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SYNTHESIS AND PROPERTIES OF UNUSUAL π-NETWORKS

CYCLOOCTA[1,2,3,4-*DEF*]BENZO[3,4]CYCLOBUTA[6,7]BIPHENYLENE[1]

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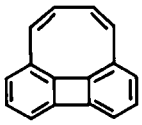
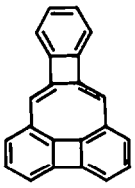
Abstract—The title compound, an example of a hydrocarbon containing three linearly fused 4n-membered rings, has been synthesized and characterized as a thermally stable species possessing no unusual chemical reactivity. Despite the presence of these conventionally antiaromatic structural units this hydrocarbon is predicted to have a net diamagnetic ring current. The NMR results, which are discussed in some detail, are shown to be consistent with this expectation. The impact of this result on the NMR criterion of aromaticity is discussed briefly.

Recently the analysis of π-electron networks by the so-called "algebraic structure count" method has been developed.[2] This approach has proved useful for surveying classes of molecules for members with novel properties. As a result of applying this analysis, compound **1** was selected as a potentially interesting hydrocarbon. It has recently been prepared in this laboratory and has been found to be thermally stable despite its high chemical reactivity and the presence of marked paramagnetic shifts in its proton NMR spectrum.[3] Thus **1** appears to hover at the borderline between olefinic, aromatic and antiaromatic classifications.



1

A similar search for other fused 4n-systems which might exhibit unusual properties revealed cycloocta[1,2,3,4-*def*]benzo[3,4]cyclobuta[6,7]biphenylene (**2**), cycloocta[1,2,3,4-*def*]phenanthro[6,7]biphenylene (**3**) and cycloocta[1,2,3,4-*def*]benzo[6,7]biphenylene (**4**).



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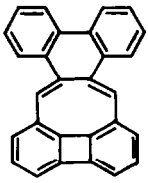

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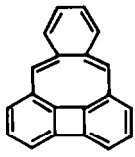

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Pople and Untch[4] have pointed out that the London[5] ring current theory predicts that 4n-membered rings should exhibit paramagnetic ring currents. In agreement with this prediction the proton NMR of **1** shows marked upfield shifts in both the olefinic and aromatic regions of the spectrum.[3] We were therefore particularly interested in the magnetic phenomena which might be expected from hydrocarbons **2**, **3** and **4**. Accordingly, ring current calculations were performed on these molecules utilizing a modification of the McWeeny ring current model.[6] In the present computations, iterated Hückel calculations were first performed to obtain π-bond orders. Bond lengths were calculated using the π-bond order—bond length correlation of Dewar and Gleicher.[7]

$$r_{ij} = 1{\cdot}504 - 0{\cdot}166P_{ij}$$

where r_{ij} is the bond length (Å) and P_{ij} is the bond order. Resonance integrals were assumed to obey the function

$$\beta = \beta_0 e^{(3{\cdot}80(1\,393 - r_{ij}))}$$

where r_{ij} is the bond length calculated above. The bond lengths obtained by this procedure are presented in Table 1.† The Hückel molecular orbitals interated to self-consistency were then used as the basis for ring current calculations using the McWeeny approach. The results of these computations for biphenylene (**5**) and hydrocarbons **1**–**4** were compiled in Table 1 (Fig. 1).

One of the interesting features of these calculated ring currents is the large variation in the paramagnetic ring currents predicted for the eight membered rings in the hydrocarbons **1**–**4**. In view of the pre-eminent position which ring currents have assumed as a criterion of aromaticity,[9] it is important to understand both the origin of the paramagnetic ring currents and the reasons for the differences among the various hydrocarbons listed in Table 2 (Fig. 1).

