Medium-sized Cyclophanes.   Part XV.   10,15-Dihydro-5*H*-tribenzo-[*a,d,g*]cyclononene and Analogues

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The preparation of the title compounds based on a novel cycloalkylation reaction of benzene is described. [1]H and [13]C N.m.r. spectra support the structures. A rigid crown conformation similar to that of cyclotriveratrylene is assigned to carbocycle (IIa) and the sulphur analogues (IId and e). On the other hand, the oxygen analogue (IIc) undergoes a ready inversion between two crown forms, which can be frozen at −90°. Ketone (IIb) is also a flexible molecule. The dependence of structural parameters on the conformational mobility is discussed. The mass spectrum of the sulphone (IIe) reveals ready extrusion of water on electron impact indicating a transannular proximity effect in the nine-membered ring.

COMPARED with the extensive studies on cyclophanes [2] and other bridged aromatics with one or two aromatic rings, only a limited number of compounds containing three or more aromatic rings have been investigated.[3] Many of these are oligomers formed as by-products during the synthesis of the lower members.[4] Compounds with three benzene rings whose conformational aspects have been studied include bridged biphenyls [5] and ter-phenyls,[6] tri-*o*-salicyclides,[7] [2.1.1]metacyclophane,[8] and cyclotriveratrylene (CTV).[9]

CTV and its derivatives have revealed interesting conformational properties with regard to the mobility and the stability of the cyclononatriene system. In order to examine other structural variations we wished to prepare the parent ring system of CTV and some heterocyclic analogues. This paper describes the preparation, ^{1}H and [13]C n.m.r. spectra, and mass spectra of 10,15-dihydro-5*H*-tribenzo[*a,d,g*]cyclononene (IIa) and the analogues (IIc—e).[10]

Synthesis.—To construct a nine-membered ring we utilized the acid-catalysed cycloalkylation of benzene with diol (I) under high dilution conditions. The procedure is that used to prepare the novel 13-membered compound [2.1.1]metacyclophane.[8]

Compound (IIa) was prepared in 75% yield by slow addition of 2,2′-bis(hydroxymethyl)diphenylmethane (Ia) as a dilute benzene solution to benzene–concentrated H_2SO_4 at room temperature. It showed a parent ion peak at m/e 270 and correctly analysed for $C_{21}H_{18}$. Similarly, 10,15-dihydrotribenzo[*b,e,h*]-oxonin (IIc) and

[1] Part XIV, T. Sato, T. Akima, and K. Uno, preceding paper.

[2] D. J. Cram, *Rec. Chem. Progr.*, 1959, **20**, 71; R. W. Griffin, jun., *Chem. Rev.*, 1963, **63**, 45; T. Sato, *Kagaku no Ryoiki*, 1969, **23**, 672, 765; *Nippon Kagaku Zasshi*, 1971, **92**, 277; D. J. Cram and J. M. Cram, *Accounts Chem. Res.*, 1971, **4**, 204; F. Vögtle and P. Neumann, *Angew. Chem., Internat. Edn.*, 1972, **11**, 73.

[3] B. H. Smith, 'Bridged Aromatic Compounds,' Academic Press, New York, 1964; N. Sommer and H. A. Staab, *Tetrahedron Letters*, 1966, 2837; T. Inazu and T. Yoshino, *Bull. Chem. Soc. Japan*, 1968, **41**, 647; H. Staab, H. Bräunling and K. Schneider, *Chem. Ber.*, 1968, **101**, 879.

[4] W. Baker, J. F. W. McOmie, and J. M. Norman, *J. Chem. Soc.*, 1951, 1114; D. J. Cram and K. C. Dewhirst, *J. Amer. Chem. Soc.*, 1959, **81**, 5963; K. Burri and W. Jenny, *Helv. Chim. Acta*, 1967, **50**, 1978; R. Flammang, H. P. Figeys, and R. H. Martin, *Tetrahedron*, 1968, **24**, 1171.

[5] F. Vögtle, *Annalen*, 1969, **728**, 17; F. Vögtle and P. Neumann, *Tetrahedron*, 1970, **26**, 5299.

[6] F. Vögtle and L. Schunder, *Annalen*, 1969, **721**, 129; F. Vögtle, *Chem. Ber.*, 1969, **102**, 1449.

[7] A. P. Downing, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc. (B)*, 1970, 24; *Chem. Comm.*, 1967, 171; 1968, 329.

[8] T. Sato, M. Wakabayashi, and K. Hata, *Bull. Chem. Soc. Japan*, 1970, **43**, 3632.

