Wittig Reactions of 1,2-Benzocyclobutadienequinone. Synthesis of 2-Thianorbiphenylene (Benzo[3,4]cyclobuta[1,2-*c*]thiophene)[1]

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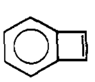
Abstract: A Wittig reaction between 1,2-benzocyclobutadienequinone (**10**) and bis(triphenylphosphoranylidenemethyl) sulfide (**11**) gave 2-thianorbiphenylene (benzo[3,4]cyclobuta[1,2-*c*]thiophene) (**12**). Oxidation of **12** with hydrogen peroxide gave first 2-thianorbiphenylene 2-oxide (**13**) and then 2-thianorbiphenylene 2,2-dioxide (**14**). On photoirradiation the sulfone **14** underwent a 2 + 2 π addition to give a dimer. A comparison of the nmr proton chemical shifts of **12**, **13**, and **14** suggests that the four-membered ring in **12** sustains a paramagnetic ring current. On bromination, the thiophene ring in **12** adds four atoms of bromine to give a mixture of tetrabromides, which can be debrominated to give **12** or dehydrobrominated to give 1,3-dibromo-2-thianorbiphenylene (**24**).

The delocalization of the π electrons in a [4*n*]annulene is predicted to raise the energy of the system,[2,3] in marked contrast to the effect of delocalization in the [4*n* + 2]annulenes in which the energy is lowered. Because of the destabilizing effect of conjugation in the [4*n*]annulenes, these systems have been termed antiaromatic.[2,3] Antiaromaticity should be most readily observed in the smallest member of the 4*n* series, cyclobutadiene, which cannot remove the interaction between the π electrons of the two double bonds by distortion from planarity. The properties of cyclobutadiene, which is a highly reactive molecule, probably having a singlet, rectangular ground state with alternating single and double bonds,[4,5] is in harmony with this expectation.

Polycyclic systems containing cyclobutadiene or potential cyclobutadiene rings also appear to be destabilized. Thus, benzocyclobutadiene (**1**) exists only as a transient intermediate[6] or as a metal complex.[7] However, a number of naphtho- and an anthrocyclobutadienes have been isolated,[6,8] such as **2**,[9] and these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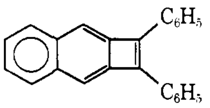

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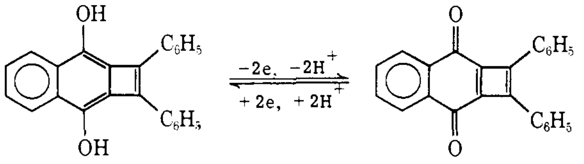
are reasonably stable compounds. The greater stability of **2**, as compared to **1**, appears to arise from the fact that compound **2** can accommodate the four-membered ring in the dimethylenecyclobutene form with only a partial disruption of the aromatic character of the naphthalene system. In accord with this view, Breslow, *et al.*,[10] have recently shown that the electrochemical oxidation of the cyclobutenonaphthohydroquinone **3** to the quinone **4** occurs less readily than either the oxidation of the corresponding cyclobutano derivative **5** or of 1,4-naphthohydroquinone itself. The destabilization due to the cyclobutadiene ring in **4** was estimated to be in the range of 12–16 kcal mol^{-1}.

In biphenylene (**6**) the dimethylenecyclobutene structure can be maintained without serious disruption of the benzene rings, and the X-ray crystallographic analysis of **6** showed that the bands between the phenyl rings are long (1.514 Å).[11] However, the high-field position (τ 3.40, 3.30) of the protons in the nmr spectrum of biphenylene[12] and the low-field position of the carbon atoms of the four-membered ring in the ^{13}C nmr spectrum[13] have both been attributed to a contribution from the potential cyclobutadiene ring. This is considered to give rise to a paramagnetic ring current,[14] which is presumed to have a shielding effect on the protons[12c] and a deshielding effect on the carbons of the four-membered ring.[13]



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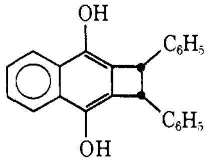

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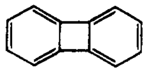
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(1) For a preliminary account of part of this work, see P. J. Garratt and K. P. C. Vollhardt, *Chem. Commun.*, 109 (1970).

(2) R. Breslow, *Chem. Eng. News*, **43** (XXVI), 90 (1965); R. Breslow, J. Brown, and J. J. Gajewski, *J. Amer. Chem. Soc.*, **89**, 4383 (1967).

(3) M. J. S. Dewar, *Advan. Chem. Phys.*, **8**, 121 (1965).

(4) See E. K. G. Schmidt, L. Brener, and R. Pettit, *J. Amer. Chem. Soc.*, **92**, 3240 (1970), and references cited therein.

(5) For theoretical calculations, see M. J. S. Dewar, M. C. Kohn, and N. Trinajstić, *ibid.*, **93**, 3437 (1971), and references cited therein.

(6) For an excellent review, see M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967.

(7) G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 131 (1965).

(8) M. P. Cava, *Chem. Soc., Spec. Publ.*, No. 21, 163 (1967).

(9) M. P. Cava, B. Y. Hwang, and J. P. Van Meter, *J. Amer. Chem. Soc.*, **85**, 4032 (1963).

(10) R. Breslow, R. Grubbs, and S.-I. Murahashi, *ibid.*, **92**, 4139 (1970).

(11) J. K. Fawcett and J. Trotter, *Acta Crystallogr.*, **20**, 87 (1966).