According to the quantum mechanical models of London[4,5] and McWeeny,[6] monocyclic polyenes with $4n + 2\pi$-electrons are predicted to exhibit a net rise in energy when subjected to a magnetic field perpendicular to the plane of the ring. This rise in energy represents a negative contribution to the magnetic susceptibility and corresponds to a diamagnetic ring current. However, as Longuet-Higgins[10] has pointed out, when there are occupied and unoccupied energy levels that mix strongly under the influence of the magnetic field, a net lowering of energy corresponding to a positive contribution to the magnetic susceptibility or a paramagnetic ring current can occur. Just such a situation is predicted in monocyclic polyenes with $4n\pi$-electrons in which the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are degenerate in the absence of bond alternation.[5] The effect also persists in molecules in which the degeneracy is removed by bond alternation, but in which the HOMO–LUMO separation remains

†The SCF bond lengths obtained from the Dewar–deLlano model (see Ref 8) for compounds **1**, **2** and **5** agree with the iterated Hückel values within a standard deviation of 0·008 Å.

Table 1. Calculated iterated-Hückel bond lengths (Å)

Bond	1	2	3	4	5
a	1.393	1.394	1.394	1.395	1.386
b	1.406	1.409	1.407	1.407	1.403
c	1.386	1.384	1.386	1.387	1.385
d	1.402	1.404	1.402	1.401	1.403
e	1.389	1.387	1.390	1.391	1.386
f	1.404	1.407	1.404	1.402	1.409
g	1.472	1.471	1.472	1.472	1.470
h	1.475	1.470	1.475	1.478	
i	1.453	1.448	1.448	1.447	
j	1.355	1.360	1.365	1.369	
k	1.448	1.463	1.453	1.450	
l		1.452	1.477	1.439	
m		1.397	1.400	1.439	
n		1.393	1.391	I.436	
o		1.396	1.397		
p		1.409	1.391		
q			1.399		
r			1.405		
s			1.448		

Table 2. Calculated ring currents

Ring*	1	2	3	4	5
A	+0.37	+0.48	+0.29	+0.17	+0.61
B	-0.75	-0.78	-0.72	-0.68	-0.81
C	+0.37	+0.48	+0.29	+0.17	+0.61
D	-0.71	-0.31	-0.91	-1.23	
E		+0.18			
F		+0.97			
G			-0.09	-0.30	
H			+0.82		
I			+0.82		
net ring current	-0.71	+1.01	+0.50	-1.88	+0.41

* Benzene = +1.00

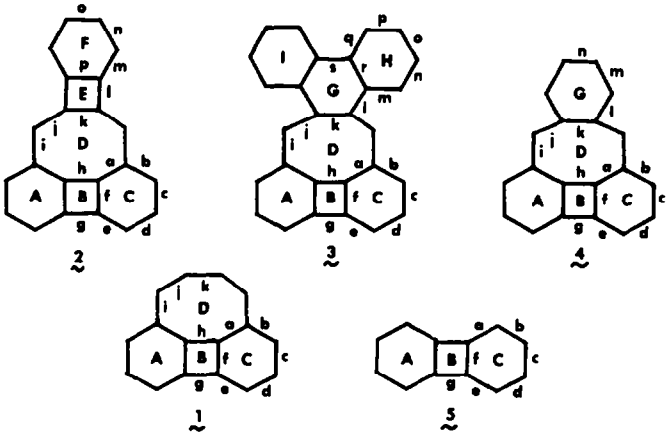


Fig. 1. Identification of bonds (lower case letters) and rings (capital letters).

small.[5,10] For *monocyclic* systems the magnitude of the magnetic response is controlled by the area of the ring times the product of the resonance integrals around the bonds of the ring.[5] Since the resonance integrals are a function of the bond lengths (*vide supra*) the magnitude of the ring current calculated for a particular monocyclic ring is sensitive to bond alternation. Furthermore, large rings are more sensitive to bond alternation as a consequence of the greater number of resonance integrals entering the product. The situation is more complicated in polycyclic systems like **1–4**, since in these systems the magnitude of the calculated ring current for a particular ring is influenced by the other rings present and cannot be related in any straightforward way to the degree of bond alternation of the particular ring in question. Thus, the ring currents in the eight membered rings of hydrocarbons **1–4** vary widely despite the rather small differences in the degree of bond alternation displayed in Table 1. Put another way, the calculated ring current is a complex function of both the individual rings and the global connectivity of the molecule.

