Oxidation of Alkoxyphenols. Part 26.[1] The Trimer of a 2,2'-Diphenoquinone (1,1'-Bicyclohexa-3,5-dienylidene-2,2'-dione)

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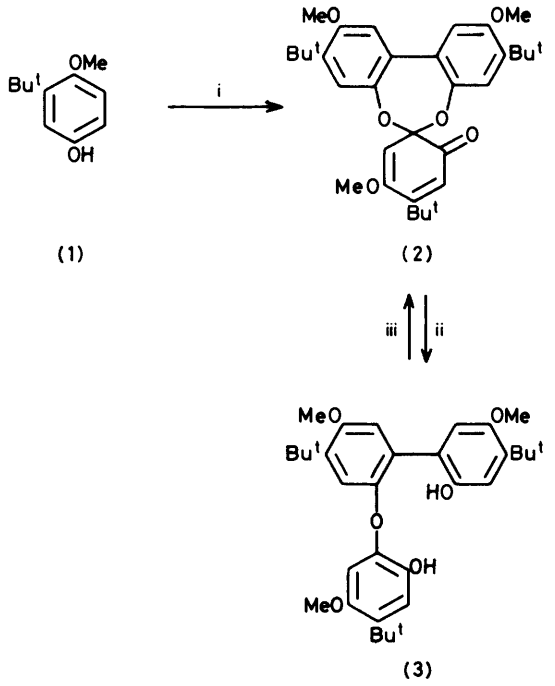
The blue material produced in the oxidation of 4-methoxy-3-t-butylphenol, formerly described as an intermediate in the formation of the dibenzo[*d,f*][1,3]dioxepin oxidation product, is shown to be 5,5'-dimethoxy-4,4'-di-t-butyl-2,2'-diphenoquinone. This quinone spontaneously condenses to a colourless trimer which, in solution in polar solvents, is shown to be in equilibrium with free radicals derived from the monomer and a dimer; that from the former regenerates the quinone. The crystal structure of the dimer has been determined as 1'-(2-hydroxy-5-methoxy-4-t-butylphenyl)-4a',5,7'-trimethoxy-4,4'-6'-tri-t-butylspiro(cyclohexa-3,5-diene-1,9'-xanthen)-2,2'(4'a*H*)-dione.

In the first paper [2] of this series it was shown that the minor component (1) of the antioxidant butylated hydroxyanisole (BHA) (1) was oxidised by alkaline ferricyanide to the dioxepin (2) in yields of up to 60%. The oxidation appeared to proceed through a blue intermediate which was precipitated if the oxidation was performed in the absence of an organic solvent. Moreover, reduction of the dioxepin to the diol (3) and reoxidation of the latter back to the dioxepin appeared to involve the same intermediate (Scheme 1). This behaviour was later shown to be quite general for 4-alkoxyphenols which contain a free 2-position and an alkyl substituent at C-5 or C-6, provided that the substituent at C-6 is not a tertiary alkyl group.[3] Investigation of the structure of the blue material was severely limited by the fact that the rate of loss of colour followed second-order kinetics, with the result that the compound could neither be recrystallised nor examined by C.W. n.m.r. spectrometry. The acquisition of Fourier transform (F.T.) n.m.r. has allowed us to re-examine the oxidation of the phenol (1), using solutions of sufficient dilution to be relatively stable, and these results are reported here.

When a freshly oxidised sample of the phenol (1) was examined in this way, within three minutes of preparation it was immediately apparent that two major sets of resonances were present (Figure 1a); one was identical with that of the dioxepin (2) and the other with that of a freshly prepared sample of the diphenoquinone (4), which has olefinic resonances at δ 6.05 and 8.28. The ratio of these two components varied with the method of preparation. The highest initial ratio of diphenoquinone to dioxepin observed was 7 : 3, obtained by rapid shaking of a dilute solution of the phenol in carbon tetrachloride with an excess of oxidant; in preparative work, addition of the phenol to the oxidant in portions, shaking vigorously but briefly each time, gave yields of dioxepin of up to 78%.

The colour and n.m.r. spectrum of the oxidation products changed with time, the colour fading to pale yellow, and the n.m.r. spectrum (Figure 1b) was apparently simplified to that of the dioxepin alone. The rate of decrease of the resonances at δ 6.05 and 8.28 confirmed the second-order kinetics reported earlier,[2] except for a very brief initial period when the rate was greater, and the concentration of dioxepin increased. Reoxidation of the reduced dioxepin (3) also gave, by F.T. n.m.r., a comparable mixture of the dioxepin (3) and the diphenoquinone (4); the blue colour faded after some hours, apparently leaving only the dioxepin. This bond cleavage (Scheme 2) is the reversal of C–O oxidative coupling, and may well proceed through the keto-tautomer (5) rather than involve a σ-radical of presumably higher energy.

As it appeared from these and earlier observations that the blue material, now identified as the diphenoquinone (4), may



Scheme 1. *Reagents*: i, $K_3Fe(CN)_6$, KOH; ii, $NaBH_4$; iii, $K_3Fe(CN)_6$, KOH

in some way undergo a redistribution reaction to the dioxepin (2), an experiment was designed that would provide unequivocal evidence for or against this Accordingly, the deuterium labelled dioxepin (7) was prepared as shown in Scheme 3. This was reduced to the diol (8). On reoxidation with alkaline ferricyanide this diol gave a blue solution which was monitored by F.T. n.m.r. The initial spectrum corresponded to a mixture of the diphenoquinone (4) and the dioxepin (7), and when the signals of the diphenoquinone had disappeared the spectrum of the dioxepin showed no trace of a resonance at the position where a cyclohexadienone methoxy-group would be expected. The diphenoquinone therefore does not rearrange to the dioxepin.

