UNUSUAL SYNTHESIS, STRUCTURE, AND THERMOCHROMIC PROPERTIES OF NOVEL STERICALLY HINDERED CYCLOHEXADIENES

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Oxidation of $4-[\alpha-morpholino-\alpha-(2-hydroxyphenyl)]methyl-2,6-di-(tert-butyl)-phenol (I) follows an unusual course, with formal loss of the benzyl carbon atom, to give 2,6-di(tert-butyl)-4-morpholino-4-(2-hydroxyphenyl)cyclohexa-2,5-dienone (II), which is thermochromic in solution. This property is due to the dissociation of (II) into morpholine and 3',5'-di(tert-butyl)-2,4'-diphenoxyquinone. The structure of (II) was established directly by x-ray diffraction, which enabled its conformational features to be related to its thermochromic properties. An x-ray examination of 3,3',5,5'-tetra(tert-butyl)-2,4'-diphenoquinone (X), together with the direct synthesis of the thermochromic analog of (II) (2,6-di(tert-butyl)-4-morpholino-4-[2-hydroxy-3,5-di(tert-butyl)phenyl]cyclohexa-2,5-dienone) (XI) from (X) and morpholine, confirmed the proposed mechanism of thermochromic dissociation.$

The oxidation of (I) has been reported previously [1] to follow an unusual course, with loss of the benzyl carbon atom and formation of 2,6-di(tert-butyl)-4-morpholino-4-(2-hydroxyphenyl)cyclohexa-2,5-dienone (II).



It has also been reported [2-4] that oxidation of hydroxydiphenylmethanes (III) affords reactive cyclopropanes (V).



It appears that reaction (1) also involves the intermediate formation of a cyclopropane derivative (VI), hydrolysis of which affords (II).

This intramolecular nucleophilic substitution (1,2-shift) with ring enlargement and hydrolysis is completed by cleavage of formaldehyde.

The structure of (II) was confirmed by elemental analysis, PMR, IR, UV, and mass spectrometry, and mass spectroscopy, and finally established by x-ray analysis. In solution, (II) undergoes a reversible thermochromic reaction.

A general view of the molecule is shown in Fig. 1. The central cyclohexadiene (CHD) fragment is nearly planar, the maximum departures of the atoms from the mean-square plane being no greater than 0.05 Å.

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Fig. 1. Molecule of (II) showing ellipsoidal thermal atom vibrations (50% probability).



Fig. 2. a) Arrangement of substituents at C⁴ and N in Newman projection along the N-C⁴ axis in (II); b) arrangement of substituents at C⁴ and N favoring hydrogen bonding, in Newman projection along axis N-C⁴.



(3)

The bond length distribution in the ring is the same as those in 1,4-benzoquinone and 2,6-dimethyl-1,4-benzoquinone [5, 6]. The tert-butyl groups occupy positions which are most sterically favored with respect to the carbonyl oxygen O^3 , with C^8 and C^{12} lying in the plane of the CHD fragment, and C^9 and C^{10} , and C^{13} and C^{14} departing from this plane and being at the maximum distance from O^3 (2.94 and 3.03, and 2.94 and 3.00 Å, respectively).

The greatest distortion of the geometry of the CHD ring is due to the sp³-hybridization of C⁴, as a result of which the endocyclic angle $C^{3}C^{4}C^{5}$ is reduced to 112.5(1)°, whereas $C^{4}C^{5}C^{6}$ and $C^{4}C^{3}C^{2}$ are increased to 125.1(2)° and 125.7(1)°. An intramolecular hydrogen bond is present between the hydrogen of the hydroxy group H²' and the nitrogen of the morpholine ring.