Interestingly, in contrast to the net paramagnetic ring currents predicted for **1** and **4**, hydrocarbons **2** and **3** are predicted to exhibit net diamagnetic ring currents in spite of the presence of multiple fused 4n-membered rings. A measurement of diamagnetic susceptibility exaltation is therefore predicted to give a negative value for **1** and **4** and a positive value for **2** and **3** even though the protons on the 8-membered rings of all four compounds are predicted to show substantial upfield shifts in the NMR.

Finally, the small diamagnetic ring currents predicted for the benzene rings in the biphenylene moieties of **3** and **4** should be pointed out. As a result of these small diamagnetic currents combined with the large paramagnetic ring currents predicted for the adjacent 4n-membered rings, these compounds would be expected to show remarkably large upfield shifts in the proton resonances of these rings.

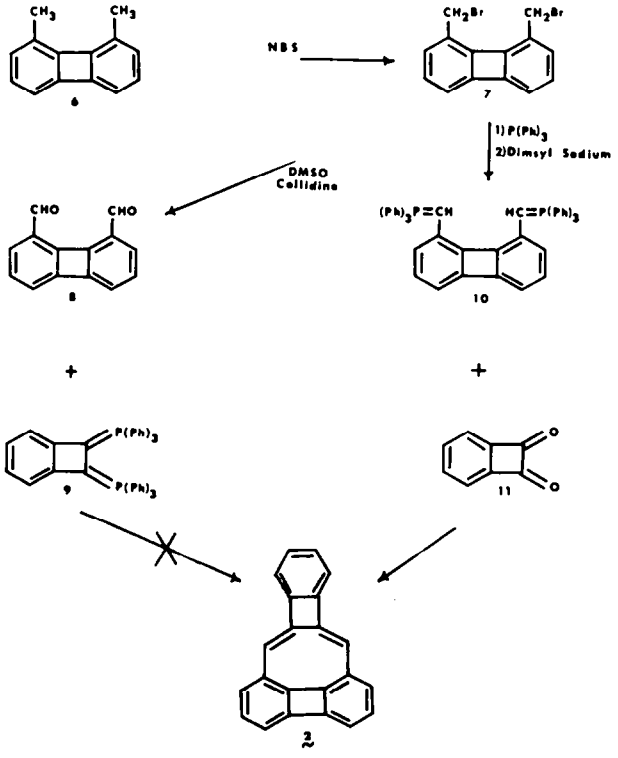
Synthesis and characterization of cycloocta[1,2,3,4-def]*benzo*-[6,7]*cyclobuta*[3,4]*biphenylene* (**2**)

A number of groups have successfully used a double Wittig reaction in the synthesis of various annelated cyclooctatetraene rings.[3,11,12] Scheme 1 outlines two alternate routes to hydrocarbon **2** in which such a reaction was attempted. Both routes utilize 1,8-dimethylbiphenylene (**6**) as the starting material, thus introducing the biphenylene moiety in the first step of the sequence and thereby avoiding the known difficulties in synthesizing biphenylenic systems.[13]

The superior reactivity of aldehydes in the Wittig reaction[14] combined with Garratt's failure to observe the formation of cyclic products in the reaction between benzocyclobutadienoquinone (**11**) and 2,2'-bis(triphenylphosphoranylidenemethyl)biphenyl[11] prompted us to direct our initial efforts along the route utilizing 1,8-biphenylenedicarboxaldehyde (**8**).