As it now became necessary to account for the disappearance of the diphenoquinone in some other way, its reactions in solution were re-examined. Previous work [4] had described the formation of the quinones (9) and (10) when the diphenoquinone was set aside in light petroleum in the dark. On repeating this experiment a different result was obtained. The blue colour of the solution slowly faded after several days,

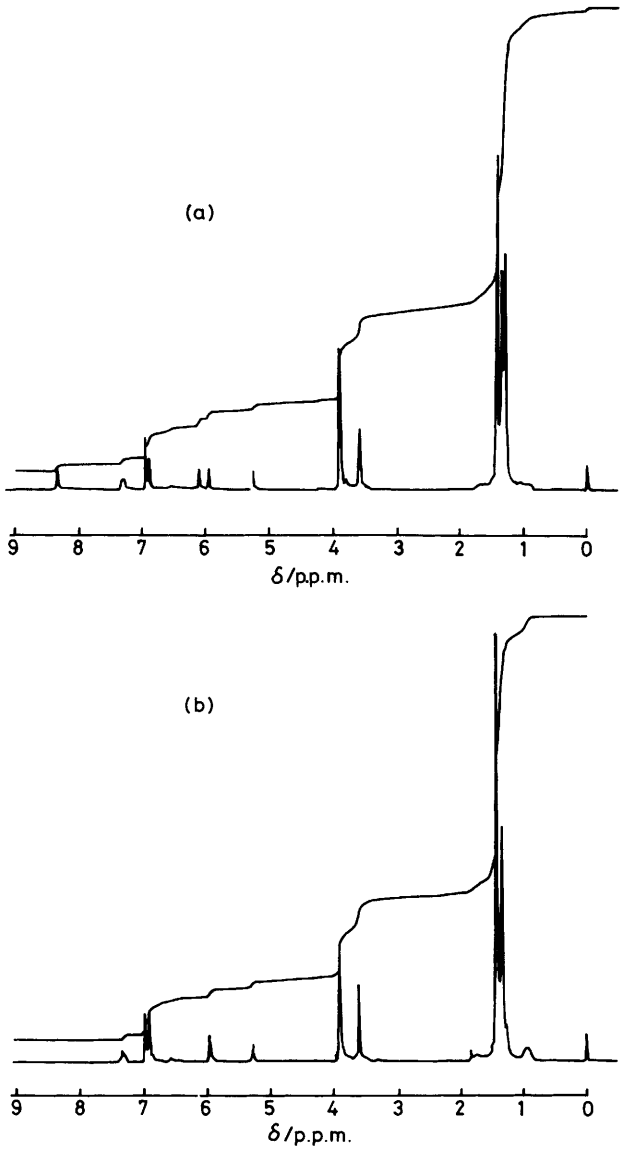
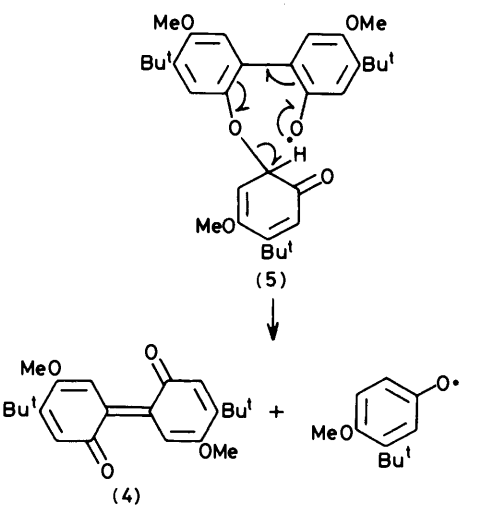
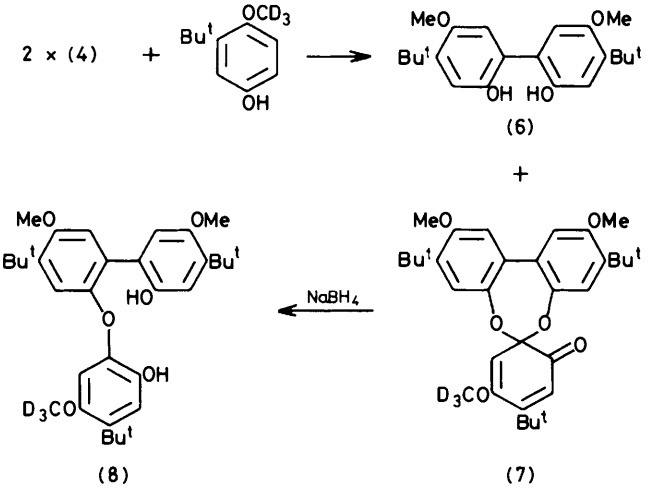


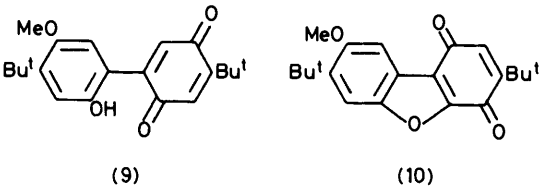
Figure 1. (a) 80 MHz F.T. n.m.r. spectrum of freshly oxidised 4-methoxy-3-t-butylphenol in CCl_4 containing 10% C_6D_6. (b) The same sample after fading of the blue colour



Scheme 2.



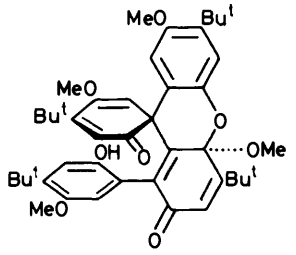
Scheme 3.



and on allowing the solvent to evaporate a colourless amorphous material (11) was obtained, which was purified by washing with and reprecipitation from light petroleum. This material gave a blue solution when heated in light petroleum. By contrast, a solution of the diphenoquinone (4) in light petroleum, shaken with a trace of hydrochloric acid, afforded an almost quantitative yield of the hydroxyphenylquinone (9). The demethylation of (4) to (9) therefore depends upon and is very susceptible to acid catalysis.

The melting point of the amorphous material (11) did not rise on successive reprecipitations, and this fact together with the sharpness of the signals in its n.m.r. spectrum made a polymeric structure unlikely. This spectrum revealed the presence of six methoxy and six t-butyl groups, as well as twelve other protons, one of which exchanged with D_2O. As there are so many separate resonances in the spectrum of this material, it is difficult to detect it in small concentrations among other components. Furthermore, the haste necessary in oxidations of the phenol (1) for n.m.r. observation of the unstable diphenoquinone undoubtedly resulted in the presence of paramagnetic material with broadened peaks. However, careful examination of the n.m.r. spectra of the faded oxidation mixtures (Figure 1b) always revealed slight increases in the integral where the amorphous material would be expected to show signals. We therefore conclude that, once the formation of dioxepin is complete, the disappearance of the blue diphenoquinone from oxidised solutions of (1) or (3) is explained by the formation of the amorphous product (11).