In spite of the fact that N...H²' [1.88(4)] and N...O² [2.670(2) Å] distances indicate a strong intramolecular hydrogen bond, the molecular geometry shows that the amino and hydroxy groups are unfavorably located to each other. The morpholine ring has the chair conformation, with bending angles along C¹⁵...C¹⁸ and C¹⁶...C¹⁷ of 54.2 and 53.0°. The ring nitrogen is pyramidally coordinated, standing out from the plane of the base of the pyramid $C^4C^{15}C^{18}$ by 0.43 Å. The relative positions of C^{15} and C^{18} (bonded to nitrogen) and C^5 , C^3 , and C^{11} (bonded to the adjacent C^4), which are rigidly sp³-hybridized, are determined by their mutual steric repulsion. Figure 2a shows the arrangement of these atoms in Newman projection along the N-C⁴ axis. It will be seen that the substituents at N and C⁴ are in the most sterically favorable skew conformation. The lone pair of the nitrogen, oriented approximately perpendicularly to the plane C⁴C¹⁵C¹⁸ base of the nitrogen pyramid, in effect expands its coordination to tetrahedral, occupying the position of a fourth substituent. In this conformation, the lone pair of the nitrogen is much further from H²', despite the maximum rotation of the phenyl group around C^4-C^{11} permitted by the steric repulsions of atoms $C^3...C^{61}$ (the torsion angle φ for C³C⁴C¹'C⁶' is 19°, and the nonvalent distance C³...C⁶ is shortened to 2.83 Å) and the rotation of the hydroxy group by 14.3° out of the plane of the benzene ring toward the lone pair. This is shown by the magnitude of the angle between H²'...N and the plane of the pyramid base C⁴C¹⁵C¹⁸, which is 70.6° rather than near 90° as would be the case when these atoms are in the most favored positions for intramolecular hydrogen bonding. The intramolecular O-H...N hydrogen bond is markedly nonlinear, the angle $O^{2}H^{2}N$ being $136(4)^{\circ}$. The six-membered ring formed by the intramolecular hydrogen bond, NC+C+C+C+O+H2+ is nonplanar, the atoms of this ring departing from the mean-square plane passing through them by 0.33 Å.

The screened conformation with a planar six-membered ring is the most favorable one for the formation of a strong intramolecular hydrogen bond (Fig. 2b). This structure would, however, be highly strained. Even in the staggered conformation, the nonvalent interatomic distances $C^5...C^{18}$ (2.85 Å), $C^{18}...C^3$ (3.05 Å), and $C^3...C^{15}$ (2.95 Å) are significantly shortened, and steric repulsion between these atoms is apparently responsible for the lengthening of the C⁴-N bond to 1.511(2) Å, as compared with the usual value for C_{sp3} -N \checkmark of 1.47-1.48 Å [7]. It is assumed that transition to the sterically strained staggered conformation occurs at elevated temperatures as a result of the increased twisting vibrations around the single bonds. In this structure, the intramolecular hydrogen bond will be the strongest, and C⁴-N the most weakened, which could be largely responsible for the $O^2 \rightarrow N$ transfer of a proton and rupture of the C⁴-N bond, that is, the thermochromic properties of (II).

Assuming structure (II), it will be seen that the colored form is the diphenoquinone (VIII), formed by loss of morpholine.



Examination of the UV spectra of (II) in various solvents shows that the positions of the absorption maxima (Fig. 3a) are independent of the solvent, but chainging from nonpolar to polar solvents results in an increase in the intensity of the long-wavelength bands (at 393 and 500 nm). Raising the temperature of the solutions results in a reversible increase in the intensities of the long-wavelength bands (Fig. 3a).

(4)



Fig. 3. Absorption spectra (in heptane) of (II) ($c = 2.41 \cdot 10^{-4}$ mole/liter; cell thickness 1.00 cm) (a); (XI) ($c = 2.58 \cdot 10^{-4}$ mole/liter; cell thickness 1.00 cm) (b) at a temperature K of: 1) 299; 2) 313; 3) 323; 4) 333; 5) 343; 6) 353; 7) 368; (X) ($c = 1.76 \cdot 10^{-4}$ mole/liter; cell thickness 0.199 cm) at 295 K (8).

In order to examine its spectral characteristics, a sample of (VIII) was obtained as follows:





Fig. 4. The (X) molecule with ellipsoids of thermal vibration of the atoms (50% probability).



Fig. 5. Charge distribution in (VIII) (numerator) and (X) (denominator).

The phenol (VII) was obtained in high yield. Oxidation of this in benzene gave a dark red solution of the quinone (VIII), but this could not be isolated in the pure state as a result of its low stability.