The dialdehyde (**8**) was prepared by room temperature oxidation of α,α-dibromo-1,8-dimethylbiphenylene (**7**) with dimethyl sulfoxide in the presence of collidine. Addition of a benzene–ether solution of **8** to an equimolar solution of **9** (prepared from *trans*-1,2-bis(triphenylphosphonio)benzocyclobutene dibromide and n-butyl lithium[15]) gave a semi-solid brown oil. Chromatography on alumina afforded triphenylphosphine oxide as the only identifiable monomeric product; the remaining material was an insoluble yellow polymer which was not investigated further.

With the failure of the reaction of **8** and **9** to give the desired cyclic hydrocarbon, the alternate reaction between benzocyclobutadienoquinone (**11**) and 1,8-bis(triphenylphosphoranylidenemethyl)biphenylene (**10**)



Scheme 1.

was investigated. The bis-ylid was prepared by reaction of α,α'-bis(triphenylphosphonio)-1,8-dimethylbiphenylene dibromide with dimsyl sodium in dimethyl sulfoxide.[3,16] Treatment of this solution with benzocyclobutadienoquinone in dry tetrahydrofuran under high dilution conditions gave a complex mixture of products from which hydrocarbon **2**, a bright red solid, could be isolated by column chromatography in 6% yield.

Hydrocarbon **2** is thermally stable: it melts at 192–193° without decomposition, and sublimes readily at 110° (0·01 torr). The high resolution mass spectrum shows a parent peak at 276·0942 (calculated for $C_{22}H_{12}$, 276·0939) with isotope peaks of the appropriate magnitude. The parent peak was the largest in the spectrum as would be expected for a hydrocarbon of low ionization potential.

The proton NMR spectrum of **2** in CCl_4 shows three groups of peaks in the ratio 2:3:1 assignable to the benzocyclobutane, biphenylene, and olefinic protons respectively. The protons of the biphenylene moiety give a complex ABC pattern with chemical shifts of 3·49, 3·37, and 3·47 and with coupling constants $J_{AB} = 8·2$ Hz, $J_{AC} = 0·82$ Hz, and $J_{BC} = 6·7$ Hz (Fig. 2 and Table 3). Thus, in contrast to the large upfield shifts observed in cycloocta[*def*]biphenylene (**1**),[3] the protons in the biphenylene moiety of **2** are shifted only slightly upfield from the positions observed in biphenylene itself. The observed chemical shifts are therefore in qualitative accord with the calculated McWeeny ring currents (Table 2). The coupling constants extracted from the NMR spectrum of **2** are in good agreement with the empirical SCF bond order—vicinal coupling constant correlation of Günther *et al.*[17] Thus, using the iterated Hückel for the SCF bond orders we calculate 8·2 Hz for J_{AB} and 6·8 Hz for J_{BC}. This agreement indicates that the actual structure of **2** is well represented as 1,2-dimethylenebenzocyclobutene attached to biphenylene. Furthermore, the uniformity of the coupling constants reported in Table 2 indicates

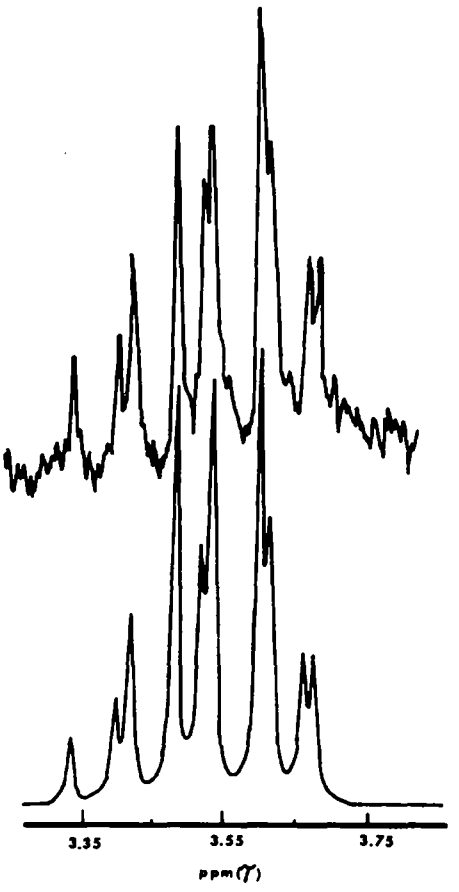
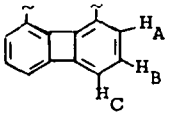


Fig. 2. Top: 100 MHz proton NMR spectrum of the biphenylene moiety of **2**. Bottom: computer simulated spectrum using the calculated chemical shifts and coupling constants in Table 2.