(12) (a) G. Fraenkel, Y. Asahi, M. J. Mitchell, and M. P. Cava, *Tetrahedron*, **20**, 1179 (1964); (b) A. R. Katritzky and R. E. Reavill, *Recl. Trav. Chim. Pays-Bas*, **83**, 1230 (1964); (c) H. P. Figeys, *Chem. Commun.*, 495 (1967).

(13) A. J. Jones and D. M. Grant, *ibid.*, 1670 (1968).

(14) J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, **88**, 4811 (1966); F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch.*, *A*, **22**, 103 (1967); H. C. Longuet-Higgins, *Chem. Soc. Spec. Publ.*, No. 21, 109 (1967).

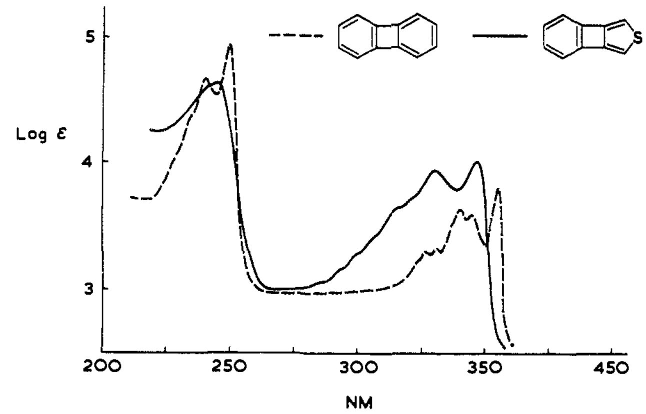
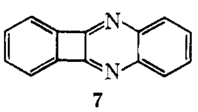


Figure 1. Electronic spectra of 2-thianorbiphenylene (**12**) and biphenylene (**6**) in ethanol.

In order to study further the magnetic and destabilizing effects of the cyclobutadiene ring in polycyclic systems, we have investigated the preparation of biphenylene analogs in which one, or both, of the benzene rings has been replaced by a different $(4n + 2)$ π-electron monocycle. The only compound of this type known when our work was commenced was 5,10-diazabenzo[*b*]biphenylene (**7**),[15] but in the intervening period the preparation of the norbiphenylene anion **8**[16] and



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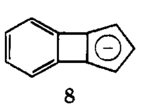

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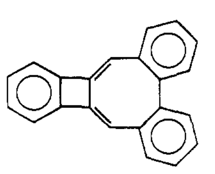
2,6- (or 2,7-) diazabiphenylene[17] has been reported.

We have previously prepared the cyclooctatetraene derivative **9**[18] by a Wittig reaction between 1,2-bis(triphenylphosphoranyl)benzocyclobutene and diphenyl-2,2′-dicarboxaldehyde. Although the alternative mode of reaction between 1,2-benzocyclobutadienoquinone (**10**) and the bis ylide derived from 2,2′-di(bromomethylene)diphenyl had not given cyclic products, we were sufficiently encouraged further to explore this type of Wittig reaction in order to determine whether this was a general method for the synthesis of biphenylene-type systems. This paper describes the successful extension of this method to the synthesis of 2-thianorbiphenylene (benzo[3,4]cyclobuta[1,2-*c*]thiophene) (**12**) and describes some properties of this and related compounds.



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A Wittig reaction between 1,2-benzocyclobutadienequinone (**10**)[15] and the bis ylide **11**,[19] derived from dimethyl thioether α,α′-bis(triphenylphosphonium) dichloride by treatment with *n*-butyllithium, gave in 14% yield 2-thianorbiphenylene (**12**), a white crystalline solid, mp 98–98.5°. The structure was assigned on the basis of the spectral and chemical properties. The mass spectrum of **12** showed a parent peak at *m/e* 158 (100) and a prominent peak at 114 due to the loss of CS, a group also lost in the mass spectral fragmentation of benzo[*b*]thiophene.[20] The electronic spectrum resembles that of biphenylene (**6**) (Table I and Figure 1), the absorption bands of **12** showing a small hypsochromic shift when compared to those of **6**. The nmr spectrum is shown in Table II and Figure 2. Desulfurization of **12** with Raney nickel gave a mixture of 1,2-dimethylbenzocyclobutene and *o*-diethylbenzene, which was separated, and the components were characterized.

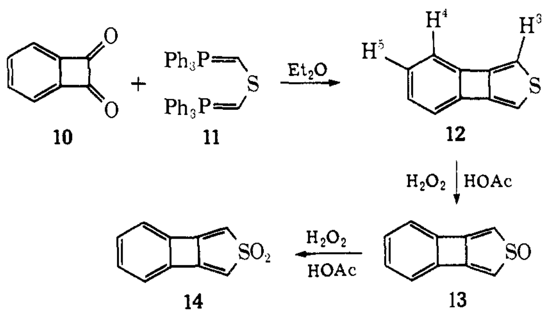
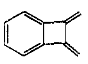


Table I. Electronic Spectra of 2-Thianorbiphenylene and Related Systems

Compd	Electronic spectrum, nm $(\epsilon)^a$		Ref
	C_2H_5OH	$(CH_3CH_2)_2O$	
12	245 (43,500), 347 (10,200)	245 (41,000), 347 (10,900)	*b*
13	246 (37,000), 337 (5070), 349 (5950)	244 sh (12,000), 310 (1900), 324.5 (1600), 369 (3000)	*b*
14	236 (66,000), 336 (10,100)	313 (4000), 321 (6550), 336 (8050)	*b*
6	250 (80,000), 360 (6300)		6
 15	230 (66,000), 392 (14,200)		6[c]
9	279 (46,200), 352 (9200)		18

[a] Only the main maxima are shown. [b] This work. [c] See also M. P. Cava, R. J. Pohl, and M. J. Mitchell, *J. Amer. Chem. Soc.*, **85**, 2080 (1963).

