Wittig Reactions of 1,2-Dihydro-1,2-bis(triphenylphosphoranylidene) benzocyclobutene. Synthesis of All-*cis*- and Mono-*trans*-1,2,3,4,6,7,8,9-octahydrodibenzo[*b,h*]benzo[3,4]cyclobuta[1,2-*e*]thionin, Analogues of Biphenylene containing a Thionin Ring [1]

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A Wittig reaction between 1,2-dihydro-1,2-bis(triphenylphosphoranylidene)benzocyclobutene (5) and 2,2'-thiobiscyclohex-1-enecarbaldehyde (4) gave both all-*cis*- (7) and mono-*trans*- (8) 1,2,3,4,6,7,8,9-octahydrodibenzo[*b,h*]benzo[3,4]cyclobuta[1,2-*e*]thionin. Oxidation of the thionins with hydrogen peroxide gave the corresponding sulphoxides. In the case of the mono-*trans*-thionin (8), two isomeric sulphoxides were isolated, which differ only in the relative orientation of the oxygen atom and the *trans*-double bond. The barrier to ring inversion in these compounds must, therefore, be relatively high.

THE fusion of a cyclic system containing $4n$ π-electrons with a cyclic $4n + 2$ π-electron system provides a molecule having a total of $4n$ π-electrons. Such systems

may be antiaromatic [2] and paratropic.[3] However, in compounds in which delocalisation of the $4n$ ring can

[1] Preliminary account, P. J. Garratt, A. B. Holmes, F. Sondheimer, and K. P. C. Vollhardt, *J. Amer. Chem. Soc.*, 1970, **92**, 4492.

[2] R. Breslow, *Chem. Eng. News*, 1965, **43**, XXVI, 90; M. J. S. Dewar, *Adv. Chem. Phys.*, 1965, **8**, 65.

[3] (*a*) P. J. Garratt, ' Aromaticity,' McGraw-Hill, London, 1971; (*b*) F. Sondheimer, *Accounts Chem. Res.*, 1972, **5**, 81.

be relieved, the destabilising effect will be diminished. Thus, benzocyclo-octene (1) is not antiaromatic,[4] the eight-membered ring having a non-planar conformation. Similarly, biphenylene (2), is much more stable than benzocyclobutene (3), presumably because dimethylenecyclobutene structures can predominate with less disruption of aromatic delocalisation.[3a] Whereas benzocyclo-octene, however, shows no unusual chemical properties, those of biphenylene are markedly different from those of biphenyl,[5] and biphenylene also

(1)   (2)   (3)
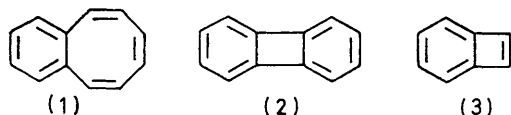
appears to be paratropic.[6] These differences presumably arise because cyclobutadiene, unlike cyclo-octatetraene, cannot relieve delocalisation by adopting a non-planar conformation.

Since it is clear that the effect of annelation by a $4n$ system will be most pronounced in the case of cyclobutadiene, we have examined the preparation of a number of biphenylene analogues in which one of the benzene rings has been replaced by another $4n + 2$