[9] A. S. Lindsey, *Chem. and Ind.*, 1963, 823; *J. Chem. Soc.*, 1965, 1685; H. Erdtman, F. Haglid, and R. Ryhage, *Acta Chem. Scand.*, 1964, **18**, 1249; A. Goldup, A. B. Morrison, and G. W. Smith, *J. Chem. Soc.*, 1965, 3864.

[10] Preliminary account, T. Sato, K. Uno, and M. Kainosho, *J.C.S. Chem. Comm.*, 1972, 579.

-thionin (IId) were prepared from the diols (Ic and d). Yields of (IIc) and (IId) were 41 and 83% respectively. The low yield of the oxonin is due to partial sulphonation. When the diol solution was added rapidly to

a; X = CH$_2$
b; X = C=O
c; X = O
d; X = S
e; X = SO$_2$
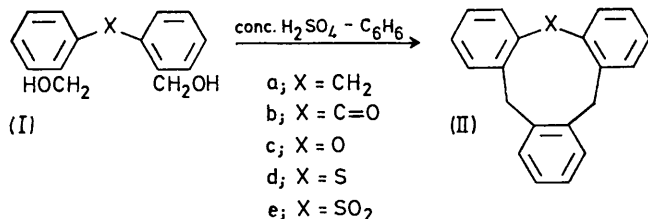
the benzene–H$_2$SO$_4$ mixture, the yield of (II) was considerably lowered. While polyphosphoric acid could be used as a condensing agent to make (IIa), trifluoroacetic acid and HSbF$_6$ were ineffective.
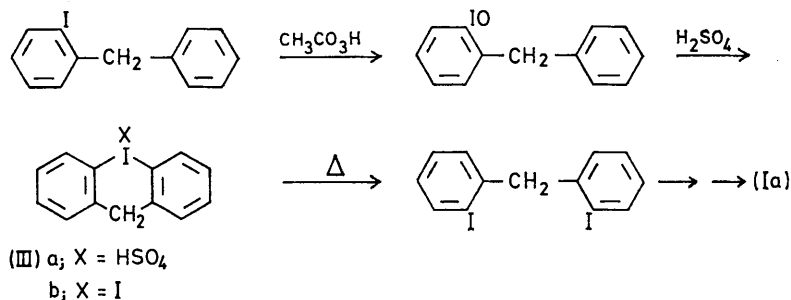
TABLE 1

M.p.s and analytical data for 10,15-dibenzo-5H-tribenzo-[a,d,g]cyclononene and analogues (II)

Compound	M.p. (°C)	Formula	Carbon (%) Calc.	Carbon (%) Found	Hydrogen (%) Calc.	Hydrogen (%) Found
(IIa)	274—276	C$_{21}$H$_{18}$	93·3	93·3	6·7	6·65
(IIb)	214·5—216	C$_{21}$H$_{16}$O	88·7	88·4	5·65	5·75
(IIc)	194·5—195	C$_{20}$H$_{16}$O	88·2	88·2	5·9	6·05
(IId)	218—219	C$_{20}$H$_{16}$S ^{a}	83·3	83·7	5·6	5·65
(IIe)	208·5—210	C$_{20}$H$_{16}$O$_2$S ^{b}	75·95	74·95	5·05	5·1

^{a} Found: S, 10·9. C$_{20}$H$_{16}$S requires S, 11·1%. ^{b} Found: S, 10·0. C$_{20}$H$_{16}$O$_2$S requires 10·0%.

Oxidation of (IIa) gave the monoketone (IIb), which showed carbonyl absorption at 1640 cm^{-1} and u.v. maxima at 245·5, 268·5, 294, and 303 nm (hexane). The sulphone (IIe), $\nu_{max.}$ 1315, 1298, and 1150 cm^{-1}, was obtained by oxidation of compound (IId). Table 1 lists the m.p.s, molecular weights, and analytical data

iodide in the same way as with dibenziodolium halides [12,13] gave a high yield of 2,2′-di-iododiphenylmethane, from which compound (Ia) was prepared by the sequence I $\longrightarrow$ CN $\longrightarrow$ CO$_2$Me $\longrightarrow$ CH$_2$OH. Compounds (Ic and d) were prepared from 2,2′-dimethyldiphenyl oxide and sulphide respectively. Bisbromomethyl derivatives obtained by treatment with N-bromosuccinimide were converted into the diacetates, which were then hydrolysed.