Table 3. NMR data for representative biphenylenes

Compound	Chemical Shift (τ)			Coupling Constant (Hz)		
	H_A	H_B	H_C	J_{AB}	J_{BC}	J_{AC}
Biphenylene[a]	3.4	3.4	3.3	8.3	7.0	0.84
1,8-Dimethylbiphenylene[a]	3.56	3.44	3.63	8.3	6.8	0.75
1,5-Dimethylbiphenylene[a]	3.57	3.43	3.63	8.5	6.7	0.66
1[a]	4.22	3.83	4.00	8.2	6.9	0.60
2[b]	3.49	3.37	3.47	8.2	6.7	0.82

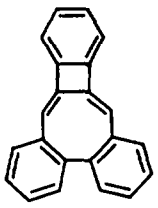
[a] Reference 3. 

[b] The spectrum was taken at 100 MHz in CCl_4 using tetramethylsilane as an internal standard (see Fig. 2). The spectrum was analyzed using a LAOCOON 3 program on an IBM 370/168 computer.

that no major geometric distortions have occurred in the biphenylene moieties of either **1** or **2**.

The olefinic protons of **2** appear as a sharp singlet at 3·85τ in CCl_4. This represents an upfield shift of 0·35 ppm relative to the olefinuic proton in *trans*-1-benzylidenebenzocyclobutene.[15] An even larger shift of 0·57 ppm is found if *cis,cis*-1,2-dibenzylidenebenzocyclobutene[15] is used as a reference. Further evidence for a substantial paramagnetic ring current in the eight-membered ring of **2** is provided by comparison with dibenzo[*a,c*]benzo[3,4]cyclobuta[1,2-*f*]cyclooctene, **12**. Garratt[11] found that the olefinic protons of **12** gave a singlet at 3·33τ in tetrahydrofuran; the protons in the benzocyclobutane moiety of **12** appeared at 2·82τ. In the same solvent the olefinic protons of **2** appear at 3·76τ while those of the benzocyclobutane moiety absorb at 2·56τ. Thus there is a paramagnetic shift of 0·43 ppm in the olefinic absorption of **2** and a diamagnetic shift of 0·38 ppm in the benzocyclobutane absorption relative to those of the same protons in hydrocarbon **12**. All of these results are in qualitative accord with the predictions based on our Hückel-McWeeny ring current calculations.

The UV-visible data for **2** and several related systems is collected in Table 4. While no rigorous analysis of the electronic spectrum has been performed, the three bands observed in the spectrum of **2** are apparently related to the three bands of biphenylene at 249 nm (log ε = 5·0), 356 nm



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(log ε = 4·0), and 392 nm (log ε = 2·4). Streitwieser's[18] empirical correlation of electronic spectra with HOMO–LUMO separations predicts that **2** should have an absorption in the visible range near 540 nm, in good accord with the band observed at 559 nm. Hydrogenation of **2** over 5% palladium–barium carbonate in ethyl acetate gave a yellow $C_{22}H_{16}$ hydrocarbon (m/e = 280) with an NMR characteristic of an alkylated biphenylene: 2·83τ (doublet, 4H), 3·42τ (ABC, 6H), 7·11τ (complex multiplet, 6H). In addition a mixture of hydrocarbons (m/e = 286, 284, and 282) was obtained, suggesting cleavage of the 4-membered rings.