Table II. Nmr Spectra of 2-Thianorbiphenylene (**12**) and Related Systems

Compd	Nmr, τ, $CDCl_3$, 100 MHz		Ref
	H^3	H^4,H^5	
12	3.51 (s)	3.14 (br s)	*a*
13	3.35 (s)	2.49 (m)	*a*
14	3.60 (s)	2.37 (m)	*a*
6		3.3, 3.4 (m)[b]	12a

[a] This work. [b] H^1,H^2 protons of biphenylene (**6**).

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(15) M. P. Cava, D. R. Napier, and R. J. Pohl, *J. Amer. Chem. Soc.*, **85**, 2076 (1963).

(16) M. P. Cava, K. Narasimhan, W. Zeiger, L. J. Radonovich, and M. D. Glick, *ibid.*, **91**, 2378 (1969).

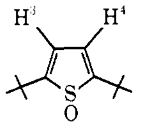
(17) J. M. Kramer and R. S. Berry, *ibid.*, **93**, 1303 (1971).

(18) P. J. Garratt, K. P. C. Vollhardt, and R. H. Mitchell, *J. Chem. Soc. C*, 2137 (1970).

(19) K. Dimroth, H. Follmann, and G. Pohl, *Chem. Ber.*, **99**, 642 (1966).

(20) See Q. N. Porter and J. Baldas, "Mass Spectrometry of Heterocyclic Compounds," Wiley-Interscience, New York, N. Y., 1971, p 264.

Oxidation of **12** with hydrogen peroxide in acetic acid gave firstly the sulfoxide **13** and then the sulfone **14**. The rate of oxidation of **13** appears to be similar to that of **12**, but **13** could be obtained as a pure, relatively unstable compound by interrupting the reaction and separating the products and starting material. When the reaction was allowed to go to completion the sulfone **14** was obtained in practically quantitative yield. The structural assignments of **13** and **14** are based on the chemical and spectral properties. The appropriate mass spectral molecular ions were observed, and the electronic and nmr spectra are shown in Tables I and II, respectively. The electronic spectrum of **13** differs from those of **12**, **14**, and other dimethylenecyclobutenes (*e.g.*, **15**) in that the spectrum is solvent dependent. In ether the absorption bands are at longer wavelength and the molar absorbtivities are lower than those in ethanol. A similar, but smaller, bathochromic shift was observed in the electronic spectrum of 2,5-di-*tert*-butylthiophene 1-oxide (**16**) on changing from a more to a less polar solvent.[21] It appears possible that in the sulfoxide **13** there is an interaction of the SO group with the dimethylenebenzocyclobutene chromophore, which is absent in the sulfone **14**. The sulfoxide group is presumably pyramidal, but such a stereochemistry does not preclude conjugative interaction if d-orbital participation is invoked.[22]



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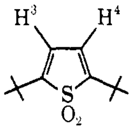

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A comparison of the nmr spectra of **12**, **13**, and **14** provides convincing evidence for the presence of a paramagnetic ring current effect in 2-thianorbiphenylene (**12**). The protons in the benzene ring of **12** appear at relatively high field, in a similar position to that of biphenylene (**6**). On oxidation to **13** the protons on the benzene ring move to significantly lower field ($\Delta\tau$ 0.65) and further oxidation to **14** results in only a small shift ($\Delta\tau$ 0.12), again to lower field. This downfield shift is that expected if oxidation of the thiophene ring fixes the dimethylenebenzocyclobutene structure and removes the paramagnetic ring current effect arising from the four-membered ring. The downfield chemical shift ($\Delta\tau$ 0.16) of the protons on the heterocyclic ring on oxidizing **12** to **13** may be accounted for by the removal of both the diamagnetic ring current of the heterocyclic ring and the paramagnetic ring current of the four-membered ring, since these effects oppose each other. However, part of this change of chemical shift, and also that observed on oxidizing **13** to **14**, may be due to the change in oxidation state of the sulfur atom. There do not appear to be any satisfactory models with which to compare the chemical shifts of the protons in these compounds. In the case of 2,5-di-*tert*-butylthiophene,[21] oxidation to the sulfoxide (**16**) causes an upfield shift of the 3,4 protons from τ 3.54 to 3.92, and further oxidation to the sulfone (**17**) causes a small downfield shift to τ 3.84. The influence of the sulfoxide group on the protons at the 2,5 positions is, however, likely to be different from its effect on the 3,4 positions.[23] We are currently reexamining the oxidation of other thiophenes[24] in an attempt to provide suitable models with which to compare these changes. Should the chemical shift differences observed on the oxidation of **12** mainly arise from changes in the ring currents, then the paramagnetic effect of the four-membered ring in **12** is considerably greater than the diamagnetic deshielding effect of the thiophene ring in this compound.

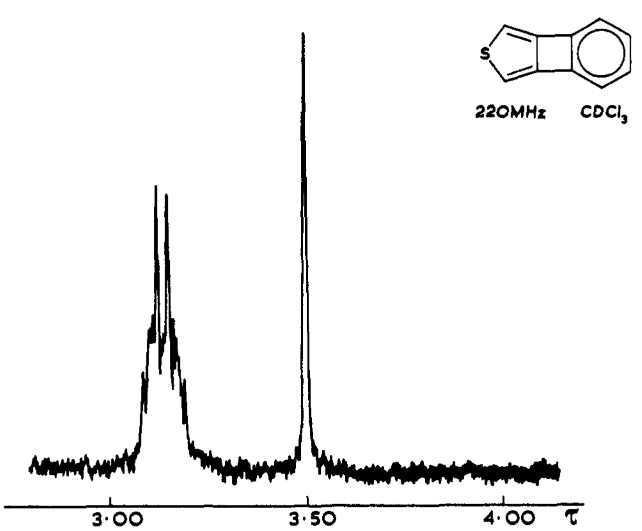

Figure 2. Nmr spectrum (220 MHz) of 2-thianorbiphenylene (**12**) in $CDCl_3$.