[13]C and [1]H N.m.r. Spectra.—The structures were confirmed by n.m.r. measurements. The conformational details were studied by variable temperature [1]H n.m.r. Table 2 shows natural abundance 25·2 MHz

TABLE 2

[13]C Chemical shifts in 10,15-dihydrotribenzo[b,e,h]-oxonin (IIc) and -thionin (IId) ^{a}

Compound	Methylene carbons	Aromatic carbons
(IIc)	35·0	121·3, 124·4, 126·4, 127·3, 129·9, 130·3, 134·4,^{b} 138·5,^{b} 156·3 ^{b}
(IId)	38·4	126·6, 127·0, 129·4, 129·9, 135·2,^{b} 136·8, 140·0,^{b} 145·8 ^{b}

^{a} Spectra were recorded for CDCl$_3$ solutions and the chemical shifts are shown in p.p.m. downfield from tetramethylsilane. ^{b} Quaternary carbons shown by comparison with the off-resonance spectra.

[13]C n.m.r. data for compounds (IIc and d). The spectral assignments were aided by wide-band proton decoupling and off-resonance methods.

The proton-decoupled spectrum of (IId) is shown in Figure 1. The aromatic carbon region is shown in Figure 2 together with the corresponding off-resonance spectrum. Both compounds (IIc and d) showed one methylene carbon and nine aromatic carbon resonances as expected from the structure. Three resonances which

(III) a; X = HSO$_4$
b; X = I

SCHEME

for compounds (IIa—e). The Scheme shows the preparation of compound (Ia) starting from 2-iododiphenylmethane. 2-Iodosyldiphenylmethane obtained by oxidation of 2-iododiphenylmethane was converted to dibenziodininium hydrogen sulphate (IIIa), from which the iodide (IIIb), was prepared by an ion exchange reaction.[11] The thermal decomposition of the iodininium

have no proton-induced splitting can be assigned to quaternary carbons.

The ^{13}C chemical shifts have been correlated with the π electron density of substituted benzenes.[14] The aromatic carbon resonances for compounds (II) can be interpreted by considering the charge density on the specific carbon atom. The lowest field signal which has

[11] J. Collette, D. McGreer, R. Crawford, F. Chubb, and R. B. Sandin, $J. Amer. Chem. Soc.$, 1956, **78**, 3819.

[12] H. Heaney and P. Lees, $Tetrahedron$, 1968, **24**, 3717.

[13] T. Sato, S. Shimada, K. Shimizu, and K. Hata, $Bull. Chem. Soc. Japan$, 1970, **43**, 1918; T. Sato, K. Shimizu, and A. Moriya, unpublished results.

[14] P. C. Lauterbur, $J. Amer. Chem. Soc.$, 1961, **83**, 1838; $J. Chem. Phys.$, 1965, **43**, 360; H. Spiesecke and W. G. Schneider, $Tetrahedron Letters$, 1961, 468; $J. Chem. Phys.$, 1961, **35**, 731; E. A. La Lancette and R. E. Benson, $J. Amer. Chem. Soc.$, 1965, **87**, 1941; V. Koptyna, A. Rezvukhin, E. Lippmaa, and T. Pehk, $Tetrahedron Letters$, 1968, 4009.

no proton-induced splitting can be assigned to carbons connected directly to the electronegative heteroatoms.

Another factor which affects ^{13}C chemical shifts is the conformational effect. This has been recognized

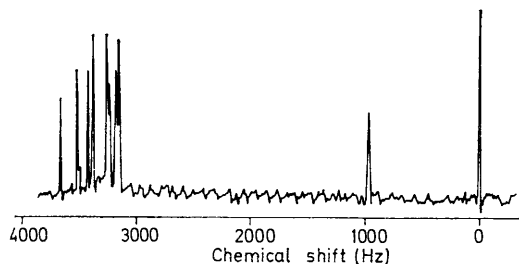FIGURE 1   The natural abundance, proton decoupled ^{13}C n.m.r. spectrum of 10,15-dihydrotribenzo[b,e,h]thionin (IId) (tetramethylsilane as reference)
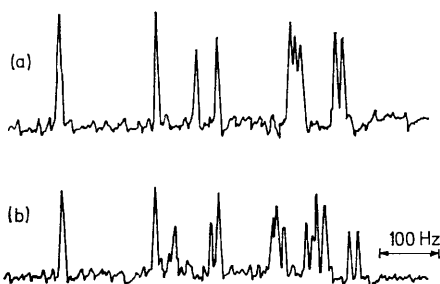
FIGURE 2   The aromatic carbon resonances of 10,15-dihydrotribenzo[b,e,h]thionin (IId): (a) proton decoupled and (b) off-, resonance spectra

for many cyclic systems, such as cyclohexanes and their heterocyclic analogues.[15] A large difference in the positions of the methylene carbon resonances (3·4 p.p.m.) between (IIc and d) indicates differences in the molecular geometry.

