Oxidation by Singlet Oxygen of 4,7-Dimethoxy-2,9-di-t-butyloxepino-[2,3-*b*]benzofuran, an Oxidation Product of the Antioxidant BHA

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Tetraphenylporphin-sensitized photo-oxidation of 4,7-dimethoxy-2,9-di-t-butyloxepino[2,3-*b*]-benzofuran (**3**) and reaction of the products with methanol cleaves the oxepine ring, producing the acetal (**9**) and its isomer (**13**), which may be derived respectively from the 1,4-endoperoxide and 1,2-dioxetane oxygen adducts of (**3**). The geometrical isomerization of (**9**) to (**14**), and the acid-catalysed hydrolysis of (**9**), (**13**) and (**14**) to the dihydrofuranylidenebenzofuranone (**18**) are described. Crystal structures were determined for compounds (**9**), (**14**), and (**18**).

BHA, consisting largely of 4-methoxy-2-t-butylphenol, is widely used as an antioxidant in the food industry. Typical one-electron oxidants convert it into the blue quinone (**1**) which has been shown to be in equilibrium with the arene oxide (**2**) and the oxepino[2,3-*b*]benzofuran (**3**).[1,2] In inhibiting autoxidation, BHA must itself be oxidized and in fact the blue colour of the quinone (**1**) has been observed in lard stabilized with BHA.[3] Since there are indications that singlet oxygen may be involved in biological oxidation,[4] it appeared of interest to examine the reaction of the oxepine (**3**), the major component of the equilibrium mixture, with this reagent. The reaction of the equilibrium mixture oxepine–benzene oxide itself with singlet oxygen has been reported[5] to yield the endoperoxide (**4**) which readily isomerizes to *trans*-benzene trioxide (**5**).

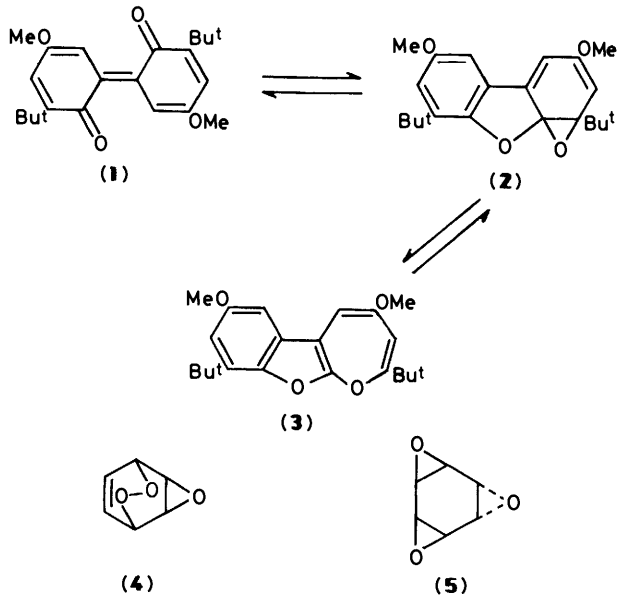
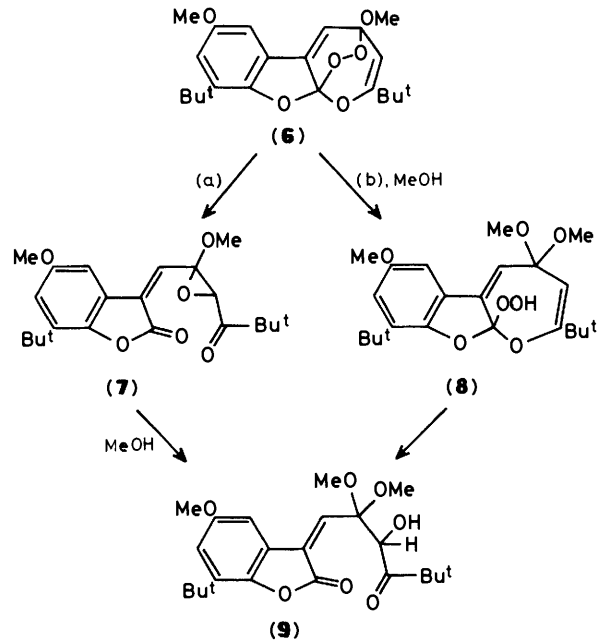


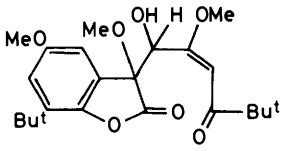
Photo-oxidation of (**1**) ⇌ (**2**) ⇌ (**3**) was initially attempted using Rose Bengal as the sensitizer, but extensive decomposition ensued. With tetraphenylporphin in acetone–methanol (99:1) a product (**9**) was obtained in 42% yield with the consumption of 1 mol equiv. of oxygen. The structure of (**9**) was established crystallographically. It is presumably the end product of nucleophilic attack by methanol on an initial endoperoxide (**6**), which may first rearrange to the epoxide (**7**). An alternative may involve the rearrangement of the hydroperoxide (**8**), for which models show the peroxidic hydroxy group to be within easy reach of the C(2)–C(3) double bond [Scheme 1, routes (a) or (b)]. Attempts to isolate intermediates by using only acetone as solvent were unsuccessful. But subsequent addition of methanol to the crude product obtained in this way also gave the acetal (**9**), indicating the presence of the endoperoxide or another intermediate in the crude product.



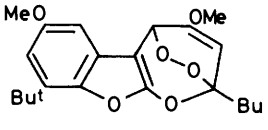
Scheme 1.

To suppress possible acid-catalysed rearrangement of the endoperoxide (**6**) the photo-oxidation was also carred out in acetone–pyridine (100:1). Again no pure material could be isolated from the crude product, but on treating this with methanol a lower yield (10%) of a compound (**13**), isomeric with (**9**), was obtained. Its structure follows from the ^{1}H n.m.r. spectrum, which like that of (**9**) shows CHOH coupling, and a higher i.r. absorption frequency at 1 815 cm^{-1} for the furanone carbonyl group, consistent with the absence of an exocyclic double bond. In comparison, the

furanone carbonyl absorption of (**9**) occurs at 1 775 cm^{-1}. Moreover, the bathochromic shift in the u.v.-visible absorption spectrum from 365 nm for compound (**9**) to 295 nm for compound (**13**) indicates that the side chain is no longer conjugated with the aromatic ring. An alternative structure (**10**) which could be formed from the isomeric endoperoxide (**11**) was excluded when it was found that acid-catalysed hydrolysis of (**9**) and (**13**) led to the same product (**18**) (see below).

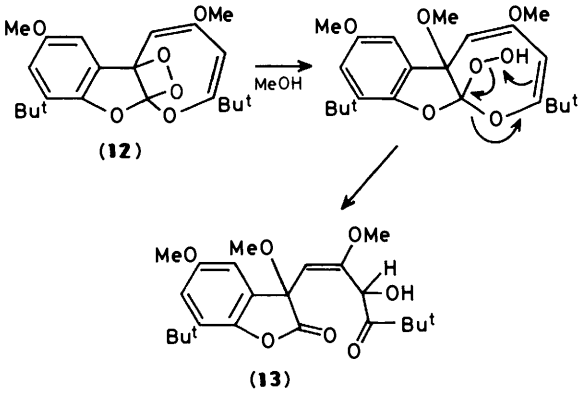


(**10**)



(**11**)

We suggest that compound (**13**) may be formed by the reaction of methanol with the dioxetane (**12**) as shown in Scheme 2, particularly as the analogous oxidation of cycloheptatriene has been reported to give both 1,2-dioxetane and endoperoxide products.[6] Formation of either (**9**) or (**13**) from the arene oxide (**2**) directly is not possible, in contrast to most of the reaction products of this equilibrium system.



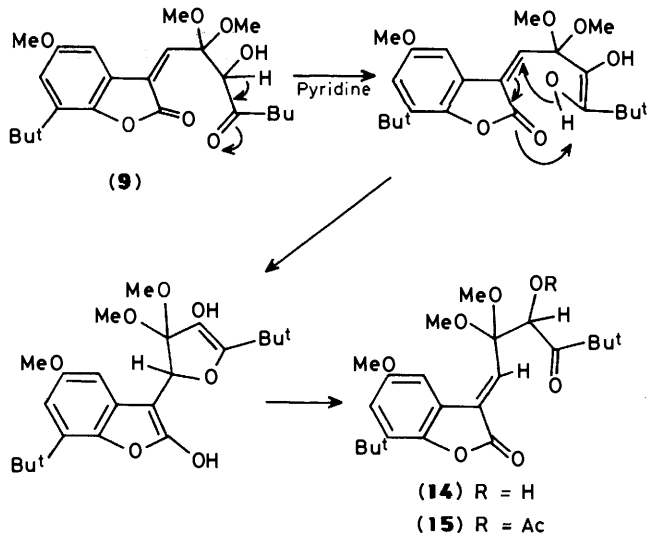
(**12**)

(**13**)

Scheme 2.

The possibility that pyridine may have caused rearrangement of acetal (**9**) to (**13**) was also examined. When (**9**) was dissolved in warm pyridine, although (**13**) was not produced, an almost quantitative transformation to the (*E*) geometric isomer (**14**) occurred. The much larger ^1H n.m.r. CHOH coupling of (**14**) at first suggested α-ketol tautomerism in the side chain, and as the paucity of hydrogens directly bonded to the side chain limited investigation by n.m.r., the structure of (**14**) was determined crystallographically. The (*Z*) geometry of the acetal (**9**) is consistent with its formation by ring opening of an endoperoxide, but apparently the (*E*) isomer (**14**) is thermodynamically more stable. This isomerization may be rationalised by enolization and temporary ring closure as in Scheme 3. Alternatively it may involve reversible Michael addition of pyridine to the α,β-unsaturated carbonyl group of (**9**). In the light of what follows the former interpretation is preferred.