phenylphosphoranylidene)benzocyclobutene (5) [13] (generated from the corresponding bisphosphonium salt and n-butyl-lithium) and 2,2'-thiobiscyclohex-1-enecarb-aldehyde (4),[14] gave a mixture from which two fractions containing cyclic materials could be obtained by chromatography. Preparative t.l.c. on silica of the first fraction gave a yellow oil, which crystallised to give the benzocyclobutathiopyran (6), m.p. 80—85°. The mass and n.m.r. spectra were consistent with the assigned structure. This compound possibly arises by a Wittig reaction between (5) and an aldehyde group of (4) followed by nucleophilic attack of sulphur on the other ylide function, or by a similar sequence of reactions on the monophosphonium salt, present as an impurity. Preparative t.l.c. on alumina of the second fraction gave the all-cis-thionin (7), m.p. 184—186°, and the mono-trans-thionin (8), m.p. 96—97°. The mass spectra confirmed the molecular structure and showed that the compounds were isomeric. The n.m.r. spectrum of (7) showed only one signal corresponding to an olefinic-type proton, whereas that of (8) showed two olefin-type signals (Table). The lower-field olefinic signal in the spectrum of (8) was attributed to H-15 and the higher-field signal to H-10 on the basis of the solvent
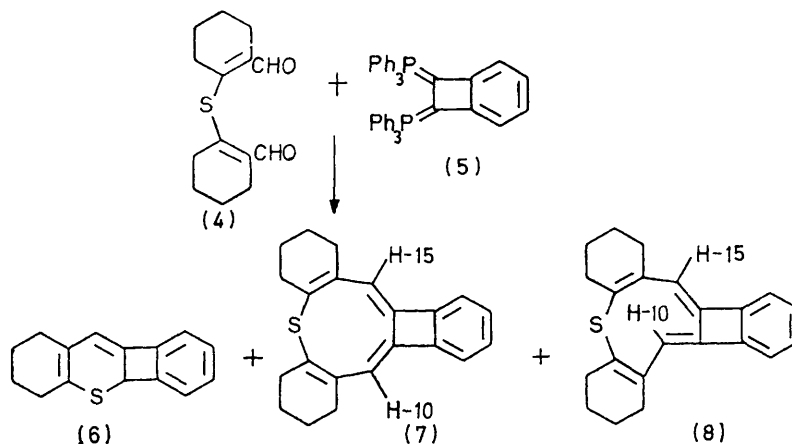
π-electron system. A number of such compounds have been described in which one of the rings has been replaced by another carbocyclic [7-9] or heterocyclic [10] 6 π-electron system. We have now extended the series by introducing the potentially aromatic, 10 π-electron thionin ring,[11] using the synthetic method we have previously described.[8,10-12]

A Wittig reaction between 1,2-dihydro-1,2-bis(tri-

dependence [15] of the chemical shifts (Table). Thus, in (8) the signal at τ 4·17 in CCl_4 moved downfield to τ 4·06 on changing the solvent to C_6D_6; a similar downfield shift was observed for the olefinic protons in (7). However the signal at τ 4·38 in (8) moved upfield to τ 4·43 with the same change of solvent.

The electronic spectrum of (7) was typical of a 1,2-dimethylene-1,2-dihydrobenzocyclobutene deriva-

[4] See J. A. Elix and M. V. Sargent, J. Amer. Chem. Soc., 1969, 91, 4734, and references therein.

[5] See M. P. Cava and M. J. Mitchell, ' Cyclobutadiene and Related Compounds,' Academic Press, New York, 1967; J. W. Barton in ' Nonbenzenoid Aromatic Compounds,' vol. 1, ed. J. P. Snyder, Academic Press, London, 1969.

[6] H. P. Figeys, Chem. Comm., 1967, 495; Angew. Chem. Internat. Edn., 1968, 7, 652.

[7] M. P. Cava, K. Narasimhan, W. Zeiger, L. J. Radonovich, and M. D. Glick, J. Amer. Chem. Soc., 1969, 91, 2378.

[8] P. J. Garratt and K. P. C. Vollhardt, Chem. Comm., 1971, 1143.

[9] L. Lombardo and D. Wege, Tetrahedron Letters, 1972, 4859.

[10] P. J. Garratt and K. P. C. Vollhardt, Chem. Comm., 1970, 109; J. Amer. Chem. Soc., 1972, 94, 7087.

[11] For a carbocyclic 10 π-electron biphenylene analogue, see P. J. Garratt and K. P. C. Vollhardt, Angew. Chem. Internat. Edn., 1971, 10, 125.

[12] P. J. Garratt, K. P. C. Vollhardt, and R. H. Mitchell, J. Chem. Soc. (C), 1970, 2137.

[13] A. T. Blomquist and V. J. Hruby, J. Amer. Chem. Soc., 1967, 89, 4996.

[14] M. Weissenfels and M. Pulst, Tetrahedron Letters, 1968, 3045.