has been assigned based on the u.v. and n.m.r. spectra.[16,17] The AB quartet of the benzyl protons does not vary at high temperatures indicating the rigidity of the geometry.[16,17] This restriction of ring inversion was demonstrated by the optical resolution of a chiral molecule related to CTV.[18]

Crown geometry can be assigned to (IIa) since it shows an AB quartet similar to that of CTV both as regards the chemical shift and the coupling constants. The quartet determined in $CDBr_3$ was unchanged up to 150° (60 MHz) suggesting a high energy barrier to inversion. Likewise, both the sulphide (IId) and sulphone (IIe) exist in the rigid crown conformation since they also show the AB quartet.

The large chemical shift difference between δ_A and δ_B is also indicative of the crown form. The lowfield methylene proton resonances in (IIa) and CTV can be assigned to the quasi-axial protons which experience steric compression[19] caused by overcrowding at the top of the crown. This was verified by the observation that the downfield shift was even greater for the sulphur analogues. The large difference in compound (IIe) (2·10 p.p.m.) suggests a van der Waals interaction of the inward sulphonyl oxygen atom with the quasi-axial protons.

On the other hand, both ketone (IIb) and oxide (IIc) showed a singlet for the methylene protons. That this was not a fortuitous coincidence in the chemical shifts was proved by running the spectra in several solvents, in all of which the resonance remained a singlet. On lowering the temperature, the singlet for (IIc) began to broaden and at −90° it separated into two broad peaks at δ 3·75 and 4·85. The chemical shifts are typical of those of crown compounds, and indicate that (IIc) is frozen in the crown form. At

TABLE 3

^{1}H N.m.r. data for 10,15-dihydro-5H-tribenzo[a,d,g]cyclononene and analogues (II) [a]

| Compound | Methylene protons | | | | T_c (°C) (Solvent) [e] | Aromatic protons |
	H_{eq}	H_{ax}	$\Delta\delta$	J/Hz		
CTV [b]	3·57 (d)	4·82 (d)	1·25	13·5	>200 (CCl_3COCCl_3)	6·89 (s)
(IIa)	3·74 (d)	4·90 (d)	1·16	13	>150 ($CDBr_3$)	7·25 (m) (AA'BB')
(IIb)	3·85 (s)				<−90 (CD_2Cl_2)	6·98—8·05 (m)
(IIc)	4·29 (s)				<−81 (CD_2Cl_2)	7·02—7·45 (m)
	3·75br [d]	4·85br [d]	1·10 [d]			
(IId)	3·78 (d)	5·65 (d)	1·89	13	>150 ($CDBr_3$)	7·05—7·80 (m)
(IIe)	3·85 (d)	5·95 (d)	2·10	14		7·12—8·12 (m)

[a] Spectra were recorded for $CDCl_3$ solutions at room temperature. Chemical shifts are in δ values (p.p.m.) downfield from tetramethylsilane.   [b] High temperature data are from ref. 16.   [e] The low and high temperature data were recorded on the 60 MHz machine using the appropriate solvent.   [d] Data at −90°.

^{1}H N.m.r. spectral data of (II) are summarized in Table 3 together with coalescence temperatures for the methylene signals. The hydrocarbon (IIa) has the same carbon skeleton as CTV, for which a crown conformation

higher temperatures (IIc) undergoes rapid inversion between two crown forms   The singlet for (IIb) remained unsplit even at −90°, though there is a five-fold increase in half-band width.

The crown form was assigned as the stable conformation of the parent ring system all-cis-cyclonona-1,4,7-triene, which undergoes a ready ring inversion between

[15] W. R. Woolfenden and D. M. Grant, J. Amer. Chem. Soc., 1966, 88, 1496;   D. K. Dalling and D. M. Grant, ibid., 1967, 89, 6612;   G. W. Buchanan, J. B. Stothers, and S.-T. Wu, Chem. Comm., 1967, 1250;   Canad. J. Chem., 1969, 47, 3113.
[16] B. Miller and B. D. Gesner, Tetrahedron Letters, 1965, 3351.
[17] N. K. Anand, R. C. Cookson, B. Halton, and I. D. R. Stevens, J. Amer. Chem. Soc., 1966, 88, 370;   R. C. Cookson, G. Halton, and I. D. R. Stevens, J. Chem. Soc. (B), 1968, 767.