Neither the sulfoxide **13** nor the sulfone **14** shows any tendency to dimerize *via* a Diels–Alder reaction, in contrast to the simple thiophene oxides which dimerize on attempted isolation.[24] This difference in behavior presumably rises because of the benzocyclobutadiene structure which would result on dimerization of **13** or **14**. Thermolysis of the sulfone **14** at 230° led to the evolution of sulfur dioxide, but only polymeric material could be isolated.[25] Photoirradiation of **14** in ether–dioxane with a medium-pressure lamp gave a dimer (mp >320° dec) to which was assigned the gross structure **20** (stereochemistry undefined).[26] The mass spectrum of **20** had a molecular ion at *m/e* 380 and the nmr spectrum (CD_2Cl_2) showed signals at τ 2.46–2.88 (m, 8 H, aromatic), 3.24 (s, 2 H, vinylic), and 5.59 (s, 2 H, cyclobutyl). The electronic spectrum (EtOH) had absorption maxima at 262 nm (ϵ 18,900), 268.5 (18,300), 295.5 (10,700), and 304 (9500). The dimer presumably arises from a 2 + 2 π addition, and the formation of similar dimers has been observed by Cava, *et al.*, on quenching the norbiphenylene anion **8**.[16] One of the dimers derived from **8** was shown to have the syn head-to-head structure **21** by an X-ray crystallographic analysis, but the stereochemistry of the dimer **20** is unknown.

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(21) W. L. Mock, *J. Amer. Chem. Soc.*, **92**, 7610 (1970).

(22) H. P. Koch and W. Moffit, *Trans. Faraday Soc.*, 47, 7 (1951).

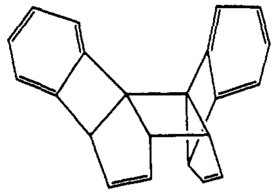
(23) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," 2nd ed, Pergamon Press, London, 1969, pp 177, 180.

(24) See W. J. Bailey and E. W. Cummins, *J. Amer. Chem. Soc.*, 76, 1932, 1936 (1954); J. L. Melles and H. J. Backer, *Recl. Trav. Chim. Pays-Bas*, 72, 491 (1953).

(25) Corresponding thermolysis of **12** gave only polymeric products together with unchanged starting material.

(26) Corresponding photoirradiation of **12** gave only polymeric material. Irradiation with a sun lamp, under the conditions used for photodimerization of biphenylene,[27] led only to recovery of starting material.

(27) N. L. Goldman and R. A. Ruden, *Tetrahedron Lett.*, 3951 (1968).



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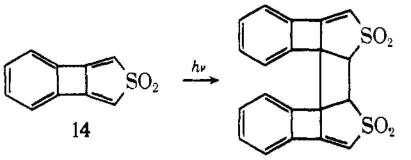

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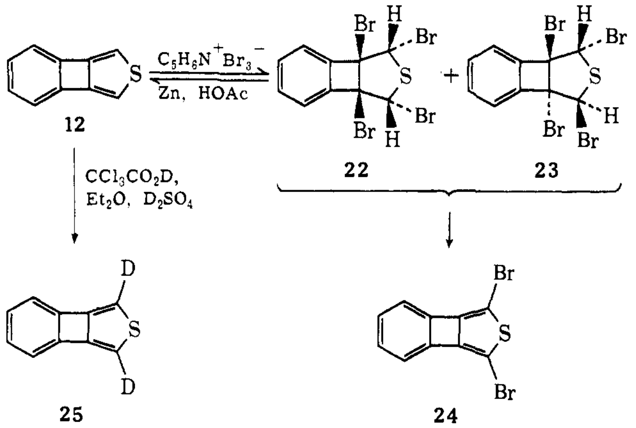
The thiophene ring of **12** is much more reactive than that of thiophene itself. Thus, treatment of **12** with bromine in carbon tetrachloride containing pyridine, or with pyridinium bromide perbromide in methylene chloride, gave a mixture of tetrabromides in which addition of bromine to both double bonds of the thiophene ring had occurred. Separation by tlc or silica of the tetrabromide mixture obtained by treatment with pyridinium bromide perbromide gave two compounds. The first compound (23%, mp 180–182°) is tentatively assigned the structure **22**. The gross structure follows from the mass and spectral properties. The stereochemical assignment was made by assuming that the bromine has added trans and by comparing the electronic spectrum of **22** with the second product. The second product (57%, mp 165–178° dec)[28] was tentatively assigned the structure **23**. The gross structure is again made on the basis of the mass and nmr spectral properties. The electronic spectrum of **22** (EtOH) shows maxima at 260 nm (sh, ϵ 1200), 268.5 (sh, 1830), 273 (2480), and 281 (2370), whereas that of **23** has maxima at 269 nm (ϵ 2240), 276 (2610), and 284 (2400). Fraenkel, *et al.*,[29] have reported that in the electronic spectrum, the more strained cis-1,2-disubstituted benzocyclobutadienes have larger molecular absorptivities than the corresponding trans compounds. In the present case, the trans-fused five-membered heterocyclic ring in **23** is assumed to provide more strain than the cis-fused ring in **22**.