Pyridine-catalysed acetylation of both (**9**) and (**14**) gave the same acetate, formulated as (**15**) in view of the isomerization shown in Scheme 3 and closer spectroscopic correspondence with the acetal (**14**). However, acetylation catalysed by sulphuric acid gave the acetate (**16**). This is formulated as the (*Z*) isomer because of the deshielding of one of the aromatic



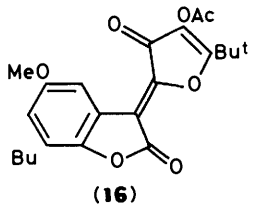
(**9**)

(**14**) R = H

(**15**) R = Ac

Scheme 3.

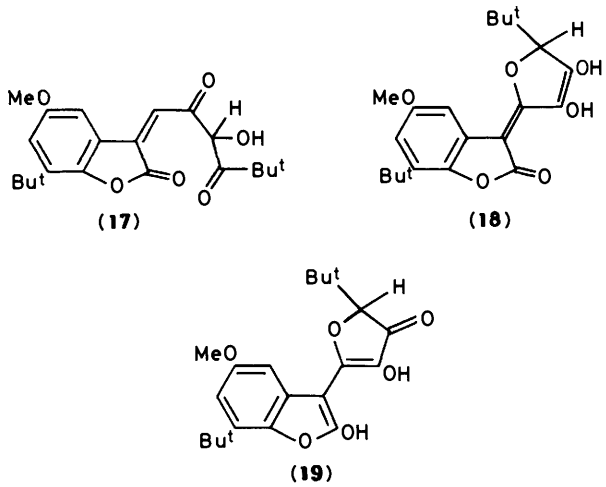
protons (δ 8.27) by the furanone carbonyl group. The formation of (**16**) also involves an oxidation. A similar oxidation in these conditions, giving the same compound without the acetoxy group, has previously been reported from this laboratory.[7]



(**16**)

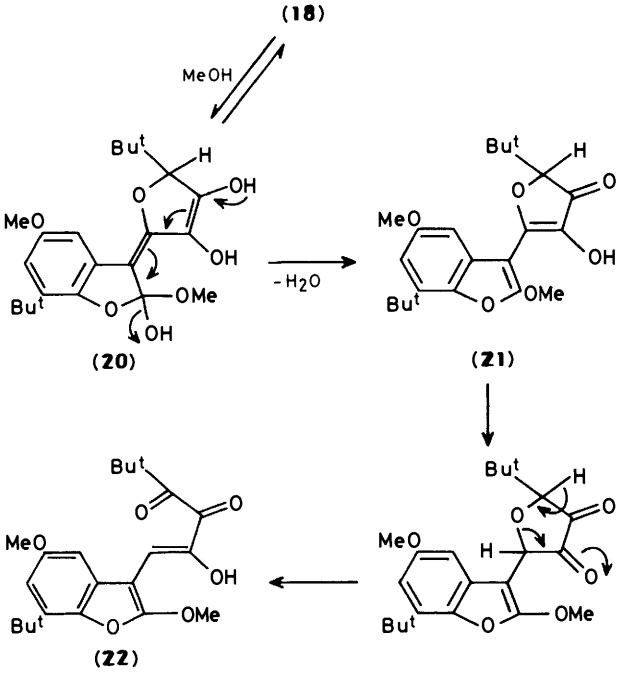
As expected, acid-catalysed hydrolysis of the acetals (**9**) and (**14**) was easy and led to the same products. Thus treatment with hydrochloric acid in acetone at room temperature gave a crude product whose ^1H n.m.r. spectrum was consistent with that expected for the ketone (**17**) or a tautomer. Attempts to isolate this product were unsuccessful. Crystallization from methanol gave material m.p. 115—117 °C. Although the hydrolysis was repeated a number of times under different conditions these products were always contaminated by paramagnetic material, and only the t-butyl and methoxy resonances could be seen in their n.m.r. spectra. Moreover, the crystals were too small for crystallographic examination. Suitable crystals, m.p. 109—110 °C, again paramagnetic, were obtained from t-butyl alcohol and were shown to have structure (**18**) solvated by t-butyl alcohol. The cyclization of (**17**) to (**18**) can be accommodated by a pathway similar to that of Scheme 3. The *E* geometry of (**18**) is presumably a consequence of intramolecular hydrogen bonding. An interesting feature of structure (**18**) is its vinylogous relationship to ascorbic acid.

The ^1H n.m.r. spectrum of (**18**) shows aliphatic and aromatic t-butyl resonances at δ 1.10 and 1.39, and another for the t-butyl alcohol of solvation at δ 1.29. The mass spectrum (M^+ 375) is characterized by the consecutive loss of two isobutene molecules. But the i.r. spectrum of a carbon tetrachloride solution lacks the characteristic furanone absorption and instead shows carbonyl absorption of 1 695 cm^{-1}. Dilution of the solution does not affect the carbonyl frequency, so it is not a feature of intermolecular hydrogen bonding. Instead, we suggest that the tautomeric structure (**19**) is favoured in this solvent.



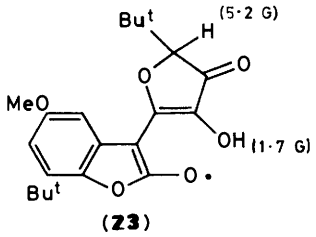
As the material, m.p. 152—155 °C, obtained from benzene–light petroleum has the same spectroscopic properties, except for the n.m.r. resonance of the solvating t-butyl alcohol, it is believed to be the unsolvated compound (**19**).

In contrast, the material, m.p. 115—117 °C, obtained from methanol has an additional methoxy resonance in the n.m.r. spectrum at δ 3.50. This is reflected in the combustion analysis which fits $C_{21}H_{26}O_6 \cdot CH_3OH$. The i.r. spectrum of a solution in carbon tetrachloride is almost indistinguishable from those of (**18**) and (**19**), but the mass spectrum is different with M^+ 388, and a base peak at *m/z* 305 comparable to that of the acetal (**9**), and corresponding to the loss of a t-butyl ketone grouping. Although this compound is converted into (**19**) on heating *in vacuo*, formulation as the methanol solvate of (**19**) is not in keeping with the mass spectrum, and on this basis the hemiacetal structure (**20**) is suggested. The fragmentation pattern can then be explained as in Scheme 4 by a preliminary loss of water (not observed) to (**21**) followed by tautomerism and ring opening to (**22**) (*M* 388).



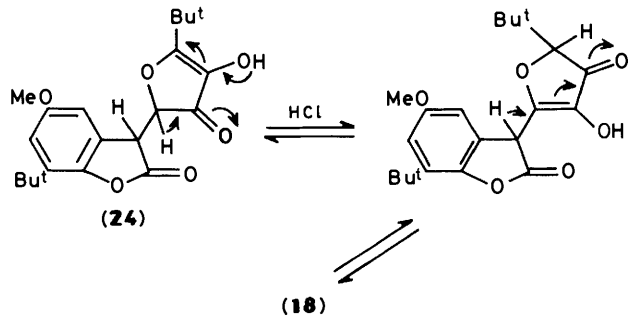
Scheme 4.

The paramagnetism of these hydrolysis products was further revealed by the e.s.r. spectrum shown by a solution of (**18**) in carbon tetrachloride. This consisted principally of a doublet of doublets with *g* 2.0039 and a_H 5.2 and 1.7 gauss. These values are reasonable for the oxygen centred radical (**23**), which appears to be of almost indefinite stability, and may have some bearing on the toxicological properties of BHA.



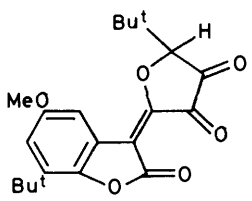
The acetal (**9**) could also be hydrolysed by brief warming with aqueous acetic acid. Here the product was not contaminated by paramagnetic material and structure (**24**) could be unambiguously assigned on the basis of its spectroscopic properties. Thus it was colourless ($\lambda_{max.}$ 295 nm); the i.r. spectrum showed furan 2(3*H*) carbonyl absorption at 1 800 cm^{-1}, a double α,β-unsaturated carbonyl absorption at 1 705 and 1 680 cm^{-1}, and a broad, bonded hydroxy absorption at 3 250 cm^{-1}. The mass spectrum, with M^+ 374, showed a major peak at *M* 289 corresponding to loss of a t-butyl ketone fragment after opening of the dihydrofuranone ring. The ^1H n.m.r. spectrum showed the 3-H to be coupled to 2′-H, 4-H, and 6-H, while the 2′-H was coupled only to 3-H. The other features of this spectrum were consistent with structure (**24**) as was the proton-coupled ^{13}C n.m.r. spectrum. A small amount, *ca.* 10%, of what appeared to be another diastereoisomer was also present, but not isolated. On warming in solution, or on contact with silica, or on melting, an orange colouration was produced, but this material was present in only trace amounts.

Crystallization of compound (**24**) from methanol containing a trace of hydrochloric acid induced quantitative conversion into the hemiacetal (**20**), again with paramagnetic contamination. The tautomeric changes of Scheme 5 suggest that (**24**) is an intermediate in the hydrolysis of the acetal (**9**) by hydrochloric acid.