[18] A. Lüttringhaus and K. C. Peters, Angew. Chem. internat. Edn., 1966, 5, 593.
[19] W. Nagata, T. Terasawa, and K. Tori, J. Amer. Chem. Soc., 1964, 86, 3746;   S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, ibid., 1965, 87, 5239.

the two possible crown forms ($\Delta E^{\ddagger} = 10$ kcal mol^{-1}).[20] Another conceivable conformation is in the form of a saddle,[20,21] but it is less stable than the crown since there is severe interaction between the inward methylene hydrogen atoms and the double bonds. The situation is similar with the tribenzo-system.* The only difference is a marked increase in the energy barrier to inversion. The energy relationship between these two conformers has been established by Cookson *et al.*,[17] who reported the thermal conversion of the kinetically controlled reduction product of the oxo-derivative of CTV from the saddle to the crown form.

Inversion of the crown form occurs *via* the saddle form, which itself undergoes a ready pseudo-rotation among six forms.[21] The crown form (IV) is converted to the saddle form (V) [or (VII)] by inverting one of the benzene rings.† Pseudorotation of (V) causes flipping of the second benzene ring to give another saddle form (VI), from which an inverted crown (IV') can be formed.

(IV)   (IV')

(V)   (VI)

(VII)
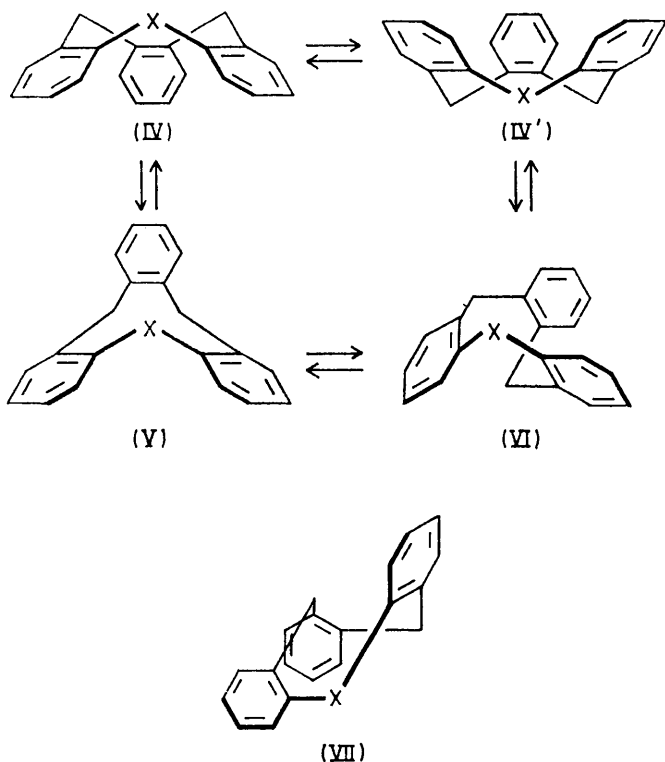
Of the various structural parameters which influence the energy barrier, *gem*-substitution and a C–X–C angle have the largest effect. A large group on the bridge makes inversion difficult since it exerts a steric influence on the *ortho*-hydrogen atoms in the transition state. An increase in the C–X–C angle lowers the barrier since the transition state, which requires flattening of the nine-membered ring, is more easily reached.

* In the saddle form, the distance between the inward hydrogen atom and the centre of the benzene ring is *ca.* 1·7 Å (from Dreiding models). Replacement of the methylene group by trigonal or bivalent atoms can relieve part of the strain.

† When X is not CH$_2$, conformers (V) and (VII) are not equivalent. With a less bulky X, the form (V) is more stable than (VII).

The importance of the angle is reflected in a marked difference between the oxide and sulphide. The C–O–C angle in (IIc) is expected to be even larger than that in diphenyl oxide ($124 \pm 5°$ [22]) owing to strain in the medium-sized ring. This will reduce the energy barrier to the saddle form. On the other hand, the crown sulphide is more stable since a longer C–S bond and a smaller C–S–C angle (di-*p*-tolyl sulphide, $109°$ [22]) makes the nine-membered ring larger and more puckered. The crown sulphone (IIe) is quite stable since it has *gem*-substituents in addition to the angle criterion.