The n.m.r. spectrum of this material (11) suggested that it was derived from three units of the diphenoquinone (4), and this trimeric structure was supported by the mass spectrum which showed a weak molecular ion at 1 068 mass units; the main fragmentation however was seen from 712 units and below. Gentle hydrolysis of (11) with one drop of hydrochloric



(12)

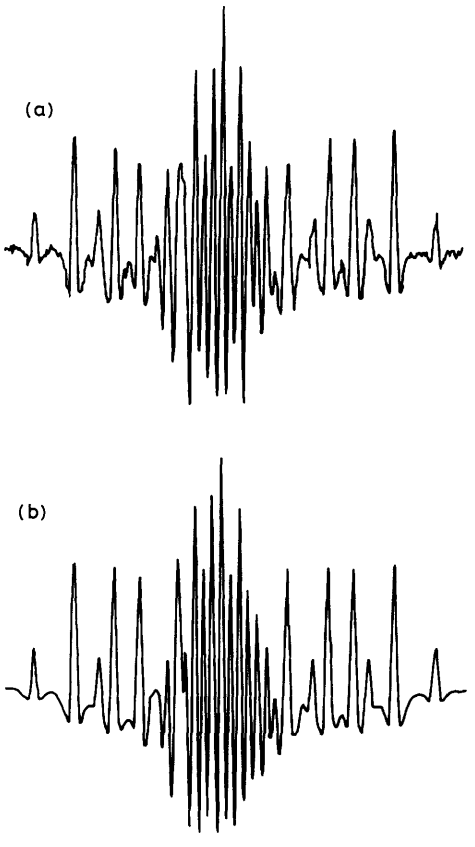


Figure 2. (a) Second-derivative e.s.r. spectrum of compound (11) in chloroform. (b) Computer simulated spectrum

acid in methanol immediately gave a yellow solution which slowly darkened and produced at least seven fractions on silica t.l.c. The two most prominent fractions were shown to be the purple hydroxyphenylquinone (9) and a yellow material (12). This material, as well as the biphenyldiol (6), could also be obtained as the major product from the brief reduction of (11) with sodium borohydride.

The hydroxyphenylquinone (9) is the acid-hydrolysis product of the quinone (4), and the biphenyldiol (6) is the reduction product of (4). These facts imply that the diphenoquinone (4) is the source of the blue colour when (11) is dissolved. This conclusion was supported by the exact match between 350 and 800 nm of the visible absorption spectra of ethanol solutions of (11) and the diphenoquinone (4). The extinction coefficient showed that in this solvent a dilute solution of (11) is dissociated to the extent of 35%.

The key to the structure of the amorphous compound (11) now appeared to lie in the yellow compound (12). This was

Table 1. E.s.r. splitting constants of the radicals observed on dissolving the trimer (11) in chloroform at 20 °C

Wider signal	a_H (mT)
doublet	1.08
doublet	0.331
quartet	0.203
$g = 2.0037$	
Narrower signal	
triplet	0.140
septet	0.089
doublet	0.046
$g = 2.0042$	

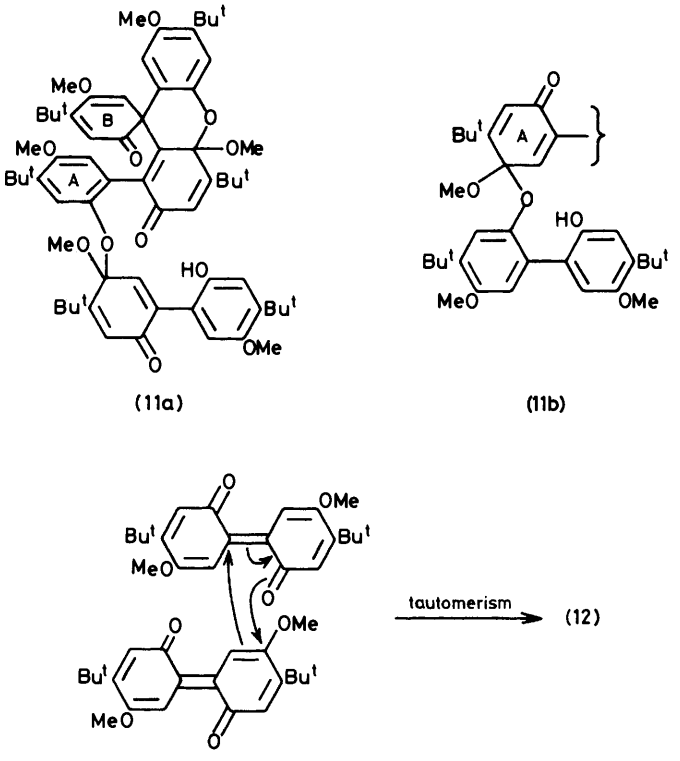
shown by n.m.r. to contain four t-butyl and four methoxy-groups, one proton that exchanged with D_2O, and seven other protons. Although we were unable to improve the yield of (12) by varying the conditions of hydrolysis, addition of phenol (1) to a solution of (11) in dichloromethane was found to give (12) in good yield, the other product being the biphenyldiol (6) which could be removed by extraction with base. Crystallographic analysis of compound (12) (see below) showed that it was a dimer of the diphenoquinone (4).

To test the reversibility of the dissociation of (11), the dimer (12) was dissolved in deuteriochloroform and a F.T. n.m.r. spectrum was recorded. A small excess of the diphenoquinone (4) was then added and the solution was re-examined by n.m.r. After 2 h when the blue colour had become faint, a good spectrum identical with that of (11) was obtained, and the spectrum of (12) was no longer visible.