[15] See N. S. Bhacca and D. H. Williams, ' Applications of NMR Spectroscopy in Organic Chemistry,' Holden-Day, San Francisco, 1964, p. 159.
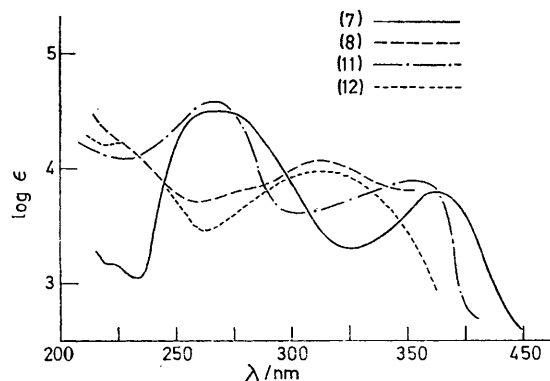
tive;[5,10,12] that of (8) was completely different (Figure), presumably owing to the nonbonded interactions which arise from the *trans*-double bond.

Proton chemical shifts of the aromatic and olefinic protons of compounds (7), (8), (11), and (12) (solid isomer) in various solvents

Solvent	Compound	Aromatic	H-10	H-15
CCl₄	(8)	2·92	4·38	4·17
CD₂Cl₂	(8)	2·84	4·37	4·06
C₆D₆	(8)	2·95	4·43	4·06
CCl₄	(12)	2·90	4·15	4·02
CD₂Cl₂	(12)	2·80	4·11	3·92
C₆D₆	(12)	3·00	4·39	3·98

Solvent	Compound	Aromatic	H-10, H-15
CCl₄	(7)	2·91	4·44
CD₂Cl₂	(7)	2·83	4·27
C₆D₆	(7)	2·99	4·30
CCl₄	(11)	2·91	4·26
CD₂Cl₂	(11)	2·69	4·13
C₆D₆	(11)	2·98	4·24

That (7) and (8) differ only in stereochemistry was confirmed by desulphurisation with Raney nickel,

Electronic spectra of compounds (7), (8), (11), and (12) (solid isomer) in ethanol

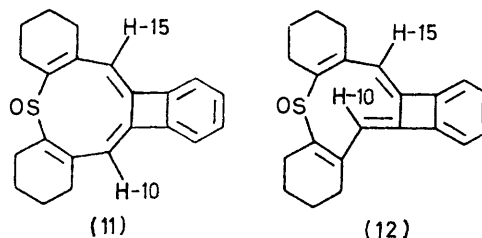which in both cases gave a mixture of compounds (9) and (10).

(9)   (10)

Oxidation of the all-*cis*-thionin (7) with hydrogen peroxide in acetic acid gave the sulphoxide (11), m.p.

252—254°. The n.m.r. spectrum of (11) again showed only one type of olefinic proton (Table) and the electronic spectrum was that expected for a 1,2-dimethylene-1,2-dihydrobenzocyclobutene (Figure). Similar oxidation of the mono-*trans*-thionin (8) gave the sulphoxide

(11)   (12)

(12) in two isomeric forms: a solid, m.p. 190—193°, and a liquid, the former in larger amount. The n.m.r. spectra of the two products were similar. Presumably these molecules are diastereoisomers which differ only in the relationship of the sulphoxide oxygen atom to the *trans*-double bond. This requires that the barriers to ring and sulphoxide inversion are relatively high. Since the resolution of sulphoxides is well documented,[16] and *trans*-cyclononene has been resolved,[17] this presumption appears justified, particularly as increasing the number of unsaturations in the nine-membered ring is likely to increase the barrier to ring inversion.

The n.m.r. chemical shifts of the thionin ring protons in (7) and (8) indicates that these are not delocalised systems, and this view is further supported by the finding that oxidation to the sulphoxide causes little change in the chemical shifts of these protons. The thionin rings in (7) and (8) have non-planar, non-delocalised structures, and thus resemble the only other known thionin derivative, dibenzo[d,f]thionin.[18] In each of these molecules the nature of the ring fusion reduces the energetic advantage of delocalisation, but nevertheless, it appears that the delocalisation energy of thionin must be small.[19] The mono-*trans*-thionin (8) represents the first example of a fully unsaturated nine-membered ring compound containing a *trans*-double bond to be isolated. The only previously known examples are the mono-*trans*-cyclononatetraenide ion, which has been characterised at low temperature,[20] and mono-*trans*-oxonin, which may also have been observed at low temperature.[21]

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. N.m.r. spectra were measured with a Varian HA-100 spectrometer, with tetramethylsilane as internal standard. Mass spectra were determined on an A.E.I. MS-9 spectrometer at 70 eV. Electronic spectra were recorded on a Unicam SP 800 spectrophotometer. Silica for preparative thin-layer chromatography (p.l.c.) was Merck Kieselgel

[16] See J. D. Morrison and H. S. Mosher, ' Asymmetric Organic Reactions,' Prentice-Hall, New Jersey, 1971, p. 335.