The ketone (IIb) is expected to be less rigid, since it contains a trigonal carbon with a formal C–C–C angle of $120°$. In fact, T_c for the methylene protons is lower than $-90°$. We could not record the frozen spectrum due to experimental limitations such as low solubility and slow molecular tumbling. Two possibilities are open: either averaging occurs between the two crown forms as with the oxide or only among the saddle forms. Cookson *et al.*[17] considered the latter possibility for the oxo-derivative of CTV. A twisted saddle form was assigned as a mean conformation to account for the u.v. data which indicated conjugation. These authors also discussed an equilibrium between the crown and saddle forms found for CTV olefins. Although we have no preference for either of the two possibilities, both a decrease in the energy barrier and an alteration in the relative stabilities between the crown and saddle forms can be expected for those compounds having an sp^2 carbon bridge.‡

Mass Spectra.—The structures of (IIa—e) were confirmed by the parent ion peaks and fragmentation patterns in the mass spectra.

In addition, the unique structural features of the nine-membered rings can be deduced. In Figure 3 the spectrum of (IIe) is shown together with that of an open-chain model, 2,2'-dimethyldiphenyl sulphone. The fragmentation of diaryl sulphones has been studied.[23] The fragmentation is characterized by the intense

‡ The conjugation energy of the Ar–X–Ar group must also be considered in the case of ketone (IIb) and sulphide (IId) where such an interaction is possible. Comparison of the u.v. spectra with those of the corresponding acyclic system A revealed that conjugation between the two aryl rings is considerably reduced in (IId), a rigid crown system, whereas the flexible
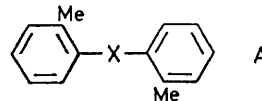
molecule (IIb) showed a similar absorption curve to that of the model compound (a general bathochromic shift due to transannular interactions was evident). The u.v. spectra of oxide (IIc) and 2,2'-dimethyldiphenyl oxide were quite similar. Detailed u.v. spectra will be described elsewhere.

[20] P. Radlick and S. Winstein, *J. Amer. Chem. Soc.*, 1963, **85**, 344; K. G. Untch and R. J. Kurland, *ibid.*, p. 346.

[21] W. R. Roth, *Annalen*, 1964, **671**, 11.

[22] S. C. Abrahams, *Quart. Rev.*, 1956, **10**, 407.

[23] P. Brown and C. Djerassi, *Angew. Chem. Internat. Edn.*, 1967, **6**, 477; S. Meyerson, H. Drews, and E. K. Fields, *Analyt. Chem.*, 1964, **36**, 1294; J. H. Bowie, D. H. Williams, S.-O. Lawesson, J. Ø. Madsen, C. Nolde, and G. Schroll, *Tetrahedron*, 1966, **22**, 3515.

peaks at $M - SO_2$, $M - HSO_2$, and $M - H_2SO_2$. Rearrangement into sulphinate followed by an S–O scission to give an $ArSO^+$ peak was also noted.
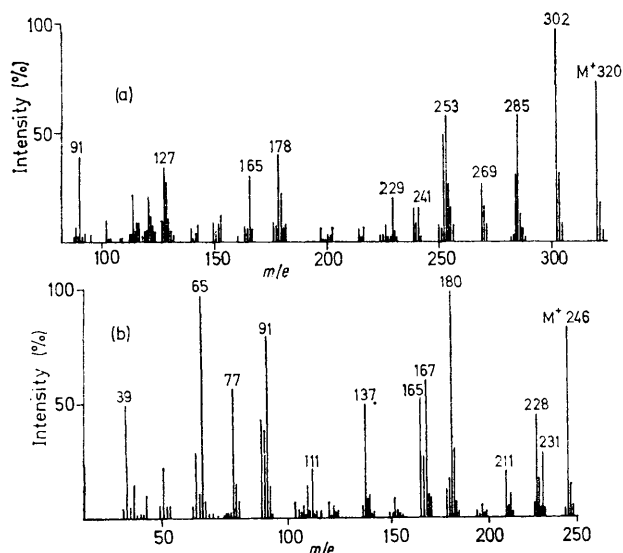

FIGURE 3 Mass spectrum of (a), 10,15-dihydrotribenzo[b,e,h]-thionin 5,5-dioxide (IIe) and (b), 2,2'-dimethyldiphenyl sulphone

For the medium-sized ring sulphone (IIe) the base peak was found to be $M - H_2O$, from which further fragments were eliminated (OH, SH, and HSO). By contrast the spectrum of 2,2'-dimethyldiphenyl sulphone showed $M - HO$, $M - H_2O$, $M - CH_3$, and $M - H_2SO_2$, among which the last peak was the strongest.

Compound (IIe) showed only a weak $M - C_7H_7$ peak, whereas in the sulphide (IId) this was the base peak.

