. The positions of the absorption bands in its UV spectrum, including long-wave ones (Fig. 1b), agreed with the corresponding bands in the spectrum of **6a**. The content of methylenequinone in equilibrium **6a** ⇄ **8a** in ethanol at 295 K was calculated according to the parameters of the spectrum of **8a** and was found to be equal to 62%. The reaction of acetic anhydride with **6a** gave the O-acetyl derivative of methylenequinone **9a**, unable to be converted to *o*-methylenequinone:



(9a) **(8a)**

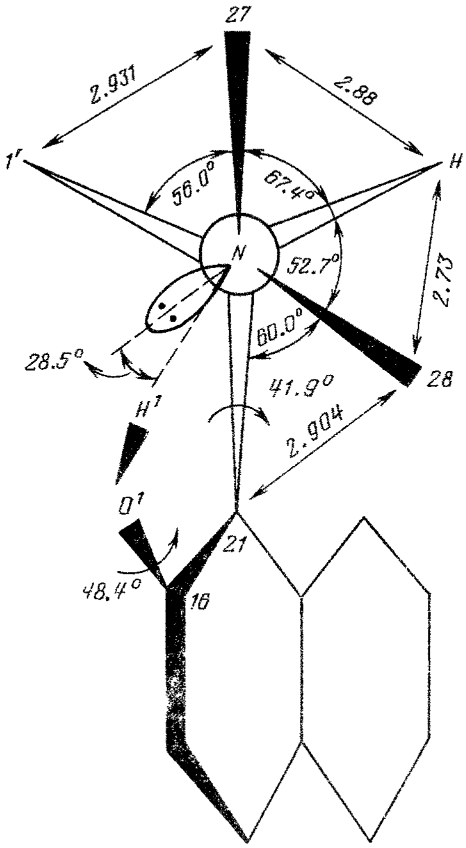


Fig. 3. Arrangement of substituents at C^{15} and N atoms in Newman projection along $N-C^{15}$ bond in the molecule of **6a.**

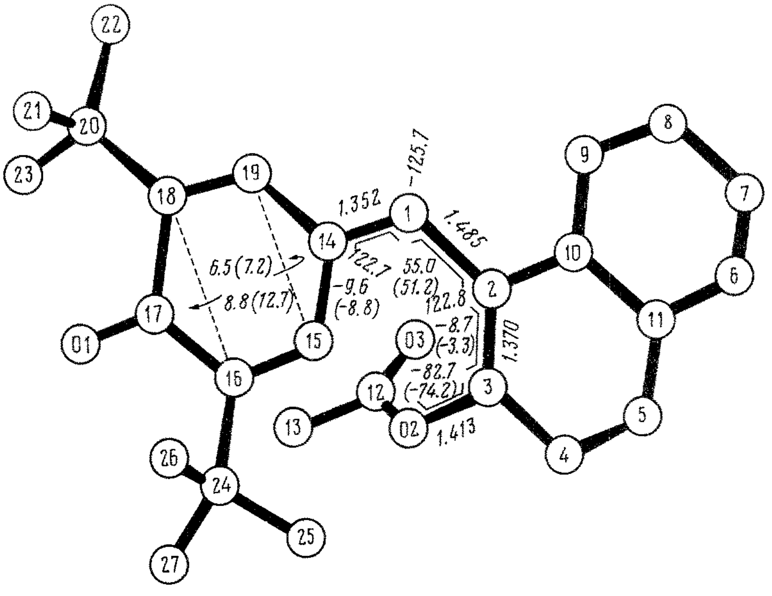


Fig. 4. Structure of molecule of **9a**. The bond lengths and valence angles averaged with respect to the two independent molecules are shown, and the torsion angles are given for each of them individually.

TABLE 1. Main Crystallographic Parameters of **6a** and **9a**

Parameter	6a	9a	Parameter	6a	9a
a, Å	12.608(3)	16.122(2)	α, deg	84.68(2)	118.55(2)
b, Å	10.919(1)	13.337(2)	β, deg	64.50(2)	93.61(1)
c, Å	10.529(3)	12.885(2)	γ, deg	76.98(2)	90.99(1)
V, Å^3	1274.5	2425.3	space group	$P\bar{1}$	$P\bar{1}$
d_{calc}, g/cm^3	1.09	1.11	Z	2	4

It was found that it does not react with morpholine, which can be considered as indirect confirmation of the involvement of the *o*-methylenequinone structure in the occurrence of equilibrium (3).