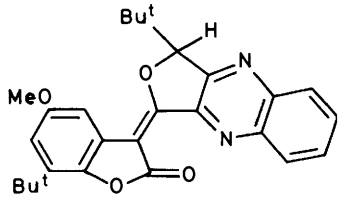


Scheme 5.

Oxidation of compound (**18**) with DDQ gave a low yield of a red compound whose mass spectrum was consistent with the trione structure (**25**), but extensive decomposition on attempted purification deterred further examination. Instead, it was characterized as the quinoxaline (**26**) by *in situ* condensation with 1,2-diaminobenzene.



(25)



(26)

Experimental

N.m.r. and i.r. spectra are for carbon tetrachloride solutions unless otherwise stated. Chemical shifts are quoted on the δ scale relative to internal tetramethylsilane. The e.s.r. spectrum was calibrated with Frémy's salt. Microanalyses are by the Australian Microanalytical Service, Melbourne, or the Canadian equivalent, Vancouver. M.p.s, taken with a Kofler hot stage, are uncorrected. Light petroleum had b.p. 65—70 °C. Extracts were dried with magnesium sulphate. Photosensitized oxidations were carried out at ambient temperature in a concentric Pyrex jacket through which oxygen was circulated through a fritted disc. This was separated from a central 600 W quartz-halogen lamp by a copper sulphate filter and a water cooled jacket. 4,7-Dimethoxy-2,9-di-t-butyloxepino[2,3-*b*]benzofuran (**3**) was prepared as described by Baltes and Volbert[1] and had m.p. 122—123 °C.

Photosensitized Oxidation of the Oxepine (**3**).—(*a*) A solution of the oxepine (**3**) (2.0 g) in acetone (400 ml) and methanol (40 ml) containing tetraphenylporphin (20 mg) was irradiated and oxygenated until the blue colour had become yellow and 1 mol equiv. of oxygen had been absorbed (40 min). The solution was evaporated under reduced pressure at < 30 °C, and the residue was subjected to rapid chromatography on silica. Elution with light petroleum–ethyl acetate (20:1) gave a fraction (1.65 g) which was crystallized twice from methanol to give (Z)-3-(3′-*hydroxy*-2′,2′-*dimethoxy*-5′,5′-*dimethyl*-4′-*oxohexylidene*)-5-*methoxy*-7-*t*-*butylbenzofuran*-2(3H)-*one* (**9**) as yellow prisms (985 mg), m.p. 132.5—133 °C (Found: C, 65.8; H, 7.5. $C_{23}H_{32}O_7$ requires C, 65.7; H, 7.7%); $\delta_H(CDCl_3)$ 1.24 (9 H, s, Bu^t), 1.36 (9 H, s, Bu^t), 3.31 (3 H, s, OMe), 3.44 (3 H, s, OMe), 3.81 (3 H, s, OMe), 4.56 (1 H, d, *J* 4.0 Hz, OH, exchanging with D_2O), 5.12 (1 H, d, *J* 4.0 Hz, C*H*OH), and 6.84 (3 H, s, 2 ArH, vinylic H); $\delta_C(CDCl_3)$ (75.5 MHz), 26.3 (q), 29.3 (q), 34.1 (s), 44.7 (s), 49.7 (q), 50.0 (q), 55.8 (q), 75.2 (d), 101.1 (d), 102.7 (s), 115.9 (d), 124.3 (s), 126.4 (s), 135.8 (s), 140.9 (d), 145.7 (s), 156.2 (s), 166.4 (s), and 213.1 (s); $\nu_{max.}$ 3 380br (bonded OH), 1 775 (furanone CO), and 1 710 cm^{-1} (ketone CO); $\lambda_{max.}$(EtOH) 252 (ε 10 600), 292 (6 350), and 365 nm (2 300); *m*/*z* (%) 420 (M^+, 3), 388 (4), 305 (31), 304 (100), 275 (26), and 247 (79). A small amount of 5,5′-dimethoxy-3,3′-di-t-butylbiphenyl-2,2′-diol, m.p. 228—229 °C (lit.,[1] m.p. 228 °C), and traces of (*E*)-5-methoxy-3-[(*E*)-2′-methoxy-5,5′-dimethyl-4′-oxohex-2′-enylidene]-7-t-butylbenzofuran-2(3*H*)-one, m.p. 180—186 °C (lit.,[8] 189.5—191 °C) were also obtained and identified spectroscopically.

(*b*) Repetition of the oxidation without the inclusion of methanol gave a dark residue which could not be purified. When set aside in methanol for several days chromatography of the resulting material gave the acetal (**9**) (500 mg) and 5,5′-dimethoxy-3,3′-di-t-butylbiphenyl-2,2′-diol (390 mg).

(*c*) Repetition of the oxidation with the inclusion of pyridine instead of methanol also gave dark, intractable material. After reaction for several days with methanol rapid chromatography on silica and elution with light petroleum–ethyl acetate (11:1) gave a fraction (470 mg) which after preparative t.l.c. and crystallization from pentane afforded 3-(3′-*hydroxy*-2′-*methoxy*-5′5′-*dimethyl*-4′-*oxohex*-1′-*enyl*)-3,5-*dimethoxy*-7-*t*-*butylbenzofuran*-2(3H)-*one* (**13**) as colourless elongated plates (230 mg), m.p. 137—138 °C (Found: C, 66.0; H, 7.6. $C_{23}H_{32}O_7$ requires C, 65.7; H, 7.7%); $\delta_H(CDCl_3)$ 1.12 (9 H, s, Bu^t), 1.39 (9 H, s, Bu^t), 2.40 (1 H, d, *J* 3.4 Hz, OH, exchanging with D_2O), 3.47 (3 H, s, OMe), 3.65 (3 H, s, OMe), 3.77 (3 H, s, OMe), 4.63 (1 H, s, vinylic H), 4.84 (1 H, d, *J* 3.4 Hz, C*H*OH), 6.85 (1 H, d, *J* 2.8 Hz, ArH), and 7.05 (1 H, d, *J* 2.8 Hz, ArH); $\nu_{max.}$ 3 600 (OH), 1 815 (furanone CO), and 1 680 cm^{-1} (ketone CO); $\lambda_{max.}$(EtOH) 295 nm (ε 2 390); *m*/*z* (%) 420 (M^+, 1), 360 (52), 335 (95), 305 (100), 304 (36), 275 (52), and 247 (47).

Base-catalysed Isomerization of the Acetal (**9**).—The acetal (**9**) (80 mg) was heated in pyridine at 60 °C for 20 min after which the mixture was poured into water and extracted with ether. Pyridine was removed by extraction with water, and the dried extract was evaporated. Crystallization of the residue from light petroleum gave the (E)-*isomer* (**14**) as yellow plates (54 mg), m.p. 135—136 °C, depressed to 110—117 °C on admixture with (**9**) (Found: C, 65.7; H, 7.6. $C_{23}H_{32}O_7$ requires C, 65.7; H, 7.7%); $\delta_H(CDCl_3)$ 1.22 (9 H, s, Bu^t), 1.33 (9 H, s, Bu^t), 3.04 (1 H, d, *J* 10 Hz, OH, exchanging with D_2O), 3.22 (3 H, s, OMe), 3.46 (3 H, s, OMe), 3.71 (3 H, s, OMe), 4.92 (1 H, d, *J* 10 Hz, C*H*OH), 6.40 (1 H, s, vinylic H), 6.77 (1 H, d, *J* 3 Hz, ArH), and 7.53 (d, *J* 3 Hz, ArH); $\delta_C(CDCl_3)$ (75.5 MHz) 27.0 (q), 29.4 (q), 34.2 (s), 44.4 (s), 48.5 (q), 50.4 (q), 55.6 (q), 72.4 (d), 103.9 (s), 108.9 (d), 116.7 (d), 121.3 (s), 129.5 (s), 135.0 (s), 137.5 (d), 148.0 (s), 155.6 (s), 168.3 (s), and 215.9 (s); $\nu_{max.}$ 3 500 br (OH), 1 783 (furanone CO), and 1 692 cm^{-1} (ketone CO); $\lambda_{max.}$(EtOH) 252 (ε 12 600), 289 (7 800), and 370 nm (2 600); *m*/*z* (%) 388 (3), 306 (26), 305 (100), 275 (17), and 247 (57).

Base-catalysed Acetylation of the Acetals (**9**) *and* (**14**).—The acetal (**9**) (70 mg) was dissolved in acetic anhydride, pyridine was added, and the solution was heated on the steam-bath for 1 h. After addition of water, the product was extracted with ether and crystallized from methanol giving (E)-(3′-*acetoxy*-2′,2′-*dimethoxy*-5′,5′-*dimethyl*-4′-*oxohexylidine*)-5-*methoxy*-7-*t*-*butylbenzofuran*-2(3H)*one* (**15**) as yellow prisms (56 mg), m.p. 129—130 °C (Found: C, 64.9; H, 7.7. $C_{25}H_{34}O_8$ requires C, 64.9; H, 7.4%); δ_H 1.14 (9 H, s, Bu^t), 1.34 (9 H, s, Bu^t), 1.80 (3 H, s, OAc), 3.23 (3 H, s, OMe), 3.42 (3 H, s, OMe), 3.68 (3 H, s, OMe), 5.89 (1 H, s, 3′-H), 6.60 (1 H, s, vinylic H), 6.69 (1 H, d, *J* 3 Hz, ArH), and 7.27 (1 H, d, *J* 3 Hz, ArH); $\nu_{max.}$ 1 785 (furanone CO), 1 748 (OAc), and 1 712 cm^{-1} (ketone CO); *m*/*z* (%) 346 (21), 304 (100), 275 (17), and 247 (65). The same product was obtained on similar treatment of (**14**).