Examination of models of compound (IIe) indicated the proximity of the sulphonyl oxygen atom with the pseudo-equatorial methylene hydrogen atoms. Ready elimination of H_2O upon electron impact can be understood by invoking this proximity effect.
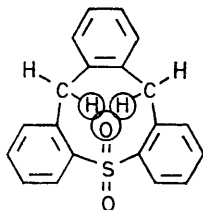
EXPERIMENTAL

[13]C N.m.r. spectra were obtained with a Varian XL-100 spectrometer operating at 25·2 MHz. Simultaneous proton decoupling was accomplished with a heteronuclear wide band decoupler. Enhancement of the signals was accomplished by a multi-scan technique (30—180 times). The assignment was aided by off-resonance spectra. [1]H N.m.r. spectra were recorded with either the XL-100 instru-

ment or a Hitachi R-20B spectrometer. Variable temperature spectra were recorded at 60 MHz with the aid of a R-202 VT unit. Mass spectra were determined by a Hitachi RMU-6E mass spectrometer with ionization current 70 eV. U.v. and i.r. spectra were recorded on Hitachi EPS-3T and EPI-G2 spectrometers.

10H-Dibenz[b,e]iodininium Iodide (IIIb).—According to the method of Collette et al.,[11] 2-iodosyldiphenylmethane, prepared by the oxidation of 2-iododiphenylmethane, was treated with concentrated H_2SO_4 to give the hydrogen sulphate (IIIa). The iodide was prepared by an ion exchange reaction, m.p. 185—186° (decomp.).

2,2'-Di-iododiphenylmethane.—The iodide (IIIb) (65 g, 0·15 mol) was heated under nitrogen at 180—200° for 30 min. Rapid decomposition occurred and was essentially complete after several min. The product was extracted with benzene, the solvent was removed and the residue was crystallized from methanol as prisms (57 g, 88%), m.p. 79—80° (Found: C, 37·25; H, 2·45; I, 59·9. $C_{13}H_{10}I$ requires C, 37·2; H, 2·4; I, 60·45%).

2,2'-Dicyanodiphenylmethane.—After the method of Friedman,[24] 2,2'-di-iododiphenylmethane (53 g, 0·13 mol), cuprous cyanide [25] (25 g, 0·33 mol), and dimethylformamide (100 ml) were refluxed for 6 h. The mixture was poured into a solution of $FeCl_3$ (100 g), concentrated HCl (25 ml), and water (150 ml) and kept at 70° for 30 h. Extraction with benzene and work-up gave prisms (22 g, 79%), m.p. 145·5—146°, $v_{max.}$ (KBr) 2200 cm^{-1} (Found: C, 82·65; H, 4·65. $C_{15}H_{10}N_2$ requires C, 82·55; H, 4·6%).

Diphenylmethane-2,2'-dicarboxylic acid.—The dicyano-compound resisted the normal conditions of hydrolysis. Potassium hydroxide (4 g) in water (5 ml) was added to the dinitrile (2 g, 0·01 mol) in 2-methoxyethanol (10 ml), and the whole was refluxed for 12 h after the method of Goldberg.[26] After acidification of the mixture, crystals were collected and were recrystallized from methanol as prisms (1·7 g, 73%), m.p. 244·5—246·5°, $v_{max.}$ (KBr) 1680 and 1305 cm^{-1} (Found: C, 70·2; H, 4·35. $C_{15}H_{12}O_4$ requires C, 70·3; H, 4·7%).

The dimethyl ester was prepared by methylation with diazomethane, m.p. 44·0—45·5° (from methanol), $v_{max.}$ (KBr) 1715, 1250, and 1075 cm^{-1} (Found: C, 72·0; H, 5·75. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·65%).

2,2'-Bis(hydroxymethyl)diphenylmethane (Ia).—The diester was reduced with lithium aluminium hydride to give the diol, m.p. 157·5—158·5°, $v_{max.}$ (KBr) 3300—3100 and 1040 cm^{-1} (Found: C, 78·75; H, 7·15. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·05%).

10,15-Dihydro-5H-tribenzo[a,d,g]cyclononene (IIa).—Compound (Ia) (250 mg, 1 mmol) in benzene (100 ml) was added to a mixture of concentrated H_2SO_4 (20 ml) and benzene (20 ml) using a modified Hershberg funnel over 24—48 h at room temperature with stirring. After additional stirring for 24 h the mixture was poured into water and after extraction with benzene, the residue was purified by column chromatography (Woelm neutral alumina, activity grade I) eluting with n-hexane. Recrystallization from n-hexane–benzene gave the product (220 mg, 75%), m.p. 274—276°, $v_{max.}$ (KBr) 3050, 3020, 2950, 1490, 1470, 1440, 750, and 715 cm^{-1}.