12 22 23 25 24

Reaction of either pure **22** or the mixture of **22** and **23** with zinc in acetic acid regenerated, in virtually quantitative yield, the compound **12**. Treatment of the mixture of **22** and **23** with 1,5-diazabicyclo[4.3.0]nonene-5 in tetrahydrofuran gave 1,3-dibromo-2-thianorbiphenylene (1,3-dibromobenzo[3,4]cyclobuta[1,2-*c*]thiophene) (**24**) (45%, mp 83–84°) identified by its mode of formation and its spectral properties. In particular the electronic spectrum of **24** [247 nm (ϵ 43,000), 332.5 (7300), 350 (7500)] is very similar to that of **12** and shows the expected small bathochromic shift.

Reaction of **12** with deuteriotrifluoroacetic acid in ether containing concentrated sulfuric acid gave 1,3-dideuterio-2-thianorbiphenylene (**25**). In the nmr spectrum the singlet absorption at τ 3.52 due to the 2,5 protons in **22** is absent. Attempts to introduce deuterium atoms into the benzene ring of **12** by increasing the acidity of the medium failed, these conditions leading only to decomposition.

The properties of **12** are similar to those of biphenylene and are consistent with the view that the potential cyclobutadiene ring destabilizes the molecule. In particular, the thiophene ring has considerable olefinic properties, as illustrated by the ready addition of bromine. The ^{13}C nmr spectrum of **12** has been investigated in collaboration with Professor A. J. Jones (University of Alberta) and this work will be reported, in conjunction with other results, elsewhere. The present synthetic method affords **12** in gram quantities from reasonably accessible precursors, and the formation of 1,3-dibromo-2-thianorbiphenylene (**24**) indicates that a variety of 2-thianorbiphenylenes should be available by this route.

Experimental Section

Melting points were determined on a Kofler hot-stage microscope and are uncorrected. Electronic spectra were determined on a Unicam SP 800 or Cary 14 recording spectrophotometer. Infrared spectra (ir) were recorded on a Unicam SP 200 or Perkin-Elmer 257 spectrophotometer. Nuclear magnetic resonance (nmr) spectra were taken on a Varian Associates HA-100 spectrometer, unless stated otherwise, and are reported in τ values relative to tetramethylsilane at τ 10.00 as internal standard. The mass spectra were recorded on an AEI MS9 or MS12 mass spectrometer.

Gas chromatography (glc) was carried out on a Hewlett-Packard FM 5750 research chromatograph. Thin-layer plates were prepared with Merck Kieselgel HF$_{254}$ or GF$_{254}$ or aluminum oxide GF$_{254}$ (type E). Thick-layer preparative chromatography (ptlc) was carried out on Merck Kieselgel PF$_{254}$ or aluminum oxide PF$_{254}$ (type E). For column chromatography, Spence Neutral Alumina, Chromatographic Alumina Type H (Laporte Ind. Ltd.), Woelm neutral alumina (activity II–III), or Silical Gel (MFC) (Hopkin and Williams) was used. Solvents were generally May and Baker "R" grade and were purified by standard methods. Petroleum ether is the fraction boiling below 40°.

Wittig Reaction between 1,2-Benzocyclobutadienequinone (10) and Bis(triphenylphosphoranylidene)methyl Sulfide (11). Synthesis of 2-Thianorbiphenylene (12). Dimethyl thioether α,α'-bis(triphenylphosphonium) dichloride[30] (10 g, 15 mmol) was dried at 110° (0.05 mm) over P$_2$O$_5$ and suspended in dry ether (2 l.) under N$_2$ with the strict exclusion of moisture. *n*-Butyllithium (2 *M*, 15 ml, 30 mmol) in hexane was added with stirring, and the resulting deep red mixture of bis(triphenylphosphoranylidene)methyl sulfide (**11**) was stirred for a further 3 hr. A solution of 1,2-benzocyclobutadienequinone (**10**) (1.98 g, 15 mmol) in dry benzene (40 ml) was added, and the mixture changed color to dark brown grey. The mixture was stirred for 1–2 hr at room temperature and then heated under reflux for 1–2 hr. After cooling to room temperature the mixture was poured into water (500 ml) and extracted with ether (200 ml), and the ethereal layer was washed with water (3 × 100 ml) and dried (MgSO$_4$). Evaporation of the solvent under reduced pressure gave an oil, which on chromatography on silica

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[28] This product contained a third isomer from which it could not be separated.

[29] See ref 12a, footnote 10.

[30] When the corresponding dimethyl thioether α,α'-bis(triphenylphosphonium) dibromide[19] was used, only a small yield (0.5%) of 2-thianorbiphenylene was obtained. Addition of lithium chloride to the reaction mixture did not increase this yield.

(200 g) eluting with petroleum ether (4 l.) gave colorless crystals. Sublimation [60° (19 mm)] and recrystallzation ($CH_3OH–H_2O$) gave 2-thianorbiphenylene (**12**) (330 mg, 2.1 mmol, 14%): mp 98–98.5°; mass spectrum *m/e* 158 (M^+, 100), 114 (M − CS, 75); ir (KBr) 1455, 1415, 1310, 1275, 1135, 1110, 1045, 980, 935, 780, 745, 730 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 242 nm sh (ϵ 41,800), 245 (43,500), 300 sh (1940), 307 sh (2660), 316 sh (4400), 322 sh (5300), 330 (8700), 347 (10,200); for the nmr spectrum, see Table I.

Anal. Calcd for $C_{10}H_6S$: C, 75.92; H, 3.82; S, 20.26. Found: C, 76.21; H, 4.03; S, 20.10.