It was now necessary to establish the attachment of the third diphenoquinone unit in such a way that facile dissociation and recombination can occur, and this was revealed by e.s.r. spectrometry. When dissolved in carbon tetrachloride, compound (11) gives a pale blue solution which becomes more intensely coloured on warming. At 60 °C this solution gave an e.s.r. signal of moderate strength. With the more polar chloroform as the solvent the colour is dark blue at room temperature, and a good e.s.r. signal (Figure 2) was obtained without heating. This spectrum is clearly that of two radicals of slightly different *g*-value. The wider component, a doublet of quartets of quartets, with the splitting constants shown in Table 1 is compatible with the phenoxy-radical derived from compound (12). This spectrum was obtained as a strong signal when a solution of (12) in chloroform was shaken with silver oxide. The narrower signal (Table 1) was similarly identified as being that of the mono-radical of the biphenyldiol (6).[5] Clearly, once this radical is produced, disproportionation can generate the diphenoquinone (4).

The formation of cyclohexadienone acetals by the oxidative coupling of phenols is known to be an easily reversible reaction, such compounds dissociating spontaneously in solution to phenoxy-radicals.[6,7] Combination of the diphenoquinone (4) with its dimer (12) in this way could give rise to the two alternative structures (11a) and (11b), which have a single phenolic hydroxy-group as required by the n.m.r. spectrum of the trimer (11).

It is difficult to decide between these structures on spectroscopic evidence. If the unusually high-field chemical shift of one of the ring protons at δ 3.95 is taken to indicate that attachment of the third diphenoquinone twists the formerly phenolic ring A so that a proton is held in the shielding zone of ring B, which appears to be the case from molecular models, then structure (11a) is supported. A firm decision between these structures seems possible, nevertheless, based



Scheme 4.

on the products of acid hydrolysis. The upper, dimeric portion of (11b) contains three methoxy-groups that should be acid labile, while the corresponding portion of (11a) contains only two. Severe acid hydrolysis of (11) gave material that was shown by n.m.r. to have a dimeric structure and to have lost only two methoxy-groups, thereby supporting structure (11a). Moreover, the results of mild acid hydrolysis also support structure (11a). Thus, on shaking a solution of (11) in dichloromethane with one drop of hydrochloric acid, the blue colour is seen to fade within the first one or two seconds. The purple colour of the hydroxyphenylquinone (9) then develops during the next few minutes. If one assumes that protonation of the acetal oxygen also occurs within the first few seconds, and as very little prior dissociation to the diphenoquinone would have occurred in this solvent, it can be concluded that most of the hydroxyphenylquinone (9) comes from the undissociated compound (11). If its structure were as shown in (11b), hydrolysis would produce the biphenyldiol (6) rather than the quinone (9).

Having established a free radical process for the formation of (11a) from (4) and (12), we have now to consider how two molecules of the diphenoquinone (4) dimerise to (12).

If the quinone (4) is regarded as an *ortho*-quinone methide there appears to be ample precedent in the literature [8,9] for its dimerization by the hetero Diels–Alder pathway shown in Scheme 4. The driving force for this dimerization must be the gain in resonance stability acquired by the formation of two aromatic rings. Similarly, the formation of the trimer (11a) involves formation of another aromatic ring, but the ready dissociation of this compound suggests that the increase in stability is here only marginal.

Experimental

M.p.s were recorded, uncorrected, using a Kofler hot-stage. N.m.r. spectra were obtained using Hitachi Perkin-Elmer R-24B, and F.T. n.m.r. using Bruker WP80 instruments. With the latter, where carbon tetrachloride is indicated, 10% [$^2H_6$]benzene was used as instrument lock. Mass spectra were recorded using a Hewlett Packard 5986 mass spectrometer and e.s.r. spectra using a Varian Associates V4500 spectrometer. Analyses were performed by the Australian Microanalytical Service. Light petroleum had b.p. 60—65 °C.

Preparation of 4-*Deuteriomethoxy*-3-*t*-*butylphenol*.—It was found that the literature yield [10] of 4-benzyloxy-2-t-butylphenol, a useful compound in the preparation of unhindered 4-alkoxyphenols such as 4-methoxy-3-t-butylphenol (1), could be considerably increased by using a two-phase system as follows.

A solution of t-butylhydroquinone (16.6 g) in methanol (50 ml) was stirred under nitrogen with benzyl bromide (17.1 g) in hexane (100 ml) and diethyl ether (50 ml). Sodium hydroxide (4.4 g) in water (40 ml) was added dropwise and the mixture was stirred overnight and then refluxed for 2 h. After separation, the upper layer was washed with water and evaporated. The product, m.p. 88 °C (18.4 g) crystallized from hexane, was used without further purification for methylation. Recrystallization from methanol–water gave white crystals, m.p. 90—91 °C (lit.,[10] 91—92 °C).

A solution of 4-benzyloxy-2-t-butylphenol (1.3 g) in dimethylformamide (8 ml) was stirred at 40 °C with deuteriodomethane (2 g) and potassium carbonate (2 g) for 4 h. Water was added and the mixture was extracted with hexane to yield, on evaporation, 4-*benzyloxy*-1-*deuteriomethoxy*-2-*t*-*butylbenzene* (0.45 g), m.p. 58—59 °C; δ (CCl_4) 1.32 (Bu^t), 4.83 (CH_2), 5.5—5.8 (3 ArH), and 7.2 (5 ArH); M^+ 273. [An undeuteriated sample prepared similarly had m.p. 59—60 °C after recrystallization, and an additional n.m.r. signal at δ 3.70 (OMe) (Found: C, 80.05; H, 8.5. $C_{18}H_{22}O_2$ requires C, 80.0; H, 8.2%; M^+, 270)].

A solution of 4-benzyloxy-1-deuteriomethoxy-2-t-butylbenzene (0.24 g) in ethanol was hydrogenated at 1 atmos. over Pd–C. The filtered solution was evaporated to an oil which crystallized from light petroleum giving 4-*deuteriomethoxy*-3-*t*-*butylphenol* (0.1 g), m.p. 60—62 °C, δ ($CDCl_3$) 1.34 (Bu^t), 4.3 (OH), and 6.52—6.82 (3 ArH), identical with the known undeuteriated phenol (lit., m.p. 62—64 °C) except that δ 3.78 (OMe) was absent; M^+ 183.