An x-ray diffraction investigation showed that the crystal of **9a** contained two symmetrically independent molecules, the differences in the geometry of which were insignificant, which makes it possible to use in the discussion the values of the geometric parameters that are average parameters for the two molecules. However, probably because of the unidentical effect of the crystalline field on each of them, the conformations of the independent molecules differ more significantly, and therefore some angles, especially the important torsion angles, are given for each molecule individually. Figure 4 shows the general form of one of the molecules of **9a** (the values of the angles for the second molecule are indicated in parentheses).

Unlike the analogous fragment in the previously investigated product of the thermal transformation of 3,3′,5,5′-tetra-*tert*-butyl-2,4′-diphenoquinone **12** [3], the quinone fragments in **9a** are nonplanar, but are deformed in the direction of a boat with 6.5° (7.2°) and 8.8° (12.7°) folds along the $C^{15}...C^{19}$ and $C^{16}...C^{18}$ lines, respectively. The C^{17} and O^1 atoms deviate from the root-mean-square $C^{15}C^{16}C^{18}C^{19}$ plane by 0.11 and 0.29 Å in one molecule and by 0.17 and 0.41 Å in the other molecule. The distribution of the bond lengths and valence angles in the quinone fragments of the molecules of **9a** and **12** agree within the limits of error.

The $C^{15}...O^2$ distances, 2.87 Å (2.91 Å), are shortened in comparison with the sum of the van der Waals radii, 2.97 Å [7]. The steric repulsions of sterically close O^2 and C^{15} atoms that appear here result, first, in an increase of the $C^1C^{14}C^{15}$, $C^2C^1C^{14}$, and $C^1C^2C^3$ valence angles to 122.7°, 125.7°, and 122.8°, respectively, and, second, in 55.0° (51.2°) unfolding about the C^1-C^2 bond and in 9.6° (8.8°) "twisting" of the $C^1{=}C^{14}$ bond, which disturbs conjugation. In addition, unlike the analogous double bond in the molecule of **12** (1.388 Å), the $C^1{=}C^{14}$ bond, 1.352 Å, remains unelongated.

We should note that the value of the $C^{14}C^1C^2C^3$ torsion angle, 55.0° (51.2°), in **9a** is close to the value of the analogous angle in the calculated optimal conformation of the 4-(4′-hydroxybenzylidene)-2,5-cyclohexadien-1-one molecule [8], 53.0°.

Thus, the structure (determined by x-ray diffraction analysis) of the O-acetyl derivative of methylenequinone **9a**, which serves as a model of a product of photo- and thermochromic transformations, confirmed the proposed mechanism of reversible dissociation of Mannich bases into colored methylenequinones and colorless morpholine.

EXPERIMENTAL

The UV spectra were recorded with a Specord M40 spectrophotometer in cuvettes with thicknesses of 0.199 and 0.201 cm with the possibility of temperature control in the range 293-369 K. The solutions were photolyzed by radiation of a DRSh-250 mercury lamp, individual lines of which were distinguished by standard filters. The IR spectra were recorded with a Specord IR-75 instrument in white mineral oil and in a CCl_4 solution. The PMR spectra were recorded with a Tesla BS 567A instrument (100 MHz) with an internal standard of hexamethyldisiloxane (HMDS).

2,6-Di-*tert*-butyl-4-[α-morpholino-α-(2-hydroxy-1-naphthyl)methyl]phenol (6a). A solution of 4.68 g (0.02 mole) of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde, 3.60 g (0.025 mole) of 2-naphthol, and 1.36 g (0.01 mole) of anhydrous zinc chloride in 10 ml of morpholine was boiled for 3 h, cooled, and diluted with water, and the recovered oily precipitate was mixed with water. The resulting crystals were filtered, washed with water, and dried. Then they were dissolved in the minimum amount

TABLE 2. Coordinates of Nonhydrogen Atoms ($\times 10^4$ and Hydrogen Atoms ($\times 10^3$) in Structure of **6a**