Desulfurization of 2-Thianorbiphenylene (12). The compound **12** (29 mg, 0.18 mmol) was dissolved in ethanol (3 ml), Raney nickel (2 g) was added, and the mixture was heated to reflux for 14 hr. The mixture was filtered, water (40 ml) was added to the filtrate, and the solution was extracted with petroleum ether (4 ml). The petroleum extract was dried ($CaCl_2$), the volume reduced by distillation, and the residue (1 ml) separated by glc (Aziepol B, 130°). Three compounds were collected. The first, in order of elution, was minor and was not identified. The second compound was *o*-diethylbenzene, identified by comparison with an authentic sample. The third compound was assigned the 1,2-dimethylbenzocyclobutene structure on the basis of its mass [*m/e* 132 (M^+, 25), 117 (M − CH_3, 100)] and electronic ($\lambda_{\max}^{\mathrm{Et_2O}}$ 253 sh, 260, 266, 273 nm) spectra.

Oxidation of 2-Thianorbiphenylene (12). Synthesis of 2-Thianorbiphenylene 2-Oxide (13) and 2-Thianorbiphenylene 2,2-Dioxide (14). Compound **12** (28 mg, 0.18 mmol) was dissolved in glacial acetic acid (3 ml), aqueous hydrogen peroxide (6%, 0.2 ml, 0.36 mmol) was added, and the mixture was stirred for 48 hr at room temperature. Water (25 ml) was added and the mixture was extracted with ether (3 × 25 ml) and dried ($MgSO_4$). After evaporation of the solvent, the resulting yellow oil was chromatographed (tlc) on silica, with petroleum ether–ethyl acetate–methanol (6:3:1), when three bands were obtained. The fastest moving band was **12** (15.6 mg). The second band consisted of colorless crystals which were recrystallized from methanol to give 2-thianorbiphenylene 2,2-dioxide (**14**) (7.4 mg, 22%): mp 213–215°; mass spectrum *m/e* 190 (M^+, 5), 126 (M − SO_2, 100); ir (KBr) 3060, 1680, 1550, 1470, 1425, 1280, 1230, 1130, 1105, 795, 765, 740, 700 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 236 nm (ϵ 66,000), 272 sh (3700), 300 sh (3130), 308 (4650), 313 (4770), 321 (7950), 328 sh (4700), 336 (10,100); for the nmr spectrum, see Table I.

Anal. Calcd for $C_{10}H_6SO_2$: C, 63.14; H, 3.18; S, 16.85. Found: C, 63.15; H, 3.41; S, 16.64.

The third band gave colorless crystals which were recrystallized from ether–methylene chloride to give 2-thianorbiphenylene 2-oxide (**13**) (4.9 mg, 16%): mp 143–145° dec; mass spectrum *m/e* 174 (M^+, 20), 158 (M − O, 100), 126 (M − SO, 80); ir (KBr) 3050, 1230, 1030, 820, 765 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 246 nm (ϵ 37,000), 337 (5070), 349 (5950); for the nmr spectrum, see Table I.

Anal. Calcd for $C_{10}H_6SO$: C, 68.94; H, 3.47. Found: C, 68.89; H, 3.58.

If the oxidation of **12**, under the conditions described above, is continued for 5 days, then an essentially quantitative conversion of **12** to **14** occurs.

Thermolysis of 12. Compound **12** (9.0 mg) was sealed in an evacuated tube and heated for 2 hr at 160° and 15 min at 230°. Mainly starting material was recovered. Heating for 2 hr at 280° gave a black tar, from which only starting material (45%) and polymer could be recovered.

Thermolysis of 14. Compound **14** was pyrolyzed under the same conditions as **12**. Sulfur dioxide was evolved but only polymeric material and unchanged **14** could be isolated.

Photoirradiation of 12. Compound **12** (9.0 mg) was dissolved in dry ether (3 ml), and the solution was flashed with N_2 and irradiated with a Hanovia medium-pressure lamp for 6 hr. Polymeric material precipitated and only starting material could be recovered. Photoirradiation in acetone for 15 hr led to complete decomposition of **12**, but no product could be isolated. Photoirradiation of **12** (25 mg) with a sun lamp (250 W) for 48 hr under the conditions of Goldman and Ruden[23] gave only recovered starting material (20 mg).

Photoirradiation of 2-Thianorbiphenylene 2,2-Dioxide (14). Compound **14** (50 mg, 0.26 mmol) was dissolved in dioxane (5 ml) in a quartz tube, and the solution was flushed with N_2. Irradiation with an Hanovia medium-pressure lamp for 4 hr gave a yellow solution, which on evaporation of the solvent and tlc on silica, eluting with Et_2O–petroleum ether–EtOAc (5:3:2), gave two bands. The faster band was compound **14** (16 mg), and the second band was eluted as a pale yellow oil, which on treatment with $CH_2Cl_2–Et_2O$ gave colorless crystals of the dimer **20** (24 mg, 70% based on recovered **14**): mp >320° dec; mass spectrum *m/e* 380 (M^+, 1) 316 (M − SO_2, 25), 252 (M − $2SO_2$, 100); ir (KBr), 1660, 1310, 1195, 1150, 1125, 1120, 1105, 1080, 760, 750 cm^{-1}; for electronic and nmr spectra, see discussion.

Anal. Calcd for $C_{20}H_{12}S_2O_4$: C, 63.14; H, 3.18; S, 16.86. Found: C, 63.03; H, 3.22; S, 16.74.