Acid-catalysed Acetylation of the Acetal (**9**).—The acetal (**9**) (75 mg) was dissolved in acetic anhydride (2 ml) and concentrated sulphuric acid (1 drop) was added to produce an immediate green colour. After being heated for 20 min on a steam-bath the solution was poured into water and extracted with ether. The extract was washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated to give a residue which was subjected to t.l.c. on silica. A dark red band on extraction and crystallization from methanol gave (Z)-3-(4′-*acetoxy*-5′-*t*-*butyl*-2′,3′-*dihydro*-3′-*oxobenzofuran*-2′-*ylidene*)-5-*methoxy*-7-*t*-*butylbenzofuran*-2(3H)-*one* (**16**) as red prisms (14 mg), m.p. 187—189 °C (Found: C, 66.7; H, 6.4. $C_{23}H_{26}O_7$ requires C, 66.6; H, 6.3%); δ_H 1.40 (18 H, s, Bu^t), 2.27 (3 H, s, OAc), 3.81 (3 H, s, OMe), 6.82 (1 H, d, *J* 3 Hz, ArH), and 8.27 (1 H, d, *J* 3 Hz, ArH); $\nu_{max.}$ 1 785 (enol acetate CO and furanone CO), 1 695 (unsaturated CO), and 1 650 cm^{-1} (C=C); $\lambda_{max.}$(EtOH) 272 (ε 9 600), 362 (10 500), and 460sh (3 000).

Hydrolysis of the Acetal (**9**).—(*a*) The acetal (**9**) (200 mg) was dissolved in acetone (5 ml) and concentrated hydrochloric acid (0.2 ml) was added. The yellow solution quickly became orange

Table 1. Non-hydrogen atom co-ordinates for compounds (**9**) and (**14**)

	(9)			(14)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
C(1)	0.149 1(3)	0.618 9(4)	0.497 4(5)	0.232 8(4)	−0.001 6(2)	0.213 9(1)
C(2)	0.067 5(3)	0.607 6(5)	0.371 0(5)	0.147 6(4)	0.063 7(2)	0.225 9(1)
C(3)	0.000 7(3)	0.471 8(5)	0.249 4(5)	0.110 3(4)	0.068 9(2)	0.271 8(1)
O(3)	−0.085 0(2)	0.440 4(3)	0.116 9(4)	0.022 9(3)	0.128 8(2)	0.288 24(8)
C(31)	−0.100 9(5)	0.556 7(7)	0.089 7(7)	−0.041 8(4)	0.181 0(2)	0.255 1(2)
C(4)	0.017 4(4)	0.354 4(5)	0.257 4(6)	0.159 9(4)	0.014 4(2)	0.305 1(1)
C(5)	0.099 3(3)	0.362 3(4)	0.379 7(5)	0.246 6(4)	−0.051 2(2)	0.294 3(1)
C(51)	0.118 1(3)	0.233 4(4)	0.378 3(6)	0.301 8(4)	−0.112 6(2)	0.330 4(1)
C(52)	0.032 5(5)	0.094 7(6)	0.236 0(9)	0.454 0(4)	−0.108 7(3)	0.329 4(1)
C(53)	0.122 2(6)	0.197 6(6)	0.542 9(9)	0.255 6(4)	−0.088 6(3)	0.379 1(1)
C(54)	0.224 0(5)	0.275 9(7)	0.353 8(12)	0.255 1(4)	−0.202 0(3)	0.320 0(1)
C(6)	0.162 8(3)	0.499 6(4)	0.500 4(5)	0.277 3(4)	−0.056 9(2)	0.247 7(1)
O(6)	0.249 5(2)	0.535 4(3)	0.639 9(4)	0.358 3(2)	−0.120 7(2)	0.229 22(8)
C(7)	0.291 2(3)	0.679 9(5)	0.735 5(6)	0.366 1(4)	−0.108 2(2)	0.182 3(1)
O(7)	0.362 6(3)	0.729 1(4)	0.868 0(5)	0.425 9(3)	−0.156 0(2)	0.158 10(8)
C(8)	0.231 3(3)	0.741 2(4)	0.644 2(5)	0.289 8(4)	−0.030 4(2)	0.170 4(1)
C(9)	0.245 4(3)	0.876 6(4)	0.682 7(5)	0.290 9(4)	−0.007 5(2)	0.125 8(1)
C(10)	0.328 9(3)	1.015 8(4)	0.821 7(5)	0.226 7(4)	0.064 6(2)	0.101 1(1)
O(101)	0.282 8(2)	1.106 6(3)	0.821 4(4)	0.199 1(3)	0.041 9(2)	0.054 47(7)
C(101)	0.337 1(5)	1.241 8(7)	0.957 2(7)	0.113 2(5)	−0.028 2(3)	0.049 4(2)
O(102)	0.358 5(2)	0.998 7(3)	0.981 0(3)	0.109 3(3)	0.083 7(2)	0.124 90(8)
C(102)	0.274 5(2)	0.930 5(6)	1.041 8(7)	0.030 2(5)	0.150 6(3)	0.108 1(2)
C(11)	0.433 9(3)	1.091 3(5)	0.789 5(6)	0.319 4(4)	0.141 1(2)	0.096 2(1)
O(11)	0.473 0(2)	0.992 8(4)	0.769 0(4)	0.351 6(3)	0.176 1(2)	0.139 08(8)
C(12)	0.422 0(2)	1.134 3(5)	0.626 3(6)	0.448 2(4)	0.119 0(3)	0.069 8(1)
O(12)	0.341 5(4)	1.059 3(3)	0.506 5(4)	0.523 7(3)	0.070 2(2)	0.087 4(1)
C(121)	0.513 7(2)	1.270 7(4)	0.622 6(6)	0.483 0(4)	0.164 7(3)	0.025 3(1)
C(122)	0.616 1(3)	1.264 3(7)	0.677 9(9)	0.373 2(6)	0.157 2(4)	−0.010 4(2)
C(123)	0.526 7(6)	1.404 8(6)	0.743 0(9)	0.501 6(6)	0.256 6(3)	0.037 6(2)
C(124)	0.491 8(5)	1.282 2(7)	0.444 3(8)	0.610 9(6)	0.131 0(4)	0.005 8(2)

and after 60 min was poured into water and extracted with ether. Evaporation of the washed and dried extract left a residue with δ_H 1.22 (9 H, s, Bu^t), 1.39 (9 H, s, Bu^t), 3.67 (1 H, s), 3.79 (3 H, s, OMe), 5.05 (1 H, s), 6.86 (1 H, d, *J* 3 Hz, ArH), 7.02 (1 H, s), and 7.91 (1 H, d, *J* 3 Hz, ArH). Crystallization from methanol gave fine yellow needles (100 mg), m.p. 115—117 °C, believed to be the *hemiacetal* (**20**) (Found: C, 64.8; H, 7.3. $C_{22}H_{30}O_7$ requires C, 65.0; H, 7.45%); δ_H 1.10 (9 H, s, Bu^t), 1.40 (9 H, s, Bu^t), 3.50 (3 H, s, OMe), and 3.70 (3 H, s, OMe); $\nu_{max.}$ 3 520, 3 080br (bonded OH), and 1 695 cm^{-1} (CO); $\lambda_{max.}$(CCl_4) 255 (ε 7 600), 273 (9 300), and 392 nm (20 000); *m*/*z* (%) 388 (2), 306 (20), 305 (100), 275 (13), and 247 (25). This material was soluble in aqueous sodium hydroxide but not in aqueous sodium hydrogen carbonate.

(*b*) The acetal (**9**) (200 mg) in acetone (9 ml) containing hydrochloric acid (1 ml) and water (1 ml) was heated under reflux for 1 h. When the solution was worked up as for (*a*) and the residue crystallized from methanol the same material (160 mg), m.p. 115—117 °C, was obtained.

A solution of this in undried t-butyl alcohol deposited yellow prisms of the t-butyl alcohol solvate of (E)-3-(3′,4′-*dihydroxy*-5′-*t*-*butyl*-2′,5′-*dihydrofuran*-2′-*ylidene*)-5-*methoxy*-7-*t*-*butyl*-*benzofuran*-2(3H)-*one* (**18**), m.p. 109—110 °C; δ_H 1.10 (9 H, s, Bu^t), 1.29 (9 H, s, Bu^t), 1.39 (9 H, s, Bu^t), and 3.68 (3 H, s, OMe); $\nu_{max.}$ 3 520, 3 050 (bonded OH), and 1 695 cm^{-1} (CO); $\lambda_{max.}$(CCl_4) 258 (ε 8 100), 275 (8 100), and 392 nm (16 000); *m*/*z* (%) 374 (*M*$^+$, 87), 319 (20), 318 (100), 317 (40), 262 (77), 261 (18), and 247 (20). Recrystallization of this from methanol gave (**20**), m.p. 115—117 °C.