The UV spectrum of the solution showed two long-wavelength bands, the absorption maxima and ratio of intensities of which were the same as for the thermochrome (II) (Fig. 3a).

The phenol (IX) was obtained by tert-butylating the phenol (VII). On oxidation, it gave the stable diphenoquinone (X), which on reaction with morpholine gave an analog of (II), namely 2,6-di(tert-butyl)-4-morpholino-4-[2-hydroxy-3,5-di(tert-butyl)phenyl]cyclo-hexa-2,5-dienone (XI).

The behavior of (XI) in solution was similar to that of (II), the color deepening considerably on heating. The positions of the absorptions in the UV spectrum of (XI) (Fig. 3b), and the changes on heating, were similar to those of (II) (Fig. 3a). However, even though the positions of the long-wavelength bands in the UV spectra of (X) (Fig. 3c) and



(XI) were nearly identical, their shapes and ratios of intensities differed markedly [1.35] for (X) and 1.89 for (XI)]. On diluting the solution of (XI), however, its long-wavelength bands became identical with those of (X).

It may be that the observed anomalies are due to the mode of reaction of the quinones (VIII) and (X) with morpholine being more complex than is shown in Scheme 4.

The structure of (X) was confirmed by x-ray diffraction. A general view of the molecule of (X) is shown in Fig. 4. The two cyclohexane rings, A and B, are linked by a double bond, $C^{1=}C^{1}$, and are rotated relative to each other by 11.5°. This structure results in strong steric interactions between rings A and B. Apparently, as a result of steric repulsion between $O^2 \dots C^6$ ', $C^6 \dots C^2$, and $H^6 \dots H^{21}$, the $C^{1=}C^{11}$ double bond is lengthened to 1.388 (4) Å, as compared with the value of 1.32 Å usual for this bond [7], the $C^{1-}C^2$ bond is lengthened to 1.501(4) Å as compared with the value for the analogous bond C^2-C^3 [1.467(5) Å], and the valence angles $C^{21}C^{11}C^1$ and $C^{11}C^{12}C^2$ are increased to 123.6 and 123.2°. Nevertheless, the intramolecular contacts $O^2 \dots C^6'$, $C^6 \dots C^{2'}$, and $H^6 \dots H^{2'}$ remain shortened at 2.86, 2.89, and 1.88 Å. The geometry and bond-length distribution in the cyclohexadiene ring A and the analogous ring in (II) are the same to within experimental error. The cyclohexadiene ring B in (X) is nonplanar, having the boat conformation with bending angles along $C^2 \dots C^6$ of 19° and along $C^3 \dots C^5$ of 4°. The C^{11} tert-butyl group, as in ring A, is in the most sterically favored position with respect to O^2 .

INDO/S calculation of the charge distribution in (VIII) and (X) (Fig. 5) shows that the most preferred electrophilic centers for the addition of morpholine are at C^1 and C^2 . The presence in the quinones (VIII) and (X) of electrophilic centers at C^2 [in (X)] and C^4 [in (VIII)] suggests that, in solution, in equilibrium with the thermochromes (II) and (XI), compounds (XII) and (XIII) may be present:

(6)



However, treatment of the spectra of (II) by the matrix ranking method [8] shows clearly that the long-wavelength absorption ($\lambda \ge 330$ nm) is due to a single absorbing component, which can only be the quinone (VIII). Consequently, addition of morpholine at the other electrophilic centers does not occur.

EXPERIMENTAL

IR spectra were obtained on a Specord IR-7 spectrophotometer, PMR spectra on a Tesla BS-567 spectrometer (internal standard hexamethyldisiloxane). UV spectra on a Specord M40, and mass spectra on a Finnigan 4021.