Bromination of 12. Compound **12** (15 mg, 0.095 mmol) was dissolved in dry CCl_4 (1 ml) and treated with a solution of bromine in CCl_4 (0.3 m, 0.39 *M*, 0.12 mmol). Addition of 1 drop of pyridine changed the solution color from red to orange. The solution was stored for 25 min, a second aliquot of bromine in CCl_4 (0.3 ml 0.12 mmol) was added, and the solution was warmed in the water bath for 15 min. CCl_4 (10 ml) was then added and the solution was extracted with aqueous $NaHCO_3$ (2 *M* 5 ml), the organic layer was washed with water (3 × 10 ml) and dried (Na_2SO_4), and the solvent was removed by evaporation. Colorless crystals of a mixture of tetrabromides (28 mg, 62%) were obtained, which, on tlc on silica eluting with ether–petroleum ether (1:9), gave two bands. The faster running band gave colorless crystals of the tetrabromide **22** (16 mg, 36%): mp 180–182°; mass spectrum *m/e* 401, 399 (18), 397, 395 (1:3:3:1, M − Br), 320, 318 (44), 316 (1:2:1, M − 2Br), 239, 237 (1:1, M − 3Br, 18), 158 (M − 4Br, 100); ir (KBr) 1240, 1145, 920, 805, 755, 655 cm^{-1}; for the electronic spectrum, see discussion; nmr (CCl_4) τ 2.58 (m, 4 H), 4.70 (s, 2 H).

Anal. Calcd for $C_{10}H_6Br_4S$: C, 25.13; H, 1.27; Br, 66.89; S, 6.71. Found: C, 25.16; H, 1.48; Br, 66.81; S, 6.53.

The second band gave colorless crystals of the tetrabromide **23** (12 mg, 26%): mp 165–178° dec; mass spectrum *m/e* 482, 480, 478 (1), 476, 474 (1:4:6:4:1, M^+), 401, 399 (30), 397, 395 (1:3:3:1, M − Br), 320, 318 (100), 316 (1:2:1, M − 2Br), 239, 237 (1:1, M − 3Br, 25), 158 (M − 4Br, 34); ir (KBr) 1155, 1140, 1045, 930, 900, 855, 815, 755, 715, 680, 645 cm^{-1}; for the electronic spectrum, see discussion; nmr (CCl_4) τ 2.42–3.00 (m, 4 H), 4.37 (s, 1.3 H), 4.42 (s, 0.7 H). This crystalline material contains a third isomeric tetrabromide as an impurity.

Anal. Calcd for $C_{10}H_6Br_4S$: C, 25.13; H, 1.27; Br, 66.89; S, 6.71. Found: C, 25.23; H, 1.38; Br, 67.25; S, 6.60.

When the bromination was carried out using pyridinium bromide perbromide (2 equiv) in dry CH_2Cl_2 for 20 hr, the removal of the solvent and chromatography of the products gave **22** (23%) and **23** (57%).

Debromination of 22 and 23. The tetrabromide mixture obtained as above (10 mg, 0.021 mmol) was dissolved in dry DMF (2 ml), and the solution was stirred with zinc powder (100 mg) under N_2. After 5 hr DMF (10 ml) was added, the mixture filtered, and the filtrate added to a mixture of water (100 ml) and ether (100 ml). The mixture was shaken, the organic layer separated, and the aqueous layer extracted with ether (3 × 20 ml). The combined organic layers were washed with water (3 × 40 ml) and dried ($MgSO_4$), and the solvent was evaporated to give **12** (3 mg, 90%), identified by comparison with an authentic sample. Debromination of pure **22** under the same conditions also gave **12** (90%).

Dehydrobromination of 22 and 23. Synthesis of 1,3-Dibromo-2-thianorbiphenylene (24). The mixture of tetrabromides **22** and **23** (36.7 mg, 0.077 mmol) was dissolved in THF (1 ml) and treated with 1,5-diazabicyclo[4.3.0]nonene-5 (50 mg, 0.38 mmol). The mixture was stirred at room temperature for 45 hr when a brown precipitate had formed. The crude product was subjected to preparative thin-layer chromatography on silica with ether–petroleum ether (3:97) as a developing medium, which gave one band consisting of 1,3-dibromo-2-thianorbiphenylene (**24**) (10.8 mg, 45%): mp 83–84°; mass spectrum *m/e* M^+ 315.836 ($C_{10}H_4Br_2S$ requires 315.838), 318, 316 (100), 314 (M^+, 1:2:1), 237, 235 (1:1, M − Br, 16), 156 (M − 2Br, 37); ir (KBr) 1305, 1110, 1055, 950, 925, 740 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 247 nm (ϵ 43,000), 264 sh (18,500), 319 sh (4300), 325 sh (4600), 322.5 (7300), 350 (7500); nmr (CCl_4) τ 3.07 (br s).

Deuterium Exchange in 12. Compound **12** (15 mg) was dissolved in a mixture of CF_3CO_2D and Et_2O (1.0 ml, 1:1) in an nmr tube, and 3 drops of D_2SO_4 were added. The solution turned pale yellow, and the tube was flushed with N_2 and sealed. The solution was monitored by its nmr spectrum, which showed a decrease in the relative integrals of the H^3 to the H^4,H^5 protons. After 40 min the relative ratios were 1:8, and the reaction was quenched with water (10 ml). The ethereal layer was washed with Na_2CO_3 (2 *N* 1 ml) and then water (5 × 20 ml) and dried ($MgSO_4$). Evaporation of the solvent gave pale yellow crystals, which on tlc on silica gave 1,3-dideuterio-2-thianorbiphenylene (**25**) (10.5 mg, 69%), mp 91–93°; mass spectrum *m/e* 160 (100), 116 (M − CS), 30; ir (KBr) 2950, 2400, 1460, 1420, 1310, 1120, 1050, 985, 950, 940, 780, 745 cm^{-1}; nmr (CCl$_4$) τ 3.2, 3.6 (11:1), *ca.* 20% undeuterated material.

If the reaction time is extended, complete deuteration of the thiophene ring occurs, but this is accompanied, however, by more extensive decomposition. Increasing the acidity of the medium in an attempt to deuterate the benzene ring led only to decomposition.