Recrystallization of either the crude hydrolysis product, or (**18**) or (**20**) from benzene–light petroleum gave small yellow plates of the *tautomer* (**19**), m.p. 152—155 °C (Found: C, 67.4; H, 7.1. $C_{21}H_{26}O_6$ requires C, 67.35; H, 7.0%); δ_H 1.10 (9 H, s, Bu^t), 1.39 (9 H, s, Bu^t), and 3.67 (3 H, s, OMe); $\nu_{max.}$ 3 520, 3 110 (bonded OH), and 1 710 and 1 700 cm^{-1} (CO); $\lambda_{max.}$(CCl_4) 255 (ε 7 400), 273 (11 500), and 392 nm (19 400); *m*/*z* 374 (*M*$^+$, 24%), 318 (39), 317 (29), 262 (37), 261 (16), and 247 (22). Recrystallization of the product from methanol gave (**20**), m.p. 115—117 °C.

Similar hydrolyses of compounds (**13**), (**14**), and (**15**) gave identical results.

(*c*) The acetal (**9**) (380 mg) was warmed in acetic acid (5 ml) and water (2.5 ml) to bring it into solution (orange) and this was set aside for 20 min. Water was added and the product was extracted with ether; the extract was then washed with aqueous sodium hydrogen carbonate and water, and dried. Evaporation left an orange residue which was crystallized from light petroleum to give colourless crystals (204 mg), m.p. 143—148 °C, to an orange liquid. Further recrystallizations from benzene–light petroleum and aqueous acetic acid deposited colourless crystals, also from orange solutions, of 3-(4′-*hydroxy*-3′-*oxo*-5′-*t*-*butyl*-2′,3′-*dihydrofuranyl*)-5-*methoxy*-7-*t*-*butyl*-*benzofuran*-2(3H)-*one* (**24**), m.p. 159—163 °C. Combustion analysis gave variable results; δ_H($CDCl_3$; 300 MHz) 0.96 (9 H, s, Bu^t), 1.36 (9 H, s, Bu^t), 3.69 (3 H, s, OMe), 4.21 (1 H, ddd, *J* 2.6 Hz, 1.0 Hz, 0.8 Hz, 3-H), 5.04 (1 H, d, *J* 2.6 Hz, 2-H), 6.32 (1 H, dd, *J* 2.7 Hz, 1.0 Hz, 4-H), 6.80 (1 H, dd, *J* 2.7 Hz, 0.8 Hz, 6-H), and 7.00 (1 H, br s, OH); δ_C($CDCl_3$; 300 MHz) 26.3 (q), 29.3 (q), 34.3 (s), 34.9 (s), 46.0 (d), 55.8 (q), 79.5 (d), 106.0 (d), 114.3 (d), 120.8 (s), 134.8 (s), 135.8 (s), 146.4 (s), 155.9 (s), 174.3 (s), 182.6 (s), and 196.0 (s); $\nu_{max.}$ 3 525, 3 250br (OH), 1 800, 1 705, and 1 680 cm^{-1} (CO); $\lambda_{max.}$(CCl_4) 254 (ε 4 700) and 295 nm (11 700); *m*/*z* (%) 374 (*M*$^+$, 7), 289 (31), 260 (6), 233 (21), 231 (21), 219 (10), 217 (13), 97 (31), and 57 (100). Recrystallization of the

Table 2. Non-hydrogen atom co-ordinates for compound (**18**)

	Molecule A			Molecule B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
C(1)	0.517 8(4)	0.492 9(3)	0.352 8(3)	0.569 2(4)	0.825 5(3)	−0.014 4(3)
C(2)	0.613 1(4)	0.511 8(3)	0.367 9(3)	0.660 0(4)	0.877 2(3)	−0.037 1(3)
C(3)	0.713 3(4)	0.469 2(3)	0.320 9(3)	0.762 6(4)	0.830 9(3)	−0.009 1(3)
O(3)	0.815 5(3)	0.479 5(3)	0.329 1(2)	0.850 7(3)	0.859 8(2)	−0.033 0(2)
C(31)	0.816 5(5)	0.542 8(4)	0.383 0(4)	0.956 4(5)	0.823 1(5)	−0.000 2(4)
C(4)	0.720 5(4)	0.411 5(3)	0.260 9(3)	0.775 6(5)	0.757 2(4)	0.040 2(3)
C(5)	0.627 2(4)	0.391 6(3)	0.243 1(3)	0.683 8(4)	0.730 4(3)	0.064 4(3)
C(51)	0.633 2(4)	0.330 0(3)	0.175 1(3)	0.697 8(5)	0.648 4(4)	0.115 7(4)
O(52)	0.606 7(5)	0.251 1(3)	0.209 3(4)	0.616 1(7)	0.675 4(5)	0.194 0(4)
C(53)	0.752 2(5)	0.296 7(4)	0.128 7(3)	0.666 1(7)	0.583 0(4)	0.070 2(5)
C(54)	0.547 3(5)	0.378 4(4)	0.116 4(3)	0.816 3(7)	0.607 1(5)	0.139 8(6)
C(6)	0.527 4(4)	0.433 5(3)	0.293 1(3)	0.583 6(4)	0.780 7(3)	0.036 5(3)
O(6)	0.423 6(3)	0.422 3(2)	0.289 3(2)	0.479 6(3)	0.767 4(2)	0.054 6(2)
C(7)	0.344 6(4)	0.475 4(3)	0.347 6(3)	0.397 2(4)	0.829 3(3)	0.015 3(3)
O(7)	0.246 3(3)	0.474 7(2)	0.354 3(2)	0.299 0(3)	0.829 9(2)	0.023 7(2)
C(8)	0.399 6(4)	0.522 3(3)	0.387 5(3)	0.450 9(4)	0.883 0(3)	−0.029 5(3)
C(9)	0.343 5(4)	0.586 5(3)	0.444 8(3)	0.396 6(4)	0.947 7(3)	−0.082 6(3)
C(10)	0.226 8(4)	0.625 7(3)	0.475 4(3)	0.284 3(4)	0.978 6(3)	−0.106 1(3)
O(10)	0.138 1(3)	0.605 3(2)	0.456 2(2)	0.196 1(3)	0.953 1(2)	−0.078 1(2)
C(11)	0.219 7(4)	0.689 0(3)	0.527 8(3)	0.279 5(4)	1.039 8(3)	−0.163 1(3)
O(11)	0.131 5(3)	0.741 5(2)	0.572 9(2)	0.193 5(3)	1.089 2(2)	−0.202 9(2)
O(12)	0.409 0(3)	0.623 7(2)	0.477 5(2)	0.461 2(3)	0.989 7(2)	−0.122 8(2)
C(12)	0.334 5(4)	0.693 5(3)	0.531 7(3)	0.392 2(4)	1.051 2(3)	−0.178 4(3)
C(121)	0.356 2(5)	0.778 1(3)	0.506 3(3)	0.456 0(4)	1.031 3(3)	−0.263 4(3)
C(122)	0.284 7(6)	0.849 8(4)	0.565 6(4)	0.463 3(6)	0.942 6(4)	−0.291 1(4)
C(123)	0.323 2(6)	0.802 9(4)	0.421 8(4)	0.391 3(6)	1.103 1(5)	−0.319 9(4)
C(124)	0.481 0(5)	0.763 3(4)	0.509 8(4)	0.575 2(5)	1.034 6(4)	−0.261 0(4)
t-Butyl alcohols						
O(1a)	0.159 0(4)	0.342 6(3)	0.315 7(2)	0.162 2(3)	0.772 4(2)	0.137 5(2)
C(1a)	0.158 4(5)	0.328 6(4)	0.232 4(3)	0.194 6(5)	0.687 5(4)	0.171 5(3)
C(11a)	0.274 3(6)	0.299 4(7)	0.192 1(6)	0.102 4(8)	0.681 6(5)	0.228 9(6)
C(12a)	0.099 8(8)	0.266 5(6)	0.222 3(5)	0.227(1)	0.624 0(6)	0.106 9(6)
C(13a)	0.092 5(9)	0.413 8(6)	0.198 7(6)	0.299(1)	0.672 0(8)	0.210 4(7)
O(1b)	−0.073 4(3)	0.745 8(3)	0.571 5(2)	−0.004 0(3)	1.076 9(3)	−0.196 9(3)
C(1b)	−0.146 1(5)	0.792 4(4)	0.514 9(4)	−0.036 8(5)	1.014 9(4)	−0.231 9(3)
C(11b)	−0.249 1(9)	0.856 3(7)	0.552 6(6)	−0.086(1)	1.048 5(6)	−0.302 3(7)
C(12b)	−0.085 0(7)	0.827 5(7)	0.452 2(6)	−0.124(1)	0.998 8(6)	−0.177 3(8)
C(13b)	−0.183 3(1)	0.727 3(7)	0.477 9(6)	0.062 8(7)	0.932 3(5)	−0.246 9(6)

product from methanol containing 1 drop of hydrochloric acid gave the hemiacetal (**20**), m.p. and mixed m.p. 115—117 °C.

3-(3′,4′-*Dioxo*-5′-*t*-*butyltetrahydrofuran*-2′-*ylidene*)-5-*methoxy*-7-*t*-*butylbenzofuran*-2(3H)-*one* (**25**).—DDQ (50 mg) was added to a stirred solution of the diol (**18**) (80 mg) in dioxane (5 ml). The solution immediately became dark crimson. After 2 h it was evaporated under reduced pressure. The dark residue was taken up in benzene and the dichlorodicyanohydroquinone was removed by filtration. Evaporation of the filtrate left a brown gum which was subjected to preparative t.l.c. on silica with light petroleum–ethyl acetate (7 : 3). A dark crimson band (12 mg) deposited small red crystals of the *trione* (**25**) from benzene–light petroleum, m.p. 174—177 °C; *m*/*z* % 372 (M^+, 5), 247 (9), and 126 (100).