Preparation of 5-*Deuteriomethoxy*-2′,10′-*dimethoxy*-3′,4,9′-*tri*-*t*-*butylspiro*(*cyclohexa*-3,5-*diene*-1,6′-*dibenzo*[d,f][1,3]*dioxepin*)-2-*one* (7).—A solution of 5,5′-dimethoxy-4,4′-di-t-butylbiphenyl-2,2′-diol (6) (0.1 g) in hexane (200 ml) was vigorously shaken for 15 s with a solution of potassium ferricyanide (1 g) and sodium hydroxide (0.5 g) in water (15 ml). Half of a solution of 4-deuteriomethoxy-3-t-butylphenol (0.05 g) in hexane (50 ml) was then added and stirred gently into the upper layer. After 10 min, the vessel was vigorously shaken again and half the remaining phenol solution was added as before. After a further 20 min, the vessel was again shaken and the remainder of the phenol solution was added. After 30 min, the vessel was again shaken. The upper layer was separated, washed once with water and evaporated under reduced pressure. The *product* (0.08 g), crystallized from light petroleum had m.p. 203—206 °C, δ (CCl_4) 1.32, 1.39 (2) (Bu^t), 3.87 (2 OMe), 5.21, 5.89 (vinyl H), 6.84, and 6.88 (ArH), identical with the known undeuteriated dioxepin [2] (lit., m.p. 209—210 °C) except that the vinylic methoxy absorbance, δ 3.58, was absent, M^+ 537.

Reduction and Reoxidation of the Deuteriated Dioxepin (7).—A solution of the dioxepin (7) (20 mg) in methanol (10 ml) was stirred with an excess of sodium borohydride until

colourless. The solution was acidified with dilute hydrochloric acid (10 ml) and extracted into carbon tetrachloride, washed with water and evaporated to a glass. N.m.r. showed only the *trimeric diol* (8), δ (CCl_4) 1.29, 1.32, 1.34 (Bu^t), 3.70, 3.80 (OMe), 5.3, 5.8 (OH), 6.34, 6.58, 6.77 (3), and 6.87 (ArH), identical with the known undeuteriated diol [2] except for the absence of the signal at δ 3.62 (OMe). This material was shaken in carbon tetrachloride (2 ml) with a solution of potassium ferricyanide (100 mg) and sodium hydroxide (100 mg) in water (2 ml) and examined by F.T. n.m.r. at intervals. Initially the spectrum was that of a mixture of the deuteriated dioxepin (7) and 5,5′-dimethoxy-4,4′-di-t-butyl-2,2′-diphenoquinone (4), δ (CCl_4) 1.30 (2 Bu^t), 3.89 (2 OMe), 6.05, and 8.28 (vinyl H). No trace of the vinylic methoxy absorbance, δ 3.58, arose as the signals due to the diphenoquinone (4) declined.

Preparation of the Trimer (11) *of 5,5′-Dimethoxy-4,4′-di-t-butyl-2,2′-diphenoquinone* (4).—The diphenoquinone (4) was prepared from 5,5′-dimethoxy-4,4′-di-t-butylbiphenyl-2,2′-diol (6) (0.5 g) in hexane solution (500 ml) by shaking it with a solution of potassium ferricyanide (1.5 g) and sodium hydroxide (1.5 g) in water (60 ml) for 2 min. The blue solution separated, washed twice with water and allowed to evaporate overnight in a gentle air stream. The residue was suspended in light petroleum (15 ml) and filtered, to give an off-white powder. This was heated in light petroleum (20 ml) and cooled to precipitate the trimeric *product* (11) (0.40 g) as a white powder, m.p. 172—175 °C (Found: C, 73.9; H, 7.9. $C_{66}H_{84}O_{12}$ requires C, 74.1; H, 7.9%); δ (CCl_4) 0.91, 1.29, 1.37 (2), 1.43, 1.48 (Bu^t), 3.23, 3.58, 3.65, 3.68, 3.85, 3.88 (OMe), 4.06 (OH), 3.96, 5.44, 6.40, 6.44, 6.52, 6.74 (2), 6.82, 6.85, 6.92, and 7.03 (ArH, vinyl H); M^+ 1068.

Preparation of the Dimer (12).—(*a*) *By hydrolysis of the trimer* (11). One drop of 10% hydrochloric acid was added to a solution of the trimer (11) (20 mg) in methanol (10 ml). The blue solution immediately became colourless, and then pale yellow, slowly darkening. Water (10 ml) was quickly added and the mixture was extracted with carbon tetrachloride. This was washed with water and evaporated. Separation by t.l.c. (silica) gave seven fractions, the major components being fraction four, the purple 2-(2-hydroxy-5-methoxy-4-t-butylphenyl)-5-t-butyl-1,4-benzoquinone (9), and fraction seven, the yellow dimer (12); δ ($CDCl_3$) 1.14, 1.32 (2), 1.49 (Bu^t), 3.26, 3.58 (2), 3.69 (OMe), 4.29 (OH), 5.29, 5.50, 6.24, 6.33, 6.53, 6.62, and 6.93 (ArH, vinyl H). The dimer decomposed on silica so that only the front portion of the band was of satisfactory purity by n.m.r.

(*b*) *By treatment of the trimer* (11) *with a phenol.* The trimer (11) (0.3 g) was dissolved in dichloromethane (2 ml) and a solution of 4-methoxy-3-t-butylphenol (1) (0.12 g) in hexane (6 ml) was added. The solution was allowed to stand for 4 h and was then washed four times with 2% aqueous sodium hydroxide solution, then with water. The upper layer was separated and allowed to evaporate to *ca.* 2 ml giving crystals (0.13 g), m.p. 222—227 °C. A small sample was recrystallized from hexane–dichloromethane by allowing the solvent to evaporate over several days to obtain crystals suitable for *X*-ray crystallography. This showed the structure to be 1′-(2-*hydroxy*-5-*methoxy*-4-*t*-*butylphenyl*)-4a′,5,7′-*trimethoxy*-4,′4,6′-*tri*-*t*-*butylspiro*(*cyclohexa*-3,5-*diene*-1,9′-*xanthen*-2,2′(4′aH)-*dione* (12).