The residue after removal of the solvent from the mother liquors was dissolved in the minimum amount of a 1:1 mixture of chloroform and hexane, and chromatographed on a column of alumina. The first, yellow, fraction afforded [3,3',5,5'-tetra-(tert-buty1)-4,4'-di-phenoquinone, 15%, mp 243-245°C], and the second, reddish, fraction was collected. The solvent was removed, and the residue recrystallized from heptane or propan-2-ol to give a further 1.3 g of (II). Total yield 8.1 g (70.5\%), mp 167-170°C. IR spectrum (Nujol mull, v, cm⁻¹): 1673, 1650 (quinone), 1607, 1590 (Ar), 1250 (t-Bu). PMR spectrum (CDCl₃, δ , ppm): 1.23 s (18H, t-Bu), 2.76 t (4H, N-CH₂), 3.85 t (4H, O-CH₂), 6.81 s (2H, quinone), 6.86-7.26 m (4H, ArH), 11.7 s (1H, OH). Mass spectrum m/z (I, \%): 385.36 (24.78) [M + 2],

Atom	X	y.	Z.	Atom	X	Ŷ	Z
$ \begin{array}{c} ()^1 \\ ()^2 \\ ()^3 \\ ($	$\begin{array}{ }\\\hline\\6131(1)\\4296(1)\\9261(1)\\6050(1)\\8434(1)\\7951(1)\\6953(1)\\6273(1)\\6874(1)\\7874(1)\\8590(1)\\8590(1)\\8011(2)\\9825(2)\\8578(3)\\8484(1)\\7777(2)\\8651(2)\\9662(2)\\5447(2)\\5130(2)\\6739(2)\\7088(2)\\5130(2)\\6739(2)\\7088(2)\\5130(2)\\6739(2)\\7088(2)\\5130(2)\\6739(2)\\7088(2)\\5130(2)\\6739(2)\\7088(2)\\5130(2)\\6739(2)\\7088(2)\\5130(2)\\6739(2)\\7088(2)\\5130(2)\\6739(2)\\7088(2)\\5130(2)\\659(2)\\746($	$\begin{array}{c} 5374 (2)\\ 9056 (2)\\ 10404 (2)\\ 7559 (2)\\ 9768 (2)\\ 9768 (2)\\ 8105 (2)\\ 7508 (2)\\ 8355 (2)\\ 9987 (2)\\ 10662 (2)\\ 7176 (2)\\ 5477 (3)\\ 7286 (3)\\ 7790 (3)\\ 12294 (2)\\ 13021 (3)\\ 13360 (2)\\ 12213 (3)\\ 13360 (2)\\ 12213 (3)\\ 13360 (2)\\ 12213 (3)\\ 13360 (2)\\ 12213 (3)\\ 13360 (2)\\ 12213 (3)\\ 13360 (2)\\ 12213 (3)\\ 13360 (2)\\ 12213 (3)\\ 13360 (2)\\ 12213 (3)\\ 13360 (2)\\ 1223 (3)\\ 8426 (2)\\ 8791 (2)\\ 8895 (3)\\ 8426 (2)\\ 8791 (2)\\ 8895 (3)\\ 8428 (3)\\ 1058 (3)\\ 638 (3)\\ 638 (3)\\ 539 (3)\\ \end{array}$	$\begin{array}{ } & 4347 (2) \\ 3647 (1) \\ 1924 (3) \\ 3251 (1) \\ 2119 (2) \\ 1208 (2) \\ 1341 (2) \\ 2362 (2) \\ 3321 (2) \\ 3254 (2) \\ 3254 (2) \\ 119 (2) \\ -645 (2) \\ 779 (3) \\ -978 (3) \\ 4306 (2) \\ 5375 (2) \\ 3600 (2) \\ 5375 (2) \\ 3700 (2) \\ 3600 (2) \\ 5375 (2) \\ 3600 (2) \\ 5375 (2) \\ 3600 (2) \\ 5375 (2) \\ 3600 (2) \\ 5375 (2) \\ 3600 (2) \\ 5375 (2) \\ 3600 (2) \\ 5375 (2) \\ 3600 (2) \\ 5375 (2) \\ 3600 (2) \\ 5375 (2) \\ 3600 (2) \\ 5375 (2) \\ 3600 (2) \\ 5375 (2) \\ 3600 (2) \\ 5375 (2) \\ 3600 (2) \\ 5375 (2) \\ 3600 (2) \\ 5375 (2) \\ 3600 (2) \\ 5375 (2) \\ 3600 (2) \\ 5375$	H ⁹ H ¹⁰ H ¹¹² H ¹¹³ H ¹¹⁴ H ¹¹⁵ H ¹¹⁶ H ¹¹⁷ H ¹⁸ H ²⁷ H ¹³ H ¹⁶ H ¹⁶ H ¹⁶ H ¹⁶ H ¹² H ¹⁶ H ¹⁶ H ¹⁷ H ¹⁸ H ¹⁶ H ¹⁷ H ¹⁸ H ¹⁶ H ¹⁷ H ¹⁸ H ¹⁸ H ¹⁷ H ¹⁸ H ¹⁷ H ¹⁸ H ¹⁸ H ¹⁸ H ¹⁷ H ¹⁸ H ¹⁸ H ¹⁸ H ¹⁸ H ¹⁸ H ¹⁷ H ¹⁸ H	$\begin{array}{c} 977 (2) \\ 906 (4) \\ 691 (3) \\ 796 (3) \\ 1003 (4) \\ 467 (2) \\ 462 (3) \\ 749 (3) \\ 746 (3) \\ 496 (4) \\ 242 (2) \\ 218 (2) \\ 384 (3) \\ 559 (2) \\ 798 (2) \\ 1027 (4) \\ 899 (3) \\ 773 (2) \\ 907 (3) \\ 956 (3) \\ 590 (2) \\ 466 (3) \\ 500 (2) \\ 466 (3) \\ 500 (2) \\ 466 (3) \\ 500 (2) \\ 466 (3) \\ 500 (2) \\ 466 (3) \\ 500 (2) \\ 466 (3) \\ 500 (2) \\ 466 (3) \\ 500 (2) \\ 466 (3) \\ 500 (2) \\ 466 (3) \\ 500 (2) \\ 466 (3) \\ 500 (2) \\ 466 (3) \\ 500 (2) \\ 466 (3) \\ 500 (2) \\ 466 (3) \\ 500 (2) \\ 466 (3) \\ 500 (2) \\ 466 (3) \\ 500 (2) \\ 466 (3) \\ 500 (2) \\ 466 (3) \\ 500 (2) \\ 466 (3) \\ 500 (2)$	$\begin{array}{c} 679 \ (3) \\ 885 \ (5) \\ 1313 \ (4) \\ 1348 \ (4) \\ 1326 \ (5) \\ 590 \ (3) \\ 606 \ (4) \\ 699 \ (4) \\ 880 \ (4) \\ 872 \ (5) \\ 910 \ (3) \\ 863 \ (3) \\ 811 \ (4) \\ 786 \ (3) \\ 502 \ (3) \\ 664 \ (5) \\ 710 \ (4) \\ 1242 \ (3) \\ 1441 \ (4) \\ 1154 \ (5) \\ 520 \ (3) \\ 404 \ (5) \\ 766 \ (3) \\ 694 \ (3) \\ 477 \ (4) \\ 841 \ (6) \\ 785 \ (5) \\ 1410 \ (5) \\ 14296 \ (4) \end{array}$	$\begin{array}{c} 142 (2) \\ -50 (4) \\ 485 (3) \\ 308 (3) \\ 574 (4) \\ 167 (3) \\ 409 (4) \\ 581 (3) \\ 400 (4) \\ 226 (3) \\ -20 (3) \\ -145 (4) \\ -31 (2) \\ 11 (3) \\ -5 (4) \\ -176 (3) \\ 600 (3) \\ 430 (3) \\ 559 (4) \\ 171 (3) \\ 278 (4) \\ 575 (3) \\ 363 (3) \\ -130 (3) \\ 144 (5) \\ -143 (4) \\ 600 (5) \\ 282 (3) \end{array}$
				1114"	1017(2)	1167 (3)	415(3)