Again, a solution of DDQ (50 mg) in dioxane was added to a solution of the diol (**18**) (70 mg) in dioxane and the mixture was stirred for 3 min; a solution of 1,2-diaminobenzene (22 mg) in dioxane was then added to give immediate discharge of the red colour. After 2 weeks water was added and the reaction mixture was extracted with ether. Evaporation of the washed and dried extract left a red gum (74 mg). This was taken up in dichloromethane and subjected to preparative t.l.c. on silica with dichloromethane. Crystallization of a red fraction (32 mg) from ethanol gave the *quinoxaline* (**26**) as bright red crystals, m.p. 219—221 °C (Found: C, 72.7; H, 6.35. $C_{27}H_{28}N_2O_4$ requires C, 72.9; H, 6.4%); $\delta_H(CDCl_3)$ 1.21 (9 H, s, Bu^t), 1.45 (9 H, s, Bu^t), 3.87 (3 H, s, OMe), 5.54 (1 H, s, 5-H), 6.87 (1 H, d, *J* 2.7 Hz, ArH), 7.45 (1 H, d, *J* 2.7 Hz, ArH), 7.88—7.91 (2 H, m, ArH), 8.14—8.18 (1 H, m, ArH), and 8.40—8.44 (1 H, m, ArH); $\nu_{max.}$ 1 775 cm^{-1} (furanone CO); *m*/*z* (%) 444 (M^+, 21), 383 (13), 373 (4), 198 (80), 197 (100), and 182 (82).

Structure Determinations.—Unique data sets were measured at 295 K within the specified $2\theta_{max.}$ limit using a Syntex $P2_1$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode (monochromatic Mo-K_α radiation, $\lambda = 0.7106_9$ Å). *N* Independent reflections were obtained, N_0 with $I > n\sigma(I)$ being considered 'observed' and used in the (large) block diagonal least-squares refinement without absorption correction after solution of the structure by direct methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (*x*, *y*, *z*, $U_{iso})_H$ were included at estimated values. Residuals on |*F*|, *R*, *R*′ at convergence are quoted using statistical weights derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0005\sigma^4(I_{diff})$. Neutral atom complex scattering factors were used;[9] computation used the XTAL 83

Table 3. Non-hydrogen interatomic distances (Å): the two values for compound (**18**) are for molecules A, B respectively

Atoms	(**9**), (**14**)	(**18**)
C(1)–C(2)	1.381(6), 1.392(5)	1.392(6), 1.360(7)
C(1)–C(6)	1.381(7), 1.391(5)	1.385(7), 1.398(7)
C(1)–C(8)	1.457(4), 1.462(5)	1.447(6), 1.479(7)
C(2)–C(3)	1.388(5), 1.386(5)	1.372(6), 1.369(7)
C(3)–C(4)	1.392(8), 1.390(5)	1.387(8), 1.410(8)
C(3)–O(3)	1.372(5), 1.384(5)	1.376(7), 1.369(7)
O(3)–C(31)	1.410(9), 1.429(5)	1.402(8), 1.416(7)
C(4)–C(5)	1.380(7), 1.397(5)	1.388(8), 1.390(9)
C(5)–C(6)	1.391(5), 1.390(5)	1.390(8), 1.357(8)
C(5)–C(51)	1.523(8), 1.535(5)	1.526(7), 1.536(8)
C(51)–C(52)	1.525(6), 1.537(6)	1.523(8), 1.546(9)
C(51)–C(53)	1.523(9), 1.537(5)	1.525(7), 1.522(12)
C(51)–C(54)	1.539(11), 1.529(6)	1.531(7), 1.496(10)
C(6)–O(6)	1.401(5), 1.410(4)	1.390(7), 1.400(7)
O(6)–C(7)	1.390(5), 1.377(4)	1.386(5), 1.376(5)
C(7)–C(8)	1.490(8), 1.498(5)	1.424(8), 1.434(8)
C(7)–O(7)	1.207(6), 1.199(5)	1.233(7), 1.223(7)
C(8)–C(9)	1.335(7), 1.343(5)	1.384(6), 1.392(6)
C(9)–C(10)	1.509(5), 1.501(5)	1.418(6), 1.417(7)
C(10)–C(11)	1.549(7), 1.541(6)	1.353(7), 1.351(7)
C(10)–O(101)	1.423(7), 1.426(4)	1.347(7), 1.350(7)
C(10)–O(102)	1.406(6), 1.405(5)	— —
O(101)–C(102)	1.438(6), 1.420(5)	— —
C(102)–C(101)	1.431(7), 1.416(5)	— —
O(11)–C(12)	1.544(8), 1.550(6)	1.480(8), 1.487(8)
C(11)–O(11)	1.424(7), 1.401(4)	1.310(5), 1.330(6)
C(9)–O(12)	— —	1.352(7), 1.352(6)
C(12)–O(12)	1.206(5), 1.203(5)	1.458(5), 1.461(5)
C(12)–C(121)	1.516(6), 1.520(5)	1.541(8), 1.539(7)
C(121)–C(122)	1.543(9), 1.522(7)	1.517(7), 1.507(9)
C(121)–C(123)	1.528(9), 1.517(6)	1.523(8), 1.538(8)
C(121)–C(124)	1.530(8), 1.508(7)	1.507(9), 1.524(9)

program system[10] implemented on a Perkin-Elmer 3240 computer by S. R. Hall. Pertinent results are given in the Figures and Tables. Thermal and hydrogen atom and t-butyl group parameters are available on request from the Cambridge Crystallographic Data Centre.*

Crystal data. (**9**). $C_{23}H_{32}O_7$, M = 420.5, Triclinic, space group $P\bar{1}$(C_i^1, No. 2), a = 15.124(14), b = 10.678(9), c = 8.619(6) Å, α = 99.40(6), β = 103.89(6), γ = 116.18(6)°, U = 1 153(1) Å^3 D_c (Z = 2) = 1.21 g cm^{-3}. F(000) = 452. μ_{Mo} = 0.96 cm^{-1}. Specimen: 0.46 × 0.34 × 0.25 mm. $2\theta_{max.}$ = 50°. N = 3 046, N_0 = 2 172 (n = 3). R = 0.064, R' = 0.069.

(**14**). $C_{23}H_{32}O_7$, M = 420.5, Orthorhombic, space group $Pbca$ (D_{2h}^{15}, No. 61) a = 10.095(5), b = 15.908(10), c = 29.00(2) Å, U = 4 657(5) Å^3. D_c (Z = 8) = 1.20 g cm^{-3}. F(000) = 1 808. μ_{Mo} = 0.95 cm^{-1}. Specimen: *ca.* 0.2 mm. $2\theta_{max.}$ = 50°, N = 2 875, N_0 = 2 023 (n = 2). R = 0.059, R' = 0.049.

(**18**). $C_{29}H_{44}O_8$, M = 520.7, Triclinic, space group $P\bar{1}$, a = 12.572(3), b = 16.361(6), c = 16.773(6) Å, α = 88.04(3), β = 83.54(2), γ = 69.13(3)°, U = 2 303(2) Å^3. D_c (Z = 4) = 1.08 g cm^{-3}. F(000) = 1 128. μ_{Mo} = 0.83 cm^{-1}. Specimen: 0.4 × 0.4 × 0.5 mm (capillary). $2\theta_{max.}$ = 40°. N = 5 578, N_0 = 4 005 (n = 2). R = 0.067, R' = 0.070.

Abnormal features. The presence of t-butyl groups presented the usual problems associated with high thermal motion. Following an initial determination of (**18**), the material was regrown to optimum size and the data measured very slowly and used at the 2σ(I) level in an effort to locate definitively the hydrogen atoms. In certain cases, (see below), it was possible to refine these, but some could not be located at all.

* See Instruction for Authors (1989), *J. Chem. Soc., Perkin Trans. 1*, 1989, Issue 1.