Bicyclo[3.3.3]undecane and 1-Azabicyclo[3.3.3]undecane. Geometry, Strain, and Spectroscopic Behavior of These Systems

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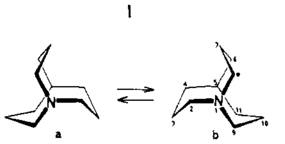
Abstract: Syntheses of bicyclo[3.3.3]undecane (manxane) (**1**) and 1-azabicyclo[3.3.3]undecane (manxine) (**2**) are reported: a multistep synthesis, involving double-ring expansion of the short bridge of bicyclo[3.3.1]non-2-en-9-one (**3**), to give manxane (**1**) and a one-step reductive fission of the short bridge of 1-azoniatricyclo[3.3.3.0]undecane bromide (**16**) with sodium in liquid ammonia to give manxine (**2**). Interesting spectroscopic properties are reported for compounds **1** and **2** and derivatives thereof. The ^{13}C and ^{1}H nmr spectra for manxane and manxine showed chemical shifts for the bridgehead carbon and hydrogen atoms at lower field than normal, and decoupling studies were used to confirm assignment of signals and structures. A "frozen" nmr spectrum was obtained (at 100 MHz) for the free base manxine (**2**) at $\sim -80°$ in keeping with the reported value for manxane (**1**). The uv spectrum of manxine (**2**) in ether had λ_{max} at 240 nm (ϵ 2935), an exceptionally long wavelength for a saturated tertiary amine, and the vapor-phase uv promised additional interest. The conjugate base of manxine (**2**) had a lower pK_a' value than related saturated tertiary amines. Most properties were rationalized on the basis of a flattening of the bridgehead regions of the molecule, affecting the hybridization of the atoms at the bridgehead; this flattening was confirmed by the X-ray study carried out in conjunction with these investigations.

Just as the quest for a compound with the diamond lattice structure led to the isolation, identification, and synthesis of adamantane,[1] so interest in eight-membered rings[2] and in conjoined arrays of eight-membered rings[3,4] has led to the synthesis of the hydrocarbon, bicyclo[3.3.3]undecane[3,4] ("manxane").[5,6] This compound has C_{3h} molecular symmetry[3] and at room temperature is in a state of rapid conformational equilibrium between two degenerate forms (**1**). Possibly

1



2

even more interesting is the related amine, 1-azabicyclo[3.3.3]undecane ("manxine"), since the two corresponding forms, **2a** and **2b**, will be dissymetric (chiral) with a C_3 axis.[7,8] We now provide details of the syntheses of "manxane" and "manxine" and some of their unusual properties.

Syntheses

Our first synthesis of manxane was accomplished by lengthening the short bridge of bicyclo[3.3.1]nonan-9-

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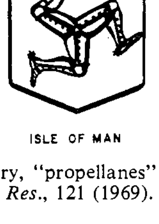
(1) R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

(2) (a) Sj. Kaarsemaker and J. Coops, *Recl. Trav. Chim. Pays-Bas*, **71**, 261 (1952); (b) A. C. Cope, S. W. Fenton, and C. F. Spencer, *J. Amer. Chem. Soc.*, **74**, 5884 (1952); (c) N. J. Leonard, R. C. Fox, M. Ōki, and S. Chiavarelli, *ibid.*, 76, 630 (1954); (d) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, Chapter 4; (e) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **86**, 4854 (1964); (f) *ibid.*, **89**, 7036 (1967); (g) K. B. Wiberg, *ibid.*, **87**, 1070 (1965); (h) N. L. Allinger and S.-E. Hu, *ibid.*, **83**, 1664 (1961); (i) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *ibid.*, **90**, 1199 (1968); (j) F. A. L. Anet and M. St. Jacques, *ibid.*, **88**, 2585, 2586 (1966); (k) A. Peake, J. A. Wyer, and L. F. Thomas, *Chem. Commun.*, 95 (1966); (l) J. E. Anderson, E. S. Glazer, D. L. Griffith, R. Knorr, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 1386 (1969); (m) P. Groth, *Acta Chem. Scand.*, **19**, 1497 (1965); (n) P. Groth, *ibid.*, **21**, 2695 (1967).

(3) M. Doyle, W. Parker, P. A. Gunn, J. Martin, and D. D. MacNicol, *Tetrahedron Lett.*, 3619 (1970).

(4) N. J. Leonard and J. C. Coll, *J. Amer. Chem. Soc.*, **92**, 6685 (1970); **93**, 287 (1971).

(5) The name suggested for this compound class was inspired by the coat of arms of the Isle of Man,[3] whose triskelion is reproduced here.



ISLE OF MAN

(6) Or, in further imagery, "propellanes" without the hub: see D. Ginsburg, *Accounts Chem. Res.*, 121 (1969).

(7) N. J. Leonard, J. C. Coll, A. H.-J. Wang, R. J. Missavage, and I. C. Paul, *J. Amer. Chem. Soc.*, **93**, 4628 (1971). For specification of molecular chirality, see R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966). Professor Prelog has very kindly pointed out to us that our system can be treated as case (78), p 408. Accordingly, **2a** receives the descriptor 1(P)$_3$ or N(P)$_3$ and **2b**, 1(M)$_3$ or N(M)$_3$, where, as designated by the helicity rule (p 391), P is plus and M is minus. For the case of substitution on one or both bridgehead carbons of **1**, specification would depend on that carbon which is higher by sequence rule.

(8) Accompanying article: A. H.-J. Wang, R. J. Missavage, S. R. Byrn, and I. C. Paul, *J. Amer. Chem. Soc.*, **94**, 7100 (1972).