Atom	X	Y	Z
O^1	8324(4)	3407(4)	5252(4)
O^2	12187(3)	3796(4)	1552(4)
O^3	7093(5)	−461(3)	1666(4)
N^1	9721(4)	3601(3)	2536(3)
C^1	8194(3)	2690(4)	2225(5)
C^2	8373(3)	1586(4)	2944(5)
C^3	8017(3)	518(4)	2800(4)
C^4	7449(3)	579(4)	1889(5)
C^5	7224(3)	1689(4)	1177(6)
C^6	7632(4)	2709(4)	1339(5)
C^7	6567(5)	1750(4)	190(5)
C^8	5312(6)	1404(5)	1040(6)
C^9	6370(6)	3110(5)	−380(6)
C^{10}	7360(5)	850(5)	−1080(6)
C^{11}	8293(4)	−728(6)	3560(5)
C^{12}	9000(6)	−546(6)	4380(5)
C^{13}	9110(6)	−1778(6)	2510(5)
C^{14}	7070(6)	−1070(6)	4630(5)
C^{15}	8556(5)	3875(4)	2411(4)
C^{16}	7478(5)	4327(4)	5035(4)
C^{17}	6527(5)	4935(5)	6232(4)
C^{18}	5660(5)	5876(5)	6089(4)
C^{19}	5723(4)	6250(5)	4744(5)
C^{20}	6674(4)	5632(5)	3536(5)
C^{21}	7564(6)	4629(5)	3679(5)
C^{22}	4836(6)	7258(6)	4604(5)
C^{23}	4868(7)	7638(6)	3320(5)
C^{24}	5808(6)	7038(6)	2100(5)
C^{25}	6677(5)	6062(5)	2209(5)
C^{26}	11881(6)	2651(6)	1420(5)
C^{27}	10700(6)	2872(4)	1322(4)
C^{28}	10070(6)	4788(4)	2614(4)
C^{29}	11258(6)	4535(5)	2710(4)
H^1	920(1)	350(1)	460(1)
H^2	876(1)	164(1)	344(1)
H^3	687(1)	−58(1)	75(1)
H^5	740(1)	362(1)	88(1)
$H^{8.1}$	516(1)	68(1)	128(1)
$H^{8.2}$	481(1)	196(1)	157(1)
$H^{8.3}$	515(1)	143(1)	43(1)
$H^{9.1}$	710(1)	315(1)	−106(1)
$H^{9.2}$	578(1)	313(1)	−63(1)
$H^{9.3}$	643(1)	384(1)	−22(1)
$H^{10.1}$	775(1)	128(1)	−170(1)
$H^{10.2}$	692(1)	51(1)	−110(1)
$H^{12.1}$	806(1)	15(1)	−116(1)
$H^{10.3}$	991(1)	40(1)	369(1)
$H^{12.2}$	849(1)	−7(1)	509(1)
$H^{12.3}$	908(1)	140(1)	500(1)
$H^{13.1}$	871(1)	−235(1)	239(1)
$H^{13.2}$	942(1)	−244(1)	269(1)
$H^{13.3}$	875(1)	−204(1)	209(1)
$H^{14.1}$	627(1)	−93(1)	501(1)
$H^{14.2}$	701(1)	−53(1)	517(1)
H^{15}	855(1)	459(1)	146(1)
H^{17}	644(1)	463(1)	696(1)
H^{18}	469(1)	623(1)	687(1)
H^{22}	411(1)	769(1)	551(1)
H^{23}	438(1)	820(1)	334(1)
H^{24}	594(1)	717(1)	137(1)
H^{25}	723(1)	579(1)	147(1)
$H^{26.1}$	1190(1)	220(1)	208(1)
$H^{26.2}$	1101(1)	281(1)	241(1)
$H^{27.1}$	1048(1)	201(1)	118(1)
$H^{27.2}$	1074(1)	331(1)	62(1)
$H^{28.1}$	935(1)	523(1)	363(1)
$H^{28.2}$	988(1)	530(1)	221(1)
$H^{29.1}$	1096(1)	412(1)	344(1)
$H^{29.2}$	1191(1)	515(1)	249(1)