Crystal Data.—$C_{44}H_{56}O_8 \cdot CHCl_3 = C_{45}H_{57}Cl_3O_8$, M = 832.3, Monoclinic, space group $P2_1/n$ (variant of C_{2h}^5, No. 14), a = 22.48(1), b = 12.401(4), c = 16.461(4) Å, β = 95.14(3), U = 4571(3) Å^3. D_m = 1.20(1), D_c = 1.21 g cm^{-3} (Z = 4). F(000) = 1768. Monochromatic Me-K_α radiation, (λ = 0.7106$_9$ Å), μ_{Mo} = 2.4 cm^{-1}. Specimen 0.18 × 0.55 × 0.10 mm. T = 295 K.

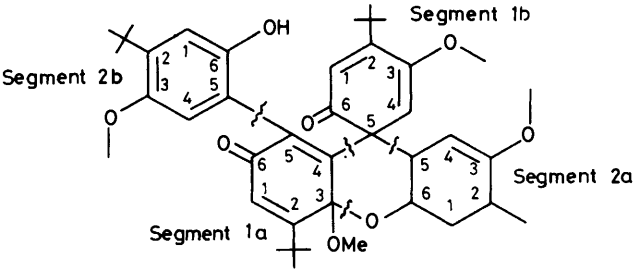


Figure 3.

Structure Determination.—A unique data set was measured to $2\theta_{max.}$ 40° using a Syntex $P2_1$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode, yielding 4 056 independent reflections. 1644 with $I > 3\sigma(I)$ were considered ' observed ' and used in the 9 × 9 block diagonal least-squares refinement, after solution of the structure by direct methods; data were corrected for absorption. Anisotropic thermal parameters were employed for the non-hydrogen atoms. For the hydrogen atoms, $(x,y,z,U)_H$ were estimated and included in the refinement as invariants. At convergence, R,R' were 0.051, 0.055, reflection weights being $[\sigma^2(F_0) + 0.0005(F_0)^2]^{-1}$. Neutral-atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f',f'').[11] Computation was carried out on a Perkin-Elmer 3240 computer using the *X*-RAY 76 programme system [12] implemented by S. R. Hall. Non-hydrogen atom labelling is as shown in Figure 3. Structure factor amplitudes, thermal parameters, and non-hydrogen atom parameters have been deposited as a Supplementary publication* (Sup. no. 23404, 16 pages).

Structural Commentary.—The structure determination establishes the stoicheiometry of compound (12) to be that of the dimer, namely $C_{44}H_{56}O_8$; one molecule of the compound comprises the asymmetric unit of the structure, together with one molecule of chloroform solvent. The hydrogen atom of the latter is involved in a hydrogen bond with a neighbouring molecule [H · · · O(6) (segment 1b) ($\frac{1}{2} + x, \frac{1}{2} < y, z - \frac{1}{2}$), 2.1$_4$ Å; C–H · · · O, 144°], while another significant intermolecular hydrogen bond is observed from H(6) (segment 2b) to O(6) (segment 1a) ($1 - x, 1 - y, 1 - z$), 1.7$_8$ Å, O–H · · · O, 137°. The structure of the molecule is shown in Figure 4; for convenience in tabulation the labelling is broken down into four segments with the same connectivity as shown. The molecule comprises five connected rings; the coplanarity of the C_6-skeletons of segments 1a, 1b, 2a, 2b is examined in Table 4, where it is seen that the two phenyl rings are reasonably planar. As expected, the methoxy-substituents lie reasonably coplanar with the rings, with the methyl groups directed away from the adjacent t-butyl substituent, which in turn is disposed so that a pair of methyl groups lie on either side of the ring plane astride the methoxy-oxygen. Normally, interactions between methoxy-methyl groups and adjacent ring hydrogen atoms cause asymmetry in the C(ring)–C(ring)–O angles on either side of the C–O bond; this situation is maintained here in spite of the proximity of the adjacent

* For details of the Supplementary publication scheme see Notices to Authors, No. 7, *J. Chem. Soc., Perkin Trans. 1* 1981, Index issue.

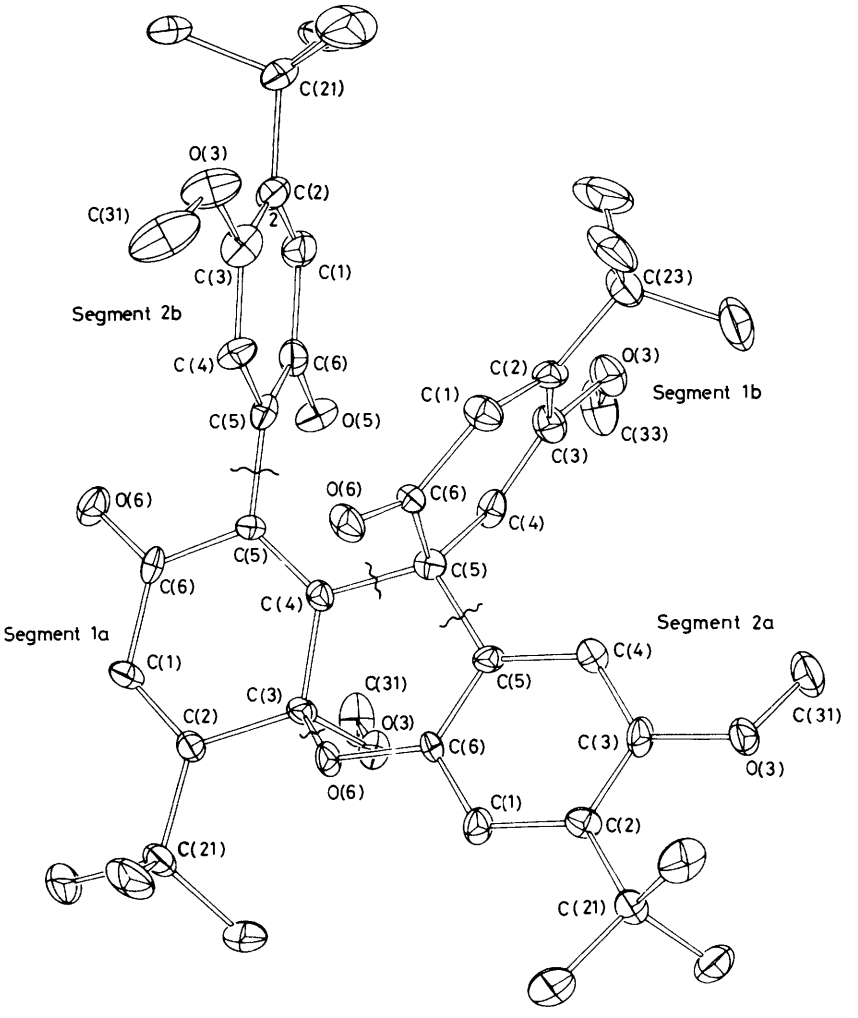


Figure 4. Molecular projection showing non-hydrogen atoms with 20% thermal ellipsoids, and segment and atom labelling