TABLE 1. Coordinates of Nonhydrogen ($\times 10^4$) and Hydrogen Atoms ($\times 10^3$) in (II)

				,			
Atom	X	Y	Z	Atom	X	Y	Z
$ \begin{array}{c} O^2 \\ O^3^2 \\ C^1 \\ C^2 \\ C^3 \end{array} $	-770(2) 4430(2) 72(2) -729(2) 4522(2)	-2598(2) 0119(3) -136(3) -1342(3)	2256 (3) 2397 (3) 1913 (3) 2445 (3)	H14 H16 H12' H16'	-236 (2) 13 (2) 157 (3) 97 (3)	55(3) 184(3) 185(4) -220(3)	316 (3) 104 (3) 87 (4) 273 (3)
C^{4} C^{5} C^{6} $C^{1'}$ $C^{2'}$	$ \begin{array}{c c} -1523(2) \\ -1704(2) \\ -1146(2) \\ -283(2) \\ 1133(2) \\ 1906(2) \end{array} $	$ \begin{array}{c} -972(3) \\ 317(3) \\ 1344(3) \\ 1110(3) \\ -199(3) \\ 992(3) \end{array} $	3081 (3) 2822 (3) 1995 (3) 1575 (3) 1888 (3) 1406 (3)	H ⁸ H ⁸ " H ⁹ 11 ⁹ '	$ \begin{array}{r} -131(3) \\ 2(3) \\ -116(3) \\ -164(3) \\ -37(3) \end{array} $	449 (4) 400 (4) 309 (4) 305 (4) 393 (4)	55 (4) 134 (4) - 10 (4) 367 (4) 340 (4)
C ³ C ⁴ C ⁵ C ⁶ C ⁷	$ \begin{array}{r} 2998(2) \\ 3428(3) \\ 2635(2) \\ 1564(2) \\ -1494(2) \end{array} $	$ \begin{array}{c} 1126(3) \\ -3(3) \\ -1293(3) \\ -1340(3) \\ 2710(3) \end{array} $	1523 (3) 2175 (3) 2583 (3) 2433 (3) 1733 (3)	H ^{9"} H ¹⁰ H ¹⁰ ' H ¹⁰ "	$ \begin{array}{r} -149(3) \\ -299(4) \\ -299(3) \\ -315(3) \\ 452(4) \end{array} $	441 (4) 177 (5) 325 (4) 177 (4) -299 (5)	$ \begin{array}{r} 282(4) \\ 40(5) \\ 93(4) \\ 192(4) \\ 560(4) \end{array} $
C^{b} C^{a} C^{1a} C^{12} C^{13}	$ \begin{array}{c c} -861(3) \\ -1234(4) \\ -2717(3) \\ -2081(2) \\ -1187(3) \\ 2020(2) \end{array} $	$ \begin{array}{r} 3684(4) \\ 3557(4) \\ 2318(4) \\ -2020(3) \\ -2444(4) \\ 3364(3) \end{array} $	818(4) 2974(4) 1188(4) 4013(3) 4953(4) 2314(4)	H ¹² ' H ¹² ' H ¹³ H ¹³ '	$ \begin{array}{r} -132(4) \\ -058(3) \\ -85(3) \\ -357(3) \\ -327(5) \end{array} $	$\begin{array}{r} -233(3) \\ -151(4) \\ -296(4) \\ -307(4) \\ -402(6) \end{array}$	538 (4) 538 (4) 440 (3) 275 (4) 385 (6)
C ¹⁴ C ¹⁵ C ¹⁶ C ¹⁷ C ¹⁸	$ \begin{array}{c c} -2920(3) \\ -2730(4) \\ 3800(2) \\ 4312(3) \\ 4698(3) \\ 3203(3) \end{array} $	$ \begin{array}{c c} -3301(3) \\ -1311(4) \\ 2408(3) \\ 1895(3) \\ 3219(3) \\ 3460(3) \end{array} $	$\begin{array}{c} 3311(4) \\ 4716(4) \\ 1024(3) \\ 45(3) \\ 2111(4) \\ 400(4) \end{array}$	H ¹³ " H ¹⁴ H ¹⁴ " H ¹⁴ "	$\begin{array}{r} -270(4) \\ -343(3) \\ -215(3) \\ -304(4) \\ 367(3) \end{array}$	$ \begin{array}{r} -394(5) \\ -116(4) \\ -50(4) \\ -193(5) \\ 136(4) \end{array} $	$ \begin{array}{r} 276(5) \\ 402(4) \\ 532(4) \\ 533(4) \\ -78(4) \end{array} $
$\begin{array}{c} C^{19} \\ C^{20} \\ C^{21} \\ C^{22} \\ H^{20} \end{array}$	$ \begin{array}{c c} 3082(3) \\ 3082(2) \\ 3860(3) \\ 3730(3) \\ 2115(3) \\ 457(3) \end{array} $	$\begin{vmatrix} -2472 (3) \\ -1927 (4) \\ -3028 (4) \\ -3752 (4) \\ -106 (4) \end{vmatrix}$	$\begin{vmatrix} 3242(3) \\ 4492(4) \\ 2409(4) \\ 3524(5) \\ 443(4) \end{vmatrix}$	H ¹⁶ H ¹⁶ H ¹⁷ H ¹⁷	470 (4) 474 (3) 451 (3) 518 (3)	$\begin{array}{c} 130(4) \\ 267(4) \\ 123(4) \\ 360(4) \\ 258(3) \end{array}$	$ \begin{array}{c} -45(4) \\ 46(3) \\ 287(4) \\ 259(3) \end{array} $
H ²⁰ ' H ²⁰ " H ²¹ H ²¹	353 (5) 423 (4) 415 (4)	-165(6) -270(6) -384(6) 222(5)	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	H ^{17"} H ¹⁸ H ¹⁸ ' H ^{18"}	526 (3) 281 (3) 260 (3) 372 (3)	416(5) 384(4) 292(4) 422(4)	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$
11	442(4)	222(3)	200(0)	H ^{21"} H ²² H ²²	310(4) 180(3) 251(5)	-350(5) -405(4) -446(7)	175 (5) 247 (4) 383 (6)
	-			H ²²	233(6)	-328(8)	430(7)