TABLE 3. Coordinates of Nonhydrogen Atoms ($\times 10^4$) and Hydrogen Atoms ($\times 10^3$ in the Structure of **9a**

Atom	Molecule A			Molecule B		
	X	Y	Z	X	Y	Z
O^1	8002(4)	1086(3)	4823(3)	3130(3)	3789(4)	5107(4)
O^2	925(5)	1738(4)	3059(4)	6160(4)	3489(5)	7244(4)
O^3	1328(4)	61(3)	1640(4)	3582(5)	4799(4)	1119(5)
C^1	-447(5)	1283(4)	1322(4)	4859(5)	3471(4)	8646(5)
C^2	294(4)	2064(5)	1518(5)	5626(4)	2865(5)	8555(4)
C^3	966(6)	2214(5)	2290(5)	6259(4)	2900(4)	7905(4)
C^5	1702(4)	2835(5)	2403(5)	7006(5)	2377(4)	7835(5)
C^4	1768(3)	3344(4)	1707(4)	7134(4)	1779(5)	8447(5)
C^6	1150(4)	3815(4)	195(4)	6660(5)	1085(4)	9755(4)
C^7	500(6)	3721(4)	9412(4)	6029(4)	1046(4)	452(5)
C^8	-272(4)	3090(6)	9292(5)	5295(6)	1558(5)	520(5)
C^9	-341(4)	2520(4)	-20(5)	5135(4)	2166(4)	-88(6)
C^{10}	354(5)	2610(5)	790(5)	5763(5)	2246(5)	9207(5)
C^{11}	1090(4)	3255(4)	908(4)	6517(5)	1702(5)	9137(4)
C^{12}	1092(5)	609(4)	2598(4)	6213(4)	4657(4)	7844(4)
C^{13}	929(6)	202(6)	3479(5)	5954(5)	5127(4)	7013(4)
C^{14}	-908(4)	1330(4)	2184(5)	4358(5)	3419(5)	7736(5)
C^{15}	-813(5)	2269(5)	3403(6)	3681(4)	4188(5)	8009(4)
C^{16}	-1210(4)	2248(4)	4274(4)	3214(5)	4285(5)	7156(4)
C^{17}	-1726(4)	1203(4)	4008(5)	3431(5)	3594(4)	5891(4)
C^{18}	-1915(5)	312(6)	2751(5)	4006(4)	2660(4)	5617(4)
C^{19}	-1517(5)	414(5)	1912(5)	4464(5)	2611(3)	6506(3)
C^{20}	-2528(6)	-693(5)	2481(4)	4076(3)	1769(3)	4287(4)
C^{21}	-3368(6)	-253(4)	2981(4)	4610(4)	778(4)	4194(4)
C^{22}	-2695(5)	-1471(4)	1130(4)	3162(4)	1208(5)	3734(4)
C^{23}	-2148(5)	-1420(5)	3006(4)	4483(4)	2365(4)	3666(4)
C^{24}	-1138(4)	3257(4)	5537(5)	2503(5)	5099(5)	7421(5)
C^{25}	-632(6)	4280(5)	5620(3)	2313(4)	5592(4)	8743(4)
C^{26}	-2029(5)	3653(4)	5900(4)	2753(6)	6103(5)	7190(4)
C^{27}	-711(4)	2920(5)	6409(5)	8295(4)	5601(4)	3378(4)
H^1	937(3)	63(4)	42(3)	468(4)	402(5)	954(4)
H^4	1221(3)	291(5)	304(5)	750(4)	247(4)	733(4)
H^5	1235(3)	381(4)	176(4)	772(5)	134(4)	837(5)
H^6	1171(3)	432(4)	28(4)	723(4)	66(5)	972(4)
H^7	1056(3)	413(4)	-113(5)	613(4)	59(4)	1095(4)
H^8	921(3)	305(4)	-131(4)	482(5)	151(4)	1108(4)
H^9	909(3)	203(4)	-10(4)	455(4)	257(4)	997(4)
$H^{13.1}$	1105(4)	-69(5)	314(4)	600(4)	604(5)	749(4)
$H^{13.2}$	1027(4)	31(5)	369(4)	533(4)	483(4)	664(5)
$H^{13.3}$	1131(4)	69(4)	431(4)	637(5)	483(4)	630(5)
H^{15}	959(4)	301(4)	361(4)	491(4)	196(5)	630(4)
H^{19}	833(4)	-23(4)	98(4)	354(4)	471(4)	892(5)
$H^{21.1}$	672(4)	30(4)	393(4)	214(4)	490(5)	891(4)
$H^{21.2}$	636(4)	23(5)	257(5)	286(4)	606(4)	931(4)
$H^{21.3}$	620(4)	-96(4)	280(4)	181(4)	616(4)	892(4)
$H^{22.1}$	788(4)	-181(4)	73(4)	288(4)	577(4)	628(4)
$H^{22.2}$	688(4)	-218(4)	95(5)	224(5)	667(4)	738(4)
$H^{22.3}$	703(4)	-99(4)	72(5)	329(4)	656(4)	776(4)
$H^{23.1}$	799(4)	-91(4)	396(5)	144(4)	358(4)	593(4)
$H^{23.2}$	744(4)	-214(4)	283(4)	162(4)	503(4)	632(4)
$H^{23.3}$	844(4)	-176(4)	262(5)	134(4)	466(5)	740(4)
$H^{25.1}$	907(4)	456(5)	502(4)	433(4)	36(4)	464(4)
$H^{25.2}$	999(4)	404(4)	536(4)	523(4)	112(5)	462(5)
$H^{25.3}$	941(5)	498(4)	651(4)	466(5)	17(5)	328(5)
$H^{26.1}$	799(5)	436(4)	677(5)	275(4)	187(4)	380(4)
$H^{26.2}$	759(4)	295(4)	585(4)	292(4)	84(4)	426(4)
$H^{26.3}$	767(4)	391(4)	527(4)	317(4)	56(5)	284(4)
$H^{27.1}$	897(4)	218(4)	638(5)	510(4)	271(4)	411(4)
$H^{27.2}$	935(4)	361(4)	730(4)	412(5)	305(4)	373(5)
$H^{27.3}$	994(4)	266(4)	615(4)	454(4)	175(4)	277(5)