Table 2. Non-hydrogen atom co-ordinates

Atom	*x*	*y*	*z*	*x*	*y*	*z*
	Segment 1a			Segment 1b		
C(1)	0.322 8(4)	0.388 0(7)	0.402 2(5)	0.393 7(4)	0.138 6(8)	0.738 9(5)
C(2)	0.301 9(3)	0.289 0(7)	0.388 7(5)	0.452 7(4)	0.112 0(7)	0.742 6(5)
C(21)	0.254 1(4)	0.262 1(7)	0.319 5(5)	0.487 9(4)	0.080 4(8)	0.822 6(5)
C(22)	0.264 8(5)	0.156 3(9)	0.276 9(6)	0.539 0(5)	0.157 0(11)	0.842 9(7)
C(23)	0.249 3(5)	0.351 7(8)	0.255 9(7)	0.511 0(5)	−0.035 9(9)	0.817 6(7)
C(24)	0.193 0(4)	0.255 5(9)	0.354 4(7)	0.449 5(5)	0.085 0(11)	0.893 9(6)
C(3)	0.329 3(4)	0.200 0(7)	0.444 9(5)	0.480 9(4)	0.111 8(7)	0.665 3(5)
O(3)	0.367 0(2)	0.133 2(4)	0.401 5(3)	0.541 5(2)	0.097 1(5)	0.673 1(3)
C(31)	0.416 1(4)	0.185 1(8)	0.368 1(6)	0.574 2(4)	0.113 2(9)	0.604 0(6)
C(4)	0.364 5(3)	0.234 9(6)	0.522 9(5)	0.449 9(3)	0.129 3(7)	0.592 8(5)
C(5)	0.382 8(3)	0.336 6(7)	0.533 7(5)	0.383 3(3)	0.141 5(7)	0.584 0(5)
C(6)	0.366 6(4)	0.417 5(7)	0.469 7(5)	0.355 5(3)	0.167 3(7)	0.665 3(5)
O(6)	0.388 8(2)	0.508 4(4)	0.472 3(4)	0.305 7(2)	0.199 4(5)	0.667 6(3)

Table 2 (*Continued*)

Atom	*x*	*y*	*z*	*x*	*y*	*z*
	Segment 2a			Segment 2b		
C(1)	0.263 0(4)	−0.050 2(7)	0.492 4(5)	0.515 3(4)	0.440 6(7)	0.672 0(6)
C(2)	0.278 3(3)	−0.149 9(7)	0.528 6(5)	0.488 6(4)	0.471 0(7)	0.741 2(5)
C(21)	0.236 7(4)	−0.247 3(7)	0.517 5(5)	0.528 0(4)	0.522 5(8)	0.813 7(6)
C(22)	0.223 0(5)	−0.292 4(8)	0.600 0(6)	0.510 2(5)	0.640 8(9)	0.822 4(6)
C(23)	0.267 1(5)	−0.336 0(8)	0.469 5(6)	0.594 2(5)	0.523 5(10)	0.798 7(7)
C(24)	0.177 3(4)	−0.220 4(8)	0.468 6(6)	0.523 1(6)	0.466 4(10)	0.895 4(6)
C(3)	0.333 7(4)	−0.154 1(7)	0.575 7(5)	0.427 4(4)	0.455 8(8)	0.743 5(5)
O(3)	0.351 5(3)	−0.253 4(5)	0.605 9(4)	0.401 6(3)	0.492 1(6)	0.810 8(4)
C(31)	0.411 9(4)	−0.270 1(8)	0.629 3(6)	0.340 2(5)	0.493 8(10)	0.810 6(7)
C(4)	0.367 8(4)	−0.062 2(7)	0.592 0(5)	0.394 8(4)	0.410 5(7)	0.676 4(5)
C(5)	0.350 7(4)	0.035 1(6)	0.558 0(5)	0.420 5(4)	0.377 6(7)	0.606 6(5)
C(6)	0.299 0(4)	0.040 0(7)	0.505 7(5)	0.481 4(4)	0.395 2(7)	0.605 0(5)
O(6) [a]	0.281 0(2)	0.133 5(4)	0.464 6(3)	0.506 8(2)	0.366 9(4)	0.534 9(3)
	Solvent					
C [b]	0.687 7(5)	0.194 2(11)	0.115 8(8)			
Cl(1)	0.713 5(2)	0.089 5(3)	0.061 3(2)			
Cl(2)	0.622 8(2)	0.244 2(4)	0.063 3(3)			
Cl(3)	0.676 3(2)	0.157 4(5)	0.210 9(3)			

[a] H(6) (Segment 2b): 0.535(—), 0.450(—), 0.522(—). [b] H(Solvent): 0.718(—), 0.255(—), 0.119(—).