TABLE 2. Coordinates of Nonhydrogen ($\times 10^4$) and Hydrogen Atoms ($\times 10^3$) in (X)

384.34 (100.00) [M + 1], 383.30 (37.82) M⁺. Found, %: C 75.30, H 8.30, N 3.23. $C_{24}H_{33}NO_{3}$. Calculated, %: C 75.16, H 8.67, N 3.65.

 $\frac{2,4'-\text{Dihydroxy-3'},5'-\text{di-(tert-butyl)diphenyl (VII).}}{(0.01 \text{ mole}) \text{ of (II) in 70 ml of alcohol and 20 ml of water was added 3.15 g (0.015 mole) of Na_2S_2O_4·2H_2O. When the dark red solution had become colorless, it was cooled and poured onto 100 g of ice. The oil which separated crystallized on rubbing to give 1.85 g (62%) of (VII), as colorless crystals mp 121-123°C (hexane or methanol). IR spectrum (v, cm⁻¹, Nujol mull): 3620, 3607, 3447 (OH). PMR spectrum (CD_2Cl_2, \delta, ppm); 1.41 s (18H, t-Bu), 5.54 s (1H, OH_a), 6.77 s (1H, OH_b), 6.87-7.37 m (6H, ArH). Found, %: C 80.52, H 8.78. C_{20}H_{26}O_2. Calculated, %: C 80.49, H. 8.78.$

2,4'-Dihydroxy-3,3',5,5'-tetra-(tert-butyl)diphenyl (IX). A solution of 2.38 g (0.008 mole) of (VIII) in 100 ml of glacial acetic acid was heated with 25 ml of tert-butanol and 15 ml of concentrated sulfuric acid for 15 h at 50°C. The mixture was diluted with 350 ml of ice water, the oil separated, and the aqueous layer extracted with hexane (2 × 15 ml) and the solvent removed. The residue was combined with the main portion of the product, dissolved in the minimum amount of a 2:1 mixture of hexane and chloroform, and chromatographed on a column of alumina, the first fraction being collected. Removal of the solvent gave 1.36 g (41.5%) of crude product. Yellow crystals, mp 171-173°C (from acetonitrile); IR spectrum (Nujol mull, v, cm⁻¹): 3640 (OH_a), 3530 (OH), 1250 (t-Bu). PMR spectrum (CDCl₃, δ , ppm): 1.35 s (9H, t-Bu), 1.48 s (9H, t-Bu), 1.49 s (18H, t-Bu), 5.38 s (1H, OH_a), 5.50 s (1H, OH_b), 7.21-7.44 (4H, ArH). Found, %: C 81.84, H 10.05. C₂₈H₄₂O. Calculated, %: C 81.95, H 10.24.