of a chloroform–hexane mixture (2:1) and passed through a column with aluminum oxide (h = 25 cm and d = 2.5 cm). The first, colorless fraction (unreacted aldehyde) was discarded, and the second, colored fraction was collected. After evaporation of the solvent, the residue was recrystallized from alcohol. Colorless crystals with mp 188-190°C in a yield of 3.6 g (40.2%). Found, %: C 77.76; H 8.21; N 3.20. $C_{29}H_{37}NO_3$. Calculated, %: C 77.81; H 8.33; N 3.13. IR spectrum: ν_{OH} = 3600 cm^{-1}. PMR spectrum ($CDCl_3$, δ, ppm): 1.36 s (18H, *t*-Bu), 2.44 t (4H, N–CH_2), 3.76 t (4H, O–CH_2), 5.0 s (1H, OH sterically hindered), 5.12 s (1H, CH), 7.12-7.92 m (9H, CH arom.), 13.12 s (1H, OH unhindered).

2,6-Di-*tert*-butyl-4-[α-morpholino-α-(2-hydroxy-6-bromo-1-naphthyl)methyl]phenol (6b). A mixture of 1.64 g (0.007 mole) of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde, 2.34 g (0.0105 mole) of 6-bromo-2-naphthol, 0.7 g (0.005 mole) of anhydrous zinc chloride, and 7 ml of morpholine was boiled for 5 h and cooled, and 30 ml of water was added. The precipitate was filtered, washed with water, and dried. The precipitate was dissolved in a chloroform−hexane mixture (2:1) and passed through a column with aluminum oxide (h = 25 cm and d = 2.5 cm). The first, colorless fraction (unreacted aldehyde) was discarded, and the second, colored fraction was collected. The dark-orange oil that formed after evaporation of the solvent was recrystallized from toluene with hexane. Colorless crystals with mp 188-189°C. Yield 1.05 g (28.5%). Found, %: C 66.06; H 7.03; Br 15.17. $C_{29}H_{36}NOBr$. Calculated, %: C 66.15; H 6.89; Br 15.17. IR spectrum: νOH = 3610 cm^{-1}.