In order to evaluate the ability of **2** to act as a diene we attempted to react **2** with tetracyanoethylene (TCNE). Every attempt to form an adduct with TCNE was unsuccessful, **2** being recovered unchanged. In this respect the behavior of **2** towards TCNE most closely resembles that of 1,2-dimethylenebenzocyclobutene[20] and hydrocarbon

Table 4. UV-visible data for **2** and related compounds

5[a]		**2**[b]		**1**[c]	
λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε
249nm	5.00	223nm	4.51	225nm	4.35
330	3.95	257	4.56	258	3.86
343	3.90	269	4.68	268	3.94
356	4.00	281	4.73	280	4.10
368	3.35	290	4.83	292	4.30
374	2.84	304	4.81	305	4.31
379	2.62	324	4.04	327	2.91
385	2.40	376	3.91	342	3.05
		398	4.02	360	3.17
		417	3.81	378	3.17
		424	3.93	402	3.07
		445	3.31	410	3.05
		479	3.16	431	3.02
		515	3.12	440	3.05
		559	2.84	463	3.00
				478	2.81
				512	2.69
				557	2.42
				621	1.63

[a] See reference 20. The solvent is hexane.

[b] The spectrum was obtained on a Cary 1605 spectrometer; solvent is is cyclohexane

[c] Reference 3 solvent is cyclohexane.

12[11] rather than that of bicyclo[6.2.0]decapentaene derivatives which have been found to give 2+2 adducts.[21] It should be noted however, that cycloocta[*def*]biphenylene also failed to react with TCNE in either a 4+2 or 2+2 manner.[3] Examination of the electronic spectrum of 2 in the presence of TCNE revealed a broad structureless charge transfer band with $\lambda_{max} = 770$ nm.

Aromaticity. Over the years a number of criteria for aromaticity have been developed.[9]† Currently there is a trend to affix a stamp of universality to the concept of aromaticity, the terms aromatic and antiaromatic being used to describe transition states,[23] electronically excited states,[24] as well as exotic orbital arrays.[25] In these contexts the term aromatic is usually understood to refer to π-electrons completing a closed shell of bonding orbitals. While such a definition has considerable heuristic value, it is not particularly satisfying for the experimentalist who wants to base his decision on the outcome of a measurement. Recently Garratt[9] has given a definition which seems to summarize the view currently adopted by most experimentalists: "Aromatic compounds are diatropic [i.e. support induced diamagnetic ring currents] cyclic molecules in which all the ring atoms are involved in a single conjugated system". Substitution of the words antiaromatic and paratropic would provide a currently acceptable definition of antiaromaticity. These definitions seem eminently satisfactory for monocyclic systems like the [4n+2]- and [4n]-annulenes, but as our results indicate, their application to polycyclic systems like 1 and 2 is fraught with hazards. A comparison of the NMR results for 2 with those for 1 show how dramatically different the magnetic response of two otherwise comparable ring systems can be. Furthermore, as our calculations indicate, the combination of 4n-membered and (4n+2)-membered rings may result in either a net paramagnetic or a net diamagnetic contribution to the total magnetic susceptibility. Taken together these facts constitute a strong caveat to the naive application of the ring current criterion.

The foregoing discussion highlights the central dilemma of aromaticity: because the concept is inherently vague and diffuse, the more intuitive and empirical information which is incorporated into a theory of aromaticity, the more acceptable the theory becomes to the chemist, whereas any attempt to reduce aromaticity to an observable is ultimately so restrictive as to be unacceptable. As a result it is difficult, if not impossible, to formulate a definition to which no objections can be raised.

EXPERIMENTAL

M.ps were determined on a Thomas Hoover Capillary Melting Point Apparatus and are uncorrected. Continuous wave proton NMR spectra were obtained on Varian A60A or HA100 spectrometers in the solvent indicated using TMS as an internal standard. Fourier transform proton NMR spectra were obtained on a Bruker HFX-90 spectrometer equipped with a Digilab computer, and chemical shifts are reported with respect to added TMS as an internal standard. Mass spectra were obtained on an AEI MS902 mass spectrometer at 70 eV. IR spectra were recorded on a Perkin Elmer 137 spectrometer. UV and visible spectra were obtained on a Cary 1605 spectrometer.