Table 4. Non-hydrogen interatomic angles (°) for compounds (**9**) and (**14**). The two values for compound (**18**) are for molecules A, B respectively

Atoms	(**9**), (**14**)	(**18**)
C(2)–C(1)–C(6)	120.8(3), 119.7(3)	120.0(4), 118.9(4)
C(2)–C(1)–C(8)	131.6(5), 133.8(3)	134.0(4), 135.5(4)
C(6)–C(1)–C(8)	107.6(4), 106.5(3)	106.0(5), 105.6(4)
C(1)–C(2)–C(3)	116.9(5), 116.9(5)	116.6(5), 118.6(5)
C(2)–C(3)–C(4)	120.4(4), 122.1(3)	122.5(5), 121.3(5)
C(2)–C(3)–O(3)	124.7(5), 123.0(3)	123.8(5), 116.0(5)
C(4)–C(3)–O(3)	114.9(3), 114.8(3)	113.7(4), 122.7(4)
C(3)–O(3)–C(31)	118.4(3), 117.4(3)	118.4(4), 120.4(4)
C(3)–C(4)–C(5)	124.4(4), 122.4(3)	122.9(4), 121.2(5)
C(4)–C(5)–C(6)	113.1(5), 113.9(5)	113.5(5), 114.5(5)
C(4)–C(5)–C(51)	122.6(3), 123.4(3)	123.3(4), 121.7(5)
C(6)–C(5)–C(51)	124.2(4), 122.7(3)	123.1(5), 123.8(6)
C(5)–C(51)–C(52)	112.5(5), 108.9(3)	109.8(4), 108.5(5)
C(5)–C(51)–C(53)	111.1(5), 111.0(3)	111.4(5), 109.6(6)
C(5)–C(51)–C(54)	108.0(4), 110.2(3)	109.6(4), 112.4(6)
C(52)–C(51)–C(53)	107.7(4), 108.1(3)	108.0(4), 109.0(7)
C(52)–C(51)–C(54)	108.3(5), 110.0(3)	110.0(5), 106.7(6)
C(53)–C(51)–C(54)	109.3(6), 108.6(3)	108.0(4), 110.4(6)
C(1)–C(6)–C(5)	124.4(4), 124.9(3)	124.5(5), 125.4(5)
C(1)–C(6)–O(6)	111.1(3), 112.0(3)	110.8(4), 110.1(4)
C(5)–C(6)–O(6)	124.5(4), 123.1(3)	124.7(5), 124.5(5)
C(6)–O(6)–C(7)	108.4(4), 107.7(3)	107.8(4), 108.8(4)
O(6)–C(7)–C(8)	107.8(3), 108.6(3)	108.4(4), 107.6(4)
O(6)–C(7)–O(7)	118.7(5), 121.1(3)	118.0(5), 119.4(5)
C(8)–C(7)–O(7)	133.5(5), 130.4(3)	133.5(4), 133.0(4)
C(1)–C(8)–C(7)	105.0(4), 105.2(3)	106.9(4), 107.9(4)
C(1)–C(8)–C(9)	125.3(4), 138.6(4)	129.1(5), 127.9(5)
C(7)–C(8)–C(9)	129.7(3), 116.3(3)	123.9(5), 124.0(5)
C(8)–C(9)–C(10)	131.9(4), 131.7(3)	132.8(5), 132.7(5)
C(9)–C(10)–C(11)	113.2(4), 112.6(3)	107.4(5), 107.6(5)
C(9)–C(10)–O(101)	103.1(4), 110.2(3)	127.1(4), 127.6(4)
C(9)–C(10)–O(102)	115.2(4), 107.1(3)	— —
C(11)–C(10)–O(101)	110.1(4), 103.4(3)	125.5(4), 124.8(4)
C(11)–C(10)–O(102)	104.1(4), 112.7(3)	— —
O(101)–C(10)–O(102)	111.3(4), 110.9(3)	— —
C(10)–O(101)–C(101)	117.0(4), 114.6(3)	— —
C(10)–O(102)–C(102)	115.5(4), 118.0(3)	— —
C(10)–C(11)–C(12)	113.3(4), 112.1(3)	109.8(4), 109.9(4)
C(10)–C(11)–O(11)	109.8(4), 112.0(3)	130.6(5), 131.1(5)
C(12)–C(11)–O(11)	105.3(4), 109.5(3)	119.6(5), 119.0(4)
C(11)–C(12)–O(12)	119.7(4), 117.9(3)	103.4(4), 103.0(4)
C(11)–C(12)–C(121)	118.1(3), 120.4(3)	119.4(4), 118.0(5)
O(12)–C(12)–C(121)	122.2(5), 121.5(4)	107.8(4), 108.4(3)
C(12)–C(121)–C(122)	110.5(5), 111.8(4)	108.2(4), 110.3(5)
C(12)–C(121)–C(123)	108.6(5), 106.9(3)	109.7(5), 108.3(4)
C(12)–C(121)–C(124)	109.7(3), 110.3(4)	108.8(4), 108.1(5)
C(122)–C(121)–C(123)	109.3(4), 109.0(4)	110.5(4), 110.7(5)
C(122)–C(121)–C(124)	108.9(5), 109.9(4)	108.9(5), 110.7(5)
C(123)–C(121)–C(124)	109.8(5), 108.9(4)	110.6(5), 108.6(6)
C(8)–C(9)–O(12)	— —	116.2(4), 116.4(4)
C(10)–C(9)–O(12)	— —	111.0(4), 110.9(4)
C(9)–O(12)–C(12)	— —	108.4(3), 108.6(4)

Structural commentary. The stoicheiometries and connectivities are consistent with those given above for compounds (**9**), (**14**), and (**18**); (**18**) is a disolvate of t-butyl alcohol. In spite of high t-butyl thermal motion, molecular skeletal geometries are tolerably precise and are compared in Tables 3 and 4. Compound (**18**) deserves special comment below; the following features may be generally noted.

(a) The usual angular asymmetry at the point of attachment of the methoxy groups at C(3) is observed in each case, the

Table 5. O · · · H, O contacts (Å) for compound (**18**)

Atoms	Molecule A	Molecule B
O(7) · · · O(10)	2.643(5)	2.657(5)
O(7) · · · H(10)	1.73(4)	1.62(4)
H(10) · · · O(10)	0.94(4)	1.06(4)
O(10) · · · H(11) · · · O(7)	164(5)	167(5)°
O(11) · · · O(1b)	2.555(6)	2.553(6)
O(11) · · · H(11)	1.33(5)	1.37(5)
O(1b) · · · H(11)	1.25(5)	1.18(5)
O(11) · · · H(11) · · · O(1b)	162(4)	176(4)°
O(7) · · · O(1a)	2.872(7)	2.789(6)
(no associated hydrogen refined)		
O(1a) · · · O(1b)*	2.700(6)	2.693(5)

* Transformation of the asymmetric unit: Molecule A: ($\bar{x}$, 1 − y, 1 − z). Molecule B: ($\bar{x}$, 2 − y, $\bar{z}$).

Table 6. Intra-dimer charge-transfer contacts for compound (**18**). The two atoms are inversion related; the criterion for inclusion is that at least one of the pairs of contacts (*i.e.* dimers A, B) is less than 3.7 Å

Atoms	Pair A	Pair B
C(3) · · · C(11)	3.512(7)	3.516(7)
C(3) · · · C(10)	3.745(7)	3.555(8)
O(3) · · · C(11)	3.707(6)	3.665(6)
O(3) · · · C(10)	3.725(6)	3.412(6)
O(3) · · · O(10)	3.846(5)	3.471(6)
C(2) · · · C(9)	3.489(7)	3.371(7)
C(2) · · · O(12)	3.406(6)	3.373(5)
C(2) · · · C(12)	3.583(7)	3.753(7)
C(2) · · · C(10)	3.685(7)	3.711(8)
C(1) · · · O(12)	3.399(5)	3.408(6)
C(1) · · · C(12)	3.587(6)	3.798(7)
C(8) · · · O(12)	3.658(5)	3.837(6)

Close contacts (H · · · C, < 3 Å) involving H(12) are to (dimer A) C(1), 2.8_9 Å; (dimer B) C(5,6), 2.9_3, 2.9_6 Å.

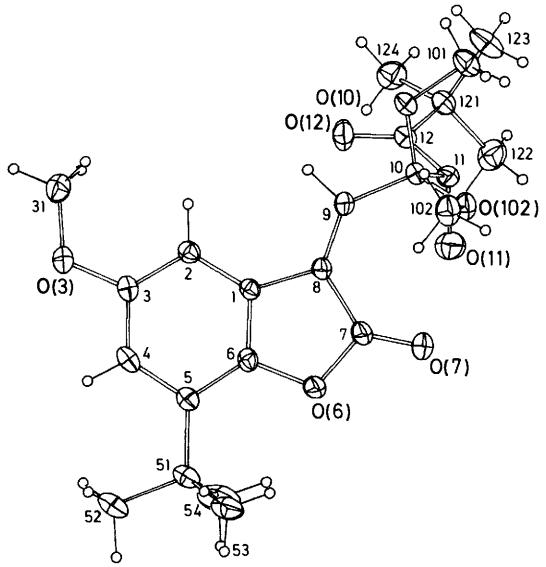


Figure 1. Projection of compound (**9**) perpendicular to the fused aromatic plane. 20% Thermal ellipsoids and atom labelling are shown for the non-hydrogen skeletal atoms. Hydrogen atoms have arbitrary radii of 0.1 Å

Table 7. Least-squares planes for compound (**18**). Least-squares planes are given in the form $pX + qY + rZ = s$; the r.h. orthogonal Å frame has X parallel to a, Z in the ac plane. Atom deviations are in Å. The angle between the two planes is 86.3°

	Molecule A	Molecule B
10^4p	374	560
10^4q	−6 535	6 296
10^4r	7 038	7 531
s	−0.903	8.948
χ^2	2 536	2 239
Defining atom deviations		
C(1)	0.04	0.05
C(2)	0.06	0.08
C(3)	0.01	0.03
C(4)	−0.08	−0.09
C(5)	−0.12	−0.13
C(6)	−0.02	−0.03
O(6)	0.00	−0.02
C(7)	0.08	0.07
C(8)	0.08	0.09
C(9)	0.04	0.05
C(10)	−0.07	−0.07
C(11)	−0.13	−0.10
C(12)	−0.08	−0.10
O(12)	0.06	0.02
Other atom deviations		
C(51)	−0.26	−0.32
O(3)	0.04	0.09
C(3)	0.00	0.20
O(7)	0.13	0.11
O(10)	−0.12	0.02
O(11)	−0.20	−0.15
C(121)	−1.271	−1.330

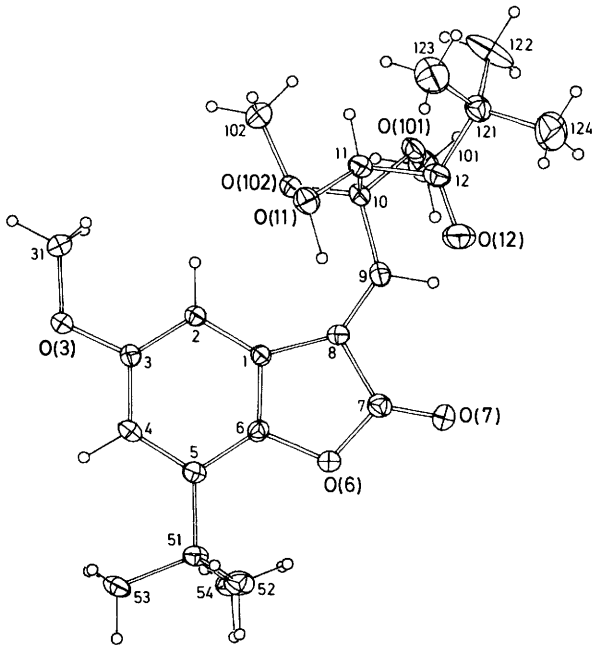


Figure 2. Projection of compound (**14**)

methoxy group being substantially co-planar with aromatic rings but, nevertheless, with the methyl crowding the nearby aromatic hydrogen.