2,6-Di-*tert*-butyl-4-α-(2-hydroxy-1-naphthyl)-1,4-methylenequinone (8a). We dissolved 0.45 g (1 mmole) of **6a** in a mixture of 2 ml of carbon disulfide and 5 ml of ethanol and left the whole at room temperature for 48 h. Then the solution was passed through a column with aluminum oxide (the eluent was chloroform), and the yellow fraction was collected. After evaporation of the solvent, the remaining oil crystallized during trituration. Mass spectrum: M^+ = 360. UV spectrum (ethanol, λ, nm; ε): 297 (ε 11,400), 414 (ε 7700). IR spectrum: νOH = 3325; νCO = 1625 cm^{-1}. The tendency of methylenequinone to capture solvents used for recrystallization prevented preparation of analytically pure samples.

2,6-Di-*tert*-butyl-4-α-(2-acetyloxy-1-naphthyl)-1,4-methylenequinone (9a). We obtained **6a** in 85% yield during boiling for 45 min in excess acetic anhydride, with subsequent dilution of the mixture by water and recrystallization of the resulting yellow precipitate from methanol or 2-propanol. Large yellow crystals with mp 143-145°C. Found, %: C 80.60; H 7.42. $C_{27}H_{30}O_3$. Calculated, %: C 80.56; H 7.51. PMR spectrum ($CDCl_3$, δ, ppm): 1.09 s (9H, *t*-Bu), 1.31 s (9H, *t*-Bu), 2.07 s (3H, CH_3), 6.90 d (1H, CH), 7.35 m (2H, CH quinone), 7.47 m (3H, CH arom.), 8.00 m (3H, CH arom.).

X-Ray Diffraction Analysis of Triclinic Crystals of 6a and 9a. The main crystallographic parameters of **6a** and **9a** are given in Table 1. The intensities of 4700 (**6a**) and 8000 (**9a**) independent reflections with $I > 2\sigma(I)$ were measured with an automated KM-4 four-circle diffractometer (CuKα radiation), and absorption was not taken into account. The structures were resolved by a direct method according to the SHELXS-86 program and refined by a complete-matrix least-squares method in an anisotropic approximation according to the SHELXS-76 program [10]. The coordinates of hydrogen atoms of the *t*-Bu groups were calculated from geometric considerations, and the remaining H atoms were localized objectively from Fourier difference syntheses. Final refinement of the coordinates was carried out by a complete-matrix least-squares method for nonhydrogen atoms in an anisotropic approximation and H atoms in an isotropic approximation to R = 0.09 (**6a**) and R = 0.08 (**9a**). The corresponding coordinates of the atoms in the structures of **6a** and **9a** are given in Tables 2 and 3.

REFERENCES

1. V. N. Komissarov and L. Yu. Ukhin, *Zh. Org. Khim.*, **25**, No. 12, 2594 (1989).
2. V. V. Ershov, G. A. Nikiforov, and A. A. Volod'kin, *Sterically Hindered Phenols* [in Russian], Khimiya, Moscow (1972), p . 26.
3. V. N. Komissarov, L. Yu. Ukhin, V. A. Kharlanov, L. V. Vetoshkina, L. E. Konstantinovskii, S. M. Aldoshin, O. S. Filipenko, M. A. Novozhilova, and L. O. Atovmyan, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 5, 1121 (1991).
4. S. M. Aldoshin, O. S. Filipenko, M. A. Novozhilova, L. O. Atovmyan, V. N. Komissarov, and L. Yu. Ukhin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 8, 808 (1991).
5. Z. V. Zvonkova, *Usp. Khim.*, **46**, No. 5, 907 (1977).
6. F. H. Allen, O. Kennard, and D. D. Watson, *J. Chem. Soc. Perkin Trans. II*, **2**, 1 (1987).
7. Yu. V. Zefirov and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, **17**, No. 6, 994 (1976).
8. S. M. Shevchenko and M. Ya. Zarubin, *Zh. Strukt. Khim.*, **27**, No. 5, 25 (1986).
9. J. Velek, B. Koutek, and L. Musil, *Collect. Czech. Chem. Commun.*, **46**, No. 4, 873 (1981).
10. G. M. Sheldrick, *Shelx-76. Program for Crystal Structure Determination*, Cambridge University, England (1976).