10,15-Dihydro-5H-tribenzo[a,d,g]cyclononen-5-one (IIb).—(IIa) (143 mg, 0·53 mmol) and sodium dichromate (179 mg, 0·6 mmol) in water (2 ml) and acetic acid (20 ml) were

[24] L. Friedman and H. Shechter, J. Org. Chem., 1961, 26, 2522.
[25] J. V. Supniewski and P. L. Salzberg, Org. Synth., Coll. Vol. I, 1956, 46.
[26] M. A. Goldberg, E. P. Odas, and G. Carsch, J. Amer. Chem. Soc., 1947, 69, 261.

refluxed for 19 h. The mixture was poured into water and the crystals which precipitated were collected. Chromatography on alumina, eluting with benzene–ether, followed by recrystallization from ethanol gave *plates* (111 mg, 74%), m.p. 214·5—216°, $\nu_{max.}$ (KBr) 1640 cm^{-1}.

2,2'-Bis(bromomethyl)diphenyl Ether.—2,2'-Dimethyldiphenyl ether [27] was brominated with N-bromosuccinimide. Distillation at 160—165° and 0·02 mmHg followed by recrystallization from n-hexane gave the *dibromide*, m.p. 86·5—87·5° (Found: C, 47·2; H, 3·4; Br, 44·4. $C_{14}H_{12}Br_2O$ requires C, 47·25; H, 3·4; Br, 44·9%).

2,2'-Bis(hydroxymethyl)diphenyl Ether (Ic).—The dibromide (10·7 g, 0·03 mol), fused sodium acetate (9·8 g, 0·12 mol), and acetic acid (16·8 g) were refluxed for 14 h. The mixture was extracted with ether and the extract was hydrolysed with NaOH in ethanol to give the *diol* (Ic) as needles (6·3 g, 90%), m.p. 96—98° (from benzene), $\nu_{max.}$ (KBr) 3300 and 1035 cm^{-1} (Found: C, 73·05; H, 6·15. $C_{14}H_{14}O_3$ requires C, 73·05; H, 6·15%).

10,15-Dihydrotribenzo[b,e,h]*oxonin* (IIc).—Following the procedure used for compound (IIa), (Ic) was treated with benzene–H_2SO_4. Compound (IIc) was obtained as needles (120 mg, 41%), m.p. 194·5—195° (from n-hexane), $\nu_{max.}$ (KBr) 3050, 3000, 2920, 1600, 1580, 1475, 1450, 1440, 1220, 780, 750, and 710 cm^{-1}.

2,2'-Bis(hydroxymethyl)diphenyl Sulphide (Id).—As with the oxide (Ic), the *sulphide* (Id) was prepared by a series of reactions from 2,2'-dimethyldiphenyl sulphide [28] as yellow needles, m.p. 101·5—103° (from benzene), $\nu_{max.}$ (KBr) 3250 and 1030 cm^{-1} (Found: C, 68·9; H, 5·6; S, 12·9. $C_{14}H_{14}O_2S$ requires C, 68·75; H, 5·75; S, 13·0%).

10,15-Dihydrotribenzo[b,e,h]*thionin* (IId).—Following the procedure used for compound (IIa), the sulphide (Id) was treated with benzene–H_2SO_4. Purification was achieved by chromatography giving *needles* (83%), m.p. 218—219° (from n-hexane), $\nu_{max.}$ (KBr) 3040, 3000, 2920, 2870, 1480, 1460, 1442, and 745 cm^{-1}.

10,15-Dihydrotribenzo[b,e,h]*thionin 5,5-Dioxide* (IIe).—Compound (IId) (115 mg, 0·4 mmol), 30% H_2O_2 (1 ml), and acetic acid (20 ml) were warmed at 95° for 3 h. Dilution of the mixture gave *crystals* (107 mg, 82%), m.p. 208·5—210° (from ethanol), $\nu_{max.}$ (KBr) 1315, 1290, and 1150 cm^{-1}.

[27] D. A. Balon, *J. Org. Chem.*, 1967, **32**, 1584; A. Factor, H. Finkbeiner, R. A. Jerussi, and D. M. White, *ibid.*, 1970, **35**, 57.
[28] F. Mauthner, *Ber.*, 1906, **39**, 3593.