α,α'-Dibromo-1,8-dimethylbiphenylene (7) *and α,α'-bis(triphenylphosphonio)-1,8-dimethylbiphenylene dibromide* were prepared as described by Wilcox *et al.*[3]

trans-1,2-*Bis(triphenylphosphonio)benzocyclobutene dibromide* was prepared as described by Blomquist and Hruby;[15] m.p. 228–229° (lit.[15] m.p. 230·5–232°).

Benzocyclobutadienoquinone (11) was prepared by the method of Cava *et al.*[26] and was sublimed (100°, 0·5 torr) twice prior to use; m.p. 125–127° (lit.[26] m.p. 126–129°).

1,8-*Biphenylenedicarboxaldehyde* (8). A soln of 1·00 g (2·96 mmol) of α,α'-1,8-dimethylbiphenylene and 2·16 g (17·0 mmol, 2·40 ml) of 2,4,6-collidine (Aldrich) in 150 ml of dry DMSO (Fisher Certified, distilled from CaH_2) was stirred at room temp under a silica gel drying tube. After 96 hr the mixture was poured into 200 ml of distilled water and extracted with six 75 ml portions of $CHCl_3$. The chloroform extracts were back extracted with distilled water and dried over Na_2SO_4. Concentration under vacuum afforded a yellow crystalline residue which was taken up in benzene and chromatographed on a 2 × 57-cm column of Florisil (100–200 mesh) using benzene as the eluent. The first four 125 ml fractions contained 0·33 g of unreacted α,α'-dibromo-1,8-dimethylbiphenylene. The remaining intensely yellow band was eluted with methylene chloride. A total of 0·22 g (34%) of 8 was obtained as a yellow solid. Crystallization from cyclohexane gave bright yellow needles: m.p. 151–152°; NMR ($CDCl_3$) τ 3·0 (multiplet, ABC, 6H), −0·27 (singlet, 2H): IR (KBr) 1675, 1370, 1240, 945, and 765 cm^{-1}; MS (rel. int.) 208(33), 180(36), 152(100).

Attempted synthesis of 2 *from* trans-1,2-*biphenylenedicarboxaldehyde* (8). 1,2-Bis(triphenylphosphonio)benzocyclobutene dibromide (0·80 g, 0·96 mmol) was suspended in 250 ml of dry diethyl ether–benzene (3:1 v/v) under an argon atmosphere, and the stoichiometric amount of n-BuLi in hexane (Foote) was added with vigorous stirring. After about 2·5 hr the dibromide had dissolved and the soln of the 9 was deep red. A soln of 1,8-biphenylenedicarboxaldehyde (0·20 g, 0·96 mmol) in 75 ml of dry diethyl ether–benzene (3:1 v/v) was added dropwise with stirring over a period of 1·25 hr. After addition was complete the mixture, which had turned a muddy brown, was refluxed for 1·5 hr. The mixture was cooled and 100 ml of distilled water was added. The organic layer was separated, washed 3 times with 100-ml portions of distilled water, and dried over K_2CO_3. Concentration under reduced pressure afforded a semi-solid yellow oil which was pre-absorbed on 25 g of alumina and chromatographed on a 2·5 × 10-cm column of Woelm Dry Column Grade alumina (100–200 mesh). Elution with benzene gave 0·40 g of triphenylphosphine oxide. The remaining material was an insoluble yellow polymeric material which was not investigated further.

Synthesis of cycloocta[1,2,3,4-def]benzo[3,4]cyclobuta[6,7]biphenylene (2). To a thoroughly dried 1-l three-necked flask fitted with an argon inlet and outlet, a serum stopper, and a magnetic stirring bar was added 0·23 g of sodium hydride (Ventron, 57% suspension in mineral oil) and 100 ml of dry pentane (Eastman technical, dried over 4 Å molecular sieves). The mixture was stirred vigorously for several minutes to dissolve the mineral oil, the sodium hydride was allowed to settle, and the pentane was withdrawn by syringe.