[17] A. C. Cope, K. Banholzer, H. Keller, B. A. Pawson, J. J. Whang, and H. J. S. Winkler, *J. Amer. Chem. Soc.*, 1965, **87**, 3644.

[18] A. P. Bindra, J. A. Elix, P. J. Garratt, and R. H. Mitchell, *J. Amer. Chem. Soc.*, 1968, **90**, 7372.

[19] For a review of the related nine-membered heterocycles, see A. G. Anastassiou, *Accounts Chem. Res.*, 1972, **5**, 281.

[20] G. Boche, D. Martens, and W. Danzer, *Angew. Chem. Internat. Edn.*, 1969, **8**, 984.

[21] S. Masamune, S. Takada, and R. T. Seidner, *J. Amer. Chem. Soc.*, 1969, **91**, 7769.

PF$_{254}$, and alumina was Merck Aluminiumoxid PF$_{254}$ (type E). Solvents were May and Baker R grade, and were purified by standard methods.

Wittig Reaction between 1,2-Dihydro-1,2-bis(triphenylphosphoranylidene)benzocyclobutene (5) *and 2,2′-Thiobiscyclohex-1-enecarbaldehyde* (4).—1,2-Dihydro-1,2-bis(triphenylphosphonio)benzocyclobutene dibromide (11·1 g, 14·3 mmol) was suspended in dry ether (1 l) under nitrogen and n-butyl-lithium (1M; 28 ml, 28 mmol) in hexane was added with stirring. The mixture was then stirred for 2 h, and 2,2′-thiobiscyclohex-1-enecarbaldehyde (4) (3·58 g, 14·3 mmol) in ether (40 ml) was added. Stirring was continued for a further 2 h, and the mixture was then heated under reflux for 2 h. After cooling, water (500 ml) and ether (200 ml) were added. The organic layer was separated, washed with water (3 × 100 ml), and dried. The solvent was removed under reduced pressure, the resulting oil was adsorbed on alumina (40 g), and the alumina was added to an alumina column (250 g). The column was eluted with light petroleum (below 40°; 1 l) to give Fraction I. Further elution with ether–light petroleum (gradient) gave Fraction II. P.l.c. (silica) of Fraction I gave a yellow oil, which on treatment with ether–methanol gave pale yellow crystals of 1,2,3,4-*tetrahydro*-5aH-*benzo*[3,4]*cyclobuta*[1,2-b][1]*benzothiopyran* (6) (63 mg, 1·9%), m.p. 80—85° (Found: M^+, 226·081. C$_{15}$H$_{14}$S requires M, 226·081), m/e 226 (M^+, 42%) and 198 (100%); τ (CCl$_4$) 2·83br (4H, s, aromatic), 4·12 (1H, s, olefinic), 5·03br (1H, s, methine), and 7·58—8·50 (m, cyclohexene); λ$_{max.}$ (EtOH) 224sh (ε 13,100), 274 (11,100), and 363 nm (6100). The second band on the p.l.c. plates was triphenylphosphine (970 mg).

P.l.c. (alumina) of Fraction II gave two components. The faster moving component was extracted and crystallised from ether–methanol at −20° to give *mono*-trans-1,2,3,-4,6,7,8,9-*octahydrodibenzo*[b,h]*benzo*[3,4]*cyclobuta*[1,2-e]*thionin* (8) (67 mg, 1·4%), m.p. 96—97° (Found: C, 82·8; H, 7·0; S, 9·85. C$_{22}$H$_{22}$S requires C, 82·95; H, 6·95; S, 10·05%); m/e 318 (M^+, 100%) and 317 (M^+ −H, 95%); τ (CCl$_4$) 2·92br (4H, s), 4·17br (1H, s), 4·38br (1H, s), 7·30—7·90 (8H, m), and 7·90—8·60 (8H, m); λ$_{max.}$ (EtOH) 224sh (ε 17,800), 285sh (6600), and 314 nm (11,400).