Table 3. Molecular non-hydrogen geometries

	Segment			
	1a	1b	2a	2b
Distances (Å)				
C(1)–C(2)	1.33(1)	1.36(1)	1.40(1)	1.39(1)
C(1)–C(6)	1.46(1)	1.45(1)	1.39(1)	1.40(1)
C(2)–C(21)	1.53(1)	1.53(1)	1.53(1)	1.56(1)
C(21)–C(22)	1.52(1)	1.51(2)	1.53(1)	1.53(1)
C(21)–C(23)	1.52(1)	1.54(2)	1.55(1)	1.53(1)
C(21)–C(24)	1.54(1)	1.52(1)	1.53(1)	1.53(1)
C(2)–C(3)	1.53(1)	1.47(1)	1.41(1)	1.39(1)
C(3)–C(4)	1.51(1)	1.35(1)	1.39(1)	1.39(1)
C(3)–O(3)	1.42(1)	1.37(1)	1.37(1)	1.37(1)
O(3)–C(31	1.43(1)	1.42(1)	1.39(1)	1.38(1)
C(4)–C(5)	1.33(1)	1.50(1)	1.37(1)	1.39(1)
C(5)–C(5′)	1.50(1)		1.55(1)	
C(5)–C(6)	1.48(1)	1.55(1)	1.39(1)	1.39(1)
C(6)–O(6)	1.23(1)	1.21(1)	1.38(1)	1.38(1)
Angles (°)				
C(2)–C(1)–C(6)	124.3(8)	125.6(8)	121.8(7)	120.7(8)
C(1)–C(2)–C(3)	116.7(7)	117.1(8)	115.9(8)	119.1(8)
C(1)–C(2)–C(21)	122.8(7)	121.9(8)	121.5(7)	118.8(8)
C(3)–C(2)–C(21)	120.6(7)	121.0(7)	122.6(7)	122.0(8)
C(2)–C(21)–C(22)	113.8(7)	110.8(8)	110.7(7)	109.2(7)
C(2)–C(21)–C(23)	110.8(7)	110.3(8)	109.3(7)	111.9(8)
C(2)–C(21)–C(24)	108.9(7)	111.7(8)	112.6(7)	114.0(8)
C(22)–C(21)–C(23)	108.5(8)	110.4(8)	109.1(7)	105.9(8)
C(22)–C(21)–C(24)	108.1(8)	106.3(8)	108.1(7)	108.3(9)
C(23)–C(21)–C(24)	108.5(8)	107.2(9)	106.9(7)	107.1(9)
C(2)–C(3)–C(4)	117.2(7)	122.4(7)	121.5(8)	119.1(8)
C(4)–C(3)–O(3)	107.6(6)	122.5(8)	121.9(7)	123.0(8)
C(2)–C(3)–O(3)	110.0(6)	115.0(7)	116.5(7)	117.8(8)
C(3)–O(3)–C(31)	116.5(6)	119.2(6)	118.5(7)	119.9(8)
C(3)–C(4)–C(5)	121.1(7)	122.5(8)	121.0(7)	123.0(8)
C(4)–C(5)–C(6)	119.5(7)	113.5(6)	118.8(7)	116.9(7)
C(4)–C(5)–C(5′)	125.1(7)	112.6(8)	122.0(7)	120.9(7)
C(6)–C(5)–C(5′)	115.4(7)	101.8(6)	118.9(7)	121.8(8)
C(1)–C(6)–C(5)	118.6(7)	115.5(7)	120.5(7)	121.1(8)
C(1)–C(6)–O(6)	119.9(7)	121.8(7)	117.3(7)	121.5(7)
C(5)–C(6)–O(6)	121.5(7)	122.3(7)	122.2(7)	117.4(7)

Other parameters:

Distances (Å)	C(1a4)–C(1b5), 1.57(1)
	C(1a3)–O(2a6), 1.42(1)
Angles (°)	O(2a6)–C(1a3)–C(1a2,4), O(1a3), 106.3(6), 108.9(6), 106.2(6)
	C(1b5)–C(1a4)–C(1a3,5), 115.1(7), 123.5(7)
	C(1a3)–O(2a6)–C(2a6), 113.7(6)
	C(1a4)–C(1b5)–C(1b4,6), C(2a5), 110.2(7), 107.4(6), 111.1(6)

Table 4. Least-squares planes [a]

	Segment			
	1a	2a	1b	2b
10^4p	8 402	−5 672	2 146	−1 381
10^4q	−1 815	2 220	9 752	9 100
10^4r	−5 110	7 931	0 534	−3 909
s	1.384	3.323	4.009	−0.7969
σ	0.08	0.03	0.08	0.01
δC(1)	−0.03	0.00	−0.02	0.00
δC(2)	−0.07	0.03	−0.06	0.00
δC(21)	−0.24	0.14	−0.22	0.00
δC(22)	0.60	1.33	0.96	1.34
δC(23)	0.07	−1.16	−1.52	−0.10
δC(24)	−1.72	0.29	−0.31	−1.12
δC(3)	0.11	−0.04	0.04	0.00
δO(3)	1.39	−0.12	0.15	0.07
δC(31)	2.52	−0.61	0.47	0.28
δC(4)	−0.06	0.01	0.06	0.01
δC(5)	−0.04	0.02	−0.12	−0.01
δC(6)	0.08	−0.03	0.11	0.01
δO(6)	0.27	−0.11	0.25	0.04

[a] Least squares planes defined by C(1)—C(6) of rings 1a, b, 2a, b are given in the form $pX + qY + rZ = s$, where the right handed orthogonal Å frame (X,Y,Z) is defined with X parallel to a, Z in the ac plane. σ (defining atoms) and atom deviations δ, are in Å.

t-butyl substituent, with no systematic significant disparity in the junction angles of the latter at the ring. The rings of segments 1a and 1b both contain a pair of double bonds, disposed in a different manner relative to the exocyclic carbonyl group. In spite of the number of sp^2-hybridized carbon atoms in these rings, the C_6-skeletons are significantly non-planar ($\chi^2 = 402$ and 430, respectively) (*cf.* 50 and 3 for rings 2a and b) and the carbonyl oxygen atom deviation is appreciable in each case. The central heterocyclic ring formed by the junction of rings 1a, 2a, and 1b is highly distorted from planarity [deviation δ C(1a3); C(1a4); C(1b5); C(2a5); C(2a6); O(2a5): 0.36, −0.15, <0.10, 0.20, <0.03, <0.28, respectively; σ 0.24 Å), comprising a pseudo-boat. Dihedral angles between this ring ' plane ' and planes 1a, 2a, and 1b are 16.3, 14.8, and 74.8° respectively, with the 1a-2a dihedral angle 22.8°.

Bond lengths are generally as expected for the structure given; the following features of interest may be noted among the angular geometry.

(i) Considerable variations are observed among the angles of rings 1a, generally consistent with the expected effects of the double bonds associated with the ring; the same may be said of ring 1b, taking cognizance of the presence of the tetrahedral spiro-carbon atom.

(ii) A considerable asymmetry is observed in the exocyclic angles at the phenolic substituent in segment 2b. Noting that the phenolic hydrogen is involved in a hydrogen bond, this may be presumed to be the cause.

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