(b) The dispositions of the t-butyl substituents at C-5 are all

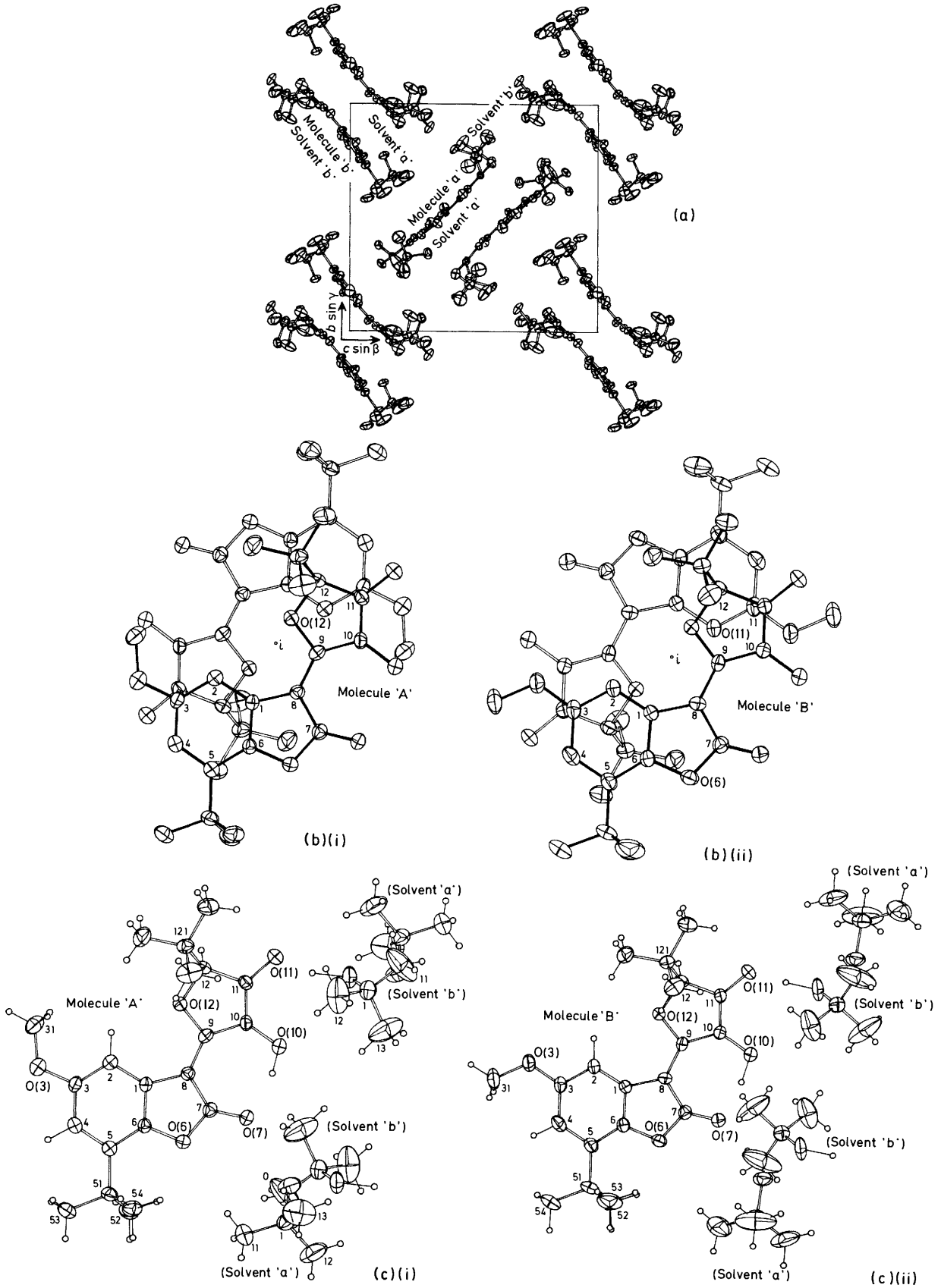


Figure 3. (*a*) Unit cell contents of compound (**18**) projected down *a*, showing the pseudo-symmetric packing, together with the dimer arrays and the two solvent molecules in association with each parent; (*b*) (*i*) (*ii*) Projection of each of the parent molecules onto the plane of its inversion image. (*c*) (*i*) (*ii*) Projection of each molecule in association with its two solvent molecules, showing also the relation of the latter with further symmetry related solvent species (parentheses)

similar with one methyl group in-plane and directed toward H(4). The intra-ring angles at C(3,5) are diminished well below the trigonal norm in all cases, and also at C(2), with compensatingly large angles observed at C(4,6).

(c) Considerable differences are observed in the geometry about CO(7) in respect of compounds (**9**) and (**14**); *cf.* (**18**), presumably a consequence of involvement in the latter in hydrogen-bonding (see below).

(d) The C(8)–C(9) bond in (**9**) and (**14**) is consistent in length with a substantially localized double bond. The exocyclic angles at C(8) in (**9**) and (**14**) differ markedly in consequence of the reorientation of the C(9) substituent.

Molecular skeletal stoicheiometry and connectivity are consistent with that given above; the hydrogen atom disposition remains somewhat dubious and is the subject of further speculative discussion below. The lattice array itself is complex and interesting. The molecules pack as centrosymmetric pairs (Figure 3), presumably a consequence of intermolecular charge-transfer contacts, the closest of these being listed in Table 5. (Non-trivial disagreement between these for the two independent dimers is assumed to be the result of differing methoxy group disposition; see below). Although the three rings of each skeleton are substantially coplanar (Table 7), it is of interest to observe the deviation from their skeletal plane by C(10—12) on the side of C(121) in each case, presumably a consequence of the need to accommodate H(12) as meat in the intermolecular sandwich. H(12) Lies toward the centre of the benzene ring at distances given in Table 6. Within the unit cell (Figure 3), packing exhibits a high degree of pseudo-symmetry; the non-achievement of potentially higher symmetry, highlighted by the well-ordered but differeing dispositions of the methoxy substituents in the two molecules, provides interesting food for thought in regard to enthalpy/entropy interactions in crystal packing.

The nature of the molecular species cannot be considered in isolation from their interactions with the solvent. H(10) Has been located in difference maps and refined in terms of its co-ordinates for each molecule; although hydrogen-bonded toward nearby O(7), it is undoubtedly localised on O(10) (Table 5) in each case, although C(10)–O(10) is similar in length to C(11)—O(11). Here, hydrogen H(11) has also been similarly located and refined, but its role is much more equivocal, being disposed in a linear hydrogen bond midway between O(11) and O(1b) in each case, with C(11)–O(11) correspondingly less than a single bond distance. A similar interaction is suggested by the proximity of O(1a) to O(7) (Table 5) but in this case no associated hydrogen atom has been located and refined and the C(13)–O(13) distance is much more definitively of integral bond order, being ketonic. Although a rational hydrogen bonding sequence can be postulated O(11)···H(11)···O(1b)···[H(1b)]···O(1a)···[H(1a)]···O(7), the inability to locate and refine the solvent atoms leaves an unresolved query in this regard. In terms of this model, the C(11)–O(11) ···H(11) bond and related lengths render a description in terms of C(11)–OH(11) inadequately simplistic.

One further peculiarity may be noted in regard to the aromatic ring geometry. The only significantly different distances between molecules A and B [apart from C(11)–O(11)] are found here, in regard to C(1)–C(2), C(3)–C(4), C(5)–C(6). In molecule A, these are impeccably aromatic, with a regular array right around the ring; in molecule B C(1)–C(2), C(5)–C(6) are short and C(3)–C(4) long. It seems unlikely that the methoxy disposition is directly responsible for this; nevertheless, it may be a secondary cause, in directing the position of H(12) of the dimer, which may account for the anomaly, since these hydrogen atoms differ rather widely in the closeness of their interaction with the benzene ring [H(12)···C(1—6): molecule A, 2.8_9, 3.0_6, 3.1_3, 3.1_2, 3.0_4, 2.8; molecule B, 3.2_1, 3.3_4, 3.2_2, 3.0_3, 2.9_3, 2.9_6 Å].

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