3,3',5,5'-Tetra-(tert-butyl)-2,4'-diphenoquinone (X). A solution of 3.5 g of K₃Fe(CN)₆ and 2.0 g of KOH in 30 ml of water was added to a solution of 0.82 g (0.002 mole) of (IX) in

7 ml of benzene, and the mixture shaken vigorously a few times. The dark red benzene layer was separated, and the solvent removed to give 0.53 g (65%) of product. Dark red-brown crystals, mp 176-178°C (from 2-propanol). IR spectrum (Nujol mull, v, cm⁻¹): 1640, 1630, 1615 (quinone), 1250 (t-Bu). PMR spectrum (CDCl₃, δ , ppm): 1.27 s (9H, t-Bu), 1.32 s (9H, t-Bu), 1.33 s (9H, t-Bu), 1.36 s (9H, t-Bu), 7.17 s (2H, H_a), 7.65 d (1H, H_b, J⁴ = 3 Hz), 8.13 d (1H, H_c, J⁴ = 3 Hz). Mass spectrum, m/z (I, %): 410.54 (6.01) [M + 2], 409.54 (10.79) [M + 1], 408.42 (5.08) M⁺. Found, %: C 82.16, H 9.99. C₂₈H₄₀O₂. Calculated, %: C 82.30, H 9.87.

 $\frac{2,6-\text{Di-tert-butyl-4-morpholino-4-[2-hydroxy-3,5-di(tert-butyl)phenyl]cyclohexa-2,5-}{\text{dienone (XI).}}$ To a suspension of 0.2 g (0.0005 mole) of (X) in 2 ml of methanol was added 2 drops of morpholine, and the mixture boiled until the quinone had dissolved. The deep red solution was cooled, and the colorless crystals which separated were filtered off and washed with 1 ml of cold methanol to give 0.18 g (72.6%) of colorless crystals, mp 157-160°C, turning pink on exposure to light. IR spectrum (Nujol mull, v, cm⁻¹): 3394 (OH), 1667, 1647, 1620 (quinone), 1593 (Ar), 1260 (t-Bu). PMR spectrum (C₆D₆, δ , ppm): 1.35 s (9H, t-Bu), 1.44 s (18H, t-Bu), 1.79 s (9H, t-Bu), 2.61 t (4H, N-CH₂), 3.57 t (4H, O-CH₂), 7.05 s (2H, quinone), 7.20 s (1H, ArH), 7.65 s, (1H, ArH), 12.20 s (1H, OH). Found, %: C 77.81, H 10.08, N 3.04. C₃₂H₄₉NO₃. Calculated, %: C 77.53, H 9.96, N 2.82.

<u>X-Ray Examination of (II) and (X).</u> The crystals of (II) and (X) were triclinic. (II), $C_{24}H_{33}NO_3$, a = 11.998(9), b = 9.718(3), c = 10.942(10) Å, $\alpha = 114.9(2)$, $\beta = 98.6(3)$, $\gamma = 96.2(2)^{\circ}$, V = 1123 Å³, Z = 2, $d_{calc} = 1.14$ g/cm³, space group PI. (X): $C_{28}H_{40}O_2$, a = 12.846(3), b = 9.767(3), c = 10.837(6) Å, $\alpha = 88.12(3)$, $\beta = 101.29(3)$, $\gamma = 107.13(3)^{\circ}$, V = 1274 Å³, Z = 2, $d_{calc} = 1.07$ g/cm³, space group PI. The experimental data for structural calculation, 2850 (F) for (II) and 1660 (F) for (X), were obtained on an RÉD-4 automatic diffractometer for CuK_{α} irradiation. Absorption was neglected. The coordinates of the nonhydrogen atoms were determined directly using the Rontgen-75 program, and refined in full-matrix least squares anisotropic approximation, and the hydrogen atoms were all located from the different synthesis of electron density. The final cycle of refinement gave the coordinates of the nonhydrogen atoms in anisotropic, and of the hydrogens in isotropic approximation to R = 0.06 (II) and 0.05 (X). The atom coordinates for (II) and (X) are given in Tables 1 and 2, respectively.

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