The slower moving component was extracted and crystallised from ether–methanol to give the all-cis-*isomer* (7) (33 mg, 0·7%), m.p. 184—186° (Found: C, 82·75; H, 6·75; S, 10·25%); m/e 318 (M^+, 100%) and 317 (M^+ − H, 70%); τ (CCl$_4$) 2·91br (4H, s), 4·44br (2H, s), 7·10—8·10 (8H, m), and 8·10—8·70 (8H, m); λ$_{max.}$ (EtOH) 223sh (ε 14,500), 268 (31,000) and 375 nm (6200).

Reaction of the Thionins (7) *and* (8) *with Raney Nickel.*—Raney nickel (*ca*. 3 g) was added to a solution of the all-*cis*-thionin (7) (10 mg, 0·031 mmol) in absolute ethanol (30 ml), and the mixture was heated under reflux for 2 h. After cooling, filtration and evaporation gave an oil (4·8 mg, 50%), which was a mixture (*ca*. 1 : 2) of 1,2-*bis*(*cyclohexylmethyl*)-1,2-*dihydrobenzocyclobutene* (9) and o-*bis*-(β-*cyclohexylethyl*)-*benzene* (10), which were separated by g.l.c. (6 ft QF$_1$ column; 200°). Compound (9) showed m/e 296 (M^+, 100%), 294, and 292; compound (10) showed m/e 298 (M^+, 100%), 296, and 294. Similar desulphurisation of the mono-*trans*-thionin (8) (10 mg, 0·031 mmol) gave a mixture (*ca*. 4 : 1) of (9) and (10) (3·9 mg. 40%), again separated by g.l.c. and identical with the samples obtained by desulphurisation of (7).

Oxidation of the Thionins (7) *and* (8).—The all-*cis*-thionin (7) (21 mg, 0·067 mmol) was added to glacial acetic acid (2·5 ml), hydrogen peroxide (6%; 0·1 ml, 0·177 mmol) was added to the stirred mixture, and stirring was continued for 3 h. Water (70 ml) was then added, and the mixture was extracted with ether (2 × 10 ml). The extracts were washed [saturated NaHCO$_3$ solution (3 × 5 ml) and water (3 × 10 ml)], dried (MgSO$_4$), and evaporated to give an oil, which on p.l.c. [alumina; elution with ether–light petroleum (80 : 20)] gave the S-*oxide* (11) (12 mg, 54%), m.p. 252—254° (CH$_2$Cl$_2$–light petroleum) (Found: C, 78·8; H, 6·5; S, 9·45. C$_{22}$H$_{22}$SO requires C, 79·0; H, 6·65; S, 9·6%), m/e 334 (M^+, 17%), 318 (M^+ − O, 90%), and 286 (M^+ − SO, 100%); τ (CCl$_4$) 2·91 br (4H, s), 4·26br (2H, s) 6·80—7·70 (8H, m), and 7·70—8·80 (8H, m); λ$_{max.}$ (EtOH) 267 (ε 37,700) and 359 nm (8000).

Similar oxidation of (8) (25·1 mg, 0·075 mmol) with hydrogen peroxide (6%; 0·1 ml, 0·177 mmol) gave, after p.l.c., the S-oxide (12) as two isomers: an *oil*, m/e 334 (M^+, 24%) and 277 (100%); τ (CD$_2$Cl$_2$) 2·76br (4H, s), 3·93br (1H, s), 4·26br (1H, s), and 7·3—8·9 (16H, m); λ$_{max.}$ (Et$_2$O) 292, 298sh, and 318sh nm; and a crystalline *solid* (9·9 mg, 40%), m.p. 190—193° (CH$_2$Cl$_2$–light petroleum) (Found: C, 78·85; H, 6·7; S, 9·5%); m/e 334 (M^+, 6%), 333 (M − H, 5%), and 277 (100%); τ (CCl$_4$) 2·90br (4H, s), 4·02br (1H, s), 4·15 (1H, s), and 7·00—8·80 (16H, m); λ$_{max.}$ (EtOH) 225 (ε 16,500) and 315 nm (9500).