Dry DMSO (750 ml, Fisher Certified, distilled from CaH_2) was added and the soln stirred until evolution of H_2 ceased and the soln became clear. α,α'-Bis(triphenylphosphonio)-1,8-dimethylbiphenylene dibromide (1·65 g) was added and the mixture was stirred for 1·5 hr during which time the dibromide gradually dissolved and the soln became deep red. A soln of 0·25 g of 11 in 50 ml dry THF (distilled from LAH) was then added dropwise over a period of 3·5 hr. Stirring was continued at room temp for 1 hr after addition was complete and the soln was then heated to 50° for an additional 1·5 hr. The mixture was cooled, poured into 1:1 of water, and extracted with four 250 ml portions of benzene. The organic extracts were dried over K_2CO_3 and concentrated under reduced pressure. The resulting red oil was pre-adsorbed on 20 g of alumina and chromatographed on 100 g of Woelm Dry Column Grade alumina (100–200 mesh). Elution with cyclohexane afforded 31·6 mg (6%) of 2 as a red solid. This material could be further purified by vacuum sublimation at 110° (0·01 torr). Two sublimations afforded 20 mg of 2, m.p. 192–193°. In subse-

†In discussing any scientific problem it is highly desirable that all the words and terms employed should be capable of precise definition... The expression aromatic character unfortunately does not satisfy this desideratum, for it is used in different connotations corresponding to different individual interests.

quent preparations purification was accomplished by preparative layer chromatography (E. Merck Silica Gel F-254, 1·5 mm, cyclohexane eluent): NMR (CCl_4) τ 2·56 (d, 4H), 3·4 (m, ABC, 6H), 3·85 (s, 2H): IR (KBr) 1465, 1410, 1370, 1320, 1180, 880, 785, 765, 720 cm^{-1}: MS 276·0942 (calculated for $C_{22}H_{12}$, 276·0939). Other physical properties of **2** are discussed in the text.

Hydrogenation of cycloocta[1,2,3,4-def]benzo[3,4]cyclobuta[6,7]biphenylene (**2**). Compound **2** (9·2 mg) in 40 ml of EtOAc (dried over 4 Å molecular sieves) was hydrogenated over 5% Pd–$BaCO_3$ (194 mg, K&K Laboratories) for 1·25 hr. The mixture was filtered through a Celite pad and concentrated under vacuum to afford a yellow oil. The products were separated by preparative layer chromatography (E. Merck Alumina F-254) using cyclohexane as the eluent. Two bands were obtained. The upper band yielded 2·3 mg of a yellow oil: FT NMR ($CDCl_3$) τ 2·83 (d, 4H), 3·42 (m, ABC, 6H), 7·11 (broad m, 6H): MS (Rel. int.) 280(100), 265(31), 250(13).

The lower band afforded 3·3 mg of a pale yellow oil: FT NMR ($CDCl_3$) τ 2·52–2·90 (broad m), 5·90–6·58 (broad m), 6·80–7·47 (m): MS (rel. int.) 286 (64), 284(72), 282(72), 271(100), 267(96).

Attempted reaction of cycloocta[1,2,3,4-def]benzo[3,4]cyclobuta[6,7]biphenylene (**2**) with tetracyanoethylene. To 3·3 mg of **2** was added 1·60 ml of an 0·016 M soln of tetracyanoethylene (Aldrich, recrystallized from chlorobenzene) in dry (distilled from LAH) THF. The reaction flask was purged with argon and sealed with a ground glass stopper wrapped with parafilm. After 24 hr at room temp TLC (Eastman silica gel) indicated that only **2** and tetracyanoethylene were present. Subsequently, the soln was heated to reflux, and after 4 hr no change was evident in the chromatogram.

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