Cyclobutarenes. Part 3.[1] Synthesis of Bromodicyclobutarenes and Some New Derivatives of the Benzocyclobutabiphenylenes

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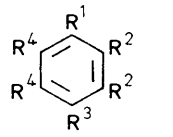
Sodium iodide debromination of tetrakis- and hexakis-(dibromomethyl)carbocycles gives bromodicyclobutarenes and/or quinodimethanes, and *o*-bis(dibromomethyl)biphenylenes give cyclobutabiphenylene derivatives. Dehydrohalogenation of these compounds generates cyclobutadienoid intermediates, some reactions of which are described.

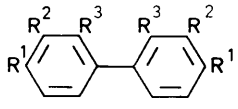
The reaction of 1,2-bis(dibromomethyl)benzene with sodium iodide in EtOH or DMF gives 1,2-dibromo-1,2-dihydrobenzocyclobutene in 60—70% yield.[2] This reaction proceeds *via* intramolecular cyclisation of an intermediate quinodimethane, 5,6-bis(bromomethylene)cyclohexa-1,3-diene, but in some analogous debrominations an anionic mechanism is indicated.[3,4] The previous papers in this series have used this method to prepare polycyclic[4] and heterocyclic cyclobutarenes,[1] and here the application of the reaction to the synthesis of di- and tricyclobutarenes is investigated. These compounds are precursors to novel anti-aromatic cyclobutadienoid systems,[5] and some cycloadditions of these intermediates are described.

Results and Discussion

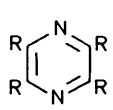
Dibromomethyl Derivatives.—At the outset of this work one point of interest lay in the question as to whether the appropriate hindered dibromomethyl precursors, particularly of benzene itself, could be prepared. 1,2,4,5-Tetrakis(dibromomethyl)benzene (**1**) has been reported,[6] but the 1,2,3,4-isomer (**2**) and hexakis(dibromomethyl)benzene (**5**) are not described in the literature. 1,2-Bis(dibromomethyl)naphthalene, in which the degree of strain is expected to be less than in (**2**), shows restricted rotation of the dibromomethyl groups with an energy barrier of *ca.* 70 kJ mol^{-1}.[4] The dodecachloro analogue of (**5**)



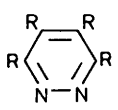
(**1**) $R^1 = R^3 = H$, $R^2 = R^4 = CHBr_2$
(**2**) $R^1 = R^2 = R^3 = CHBr_2$, $R^4 = H$
(**3**) $R^1 = R^3 = CHBr_2$, $R^2 = CH_2Br$, $R^4 = H$
(**4**) $R^1 = R^2 = CHBr_2$, $R^3 = CBr_3$, $R^4 = H$
(**5**) $R^1 = R^2 = R^3 = R^4 = CHBr_2$



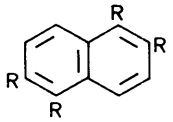
(**6**) $R^1 = H$, $R^2 = R^3 = CHBr_2$
(**7**) $R^1 = R^2 = CHBr_2$, $R^3 = H$



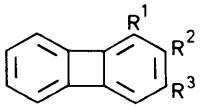
(**9**) $R = CHBr_2$



(**10**) $R = CH_2Br$



(**8**) $R = CHBr_2$



(**11**) $R^1 = R^2 = CHBr_2$, $R^3 = H$
(**12**) $R^1 = H$, $R^2 = R^3 = CHBr_2$

appears to have a completely 'locked' conformation below 180 °C (the limit of the experimental observation).[7]

Gratifyingly, both (**2**) and (**5**) can be prepared by direct photobromination of the requisite methyl benzenes. The reaction times necessary give some indication of the relative degree of difficulty of introducing bromine atoms into these hindered molecules. Thus photobromination of 1,2,3,4-tetramethylbenzene resulted in the rapid formation (< 1 h) of the hexabromide (**3**), but further substitution occurred only under dilute conditions, giving a maximum yield of the octabromide (**2**) (*ca.* 60%) after 40—50 h. In comparison, photobromination of 1,2,4,5-tetramethylbenzene under identical conditions gave the octabromide (**1**) in near-quantitative yield after 8 h. The ^{1}H n.m.r. spectrum of (**2**) shows four singlets for the dibromomethyl groups, the signal due to 1α-H appearing at 0.7 p.p.m. upfield of those due to 2α-, 3α-, and 4α-H, which are deshielded by the surrounding bromine atoms. A similar effect was observed in the spectra of 1,2-bis(dibromomethyl)naphthalene and 9,10-bis(dibromomethyl)phenanthrene.[4] Formation of the octabromide (**2**) was accompanied by 20—30% of the nonabromide (**4**); substitution occurring at the least hindered position, 1α-H. Attempts to suppress the formation of (**4**) were unsuccessful; the reaction was monitored by n.m.r. spectroscopy and stopped when the characteristic 1α-H singlet reached maximum intensity.

Photobromination of hexamethylbenzene was initially rapid and exothermic, giving hexakis(bromomethyl)benzene[8] after *ca.* 30 min, but then proceeded slowly to give a product analysed as the undecabromide after *ca.* 200 h. Reaction for a further 200—250 h gave the dodecabromide (**5**) in quantitative yield; the insolubility of this compound prevented the recording of n.m.r. spectra.

The ^{1}H n.m.r. spectrum of 2,2′3,3′-tetrakis(dibromomethyl)-biphenyl (**6**) is also suggestive of restricted rotation of the substituents, showing signals of equal intensity at δ 6.42 (s, 2α-, 2′α-H), 7.07 (dd, 6-, 6′-H), 7.55 (t, 5-, 5′-H), 7.80 (s, 3α-, 3′α-H), and 8.26 (dd, 4-, 4′-H). The phenyl groups are probably twisted with respect to each other, so the shielding effect of the adjacent ring may contribute to the high-field shift of 2α- and 2′α-H. The low-field shift of 3α-, 3′α-H again reflects the deshielding influence of the 'enveloping' bromine atoms. In contrast the dibromomethyl protons of the octabromo isomer (**7**), which can rotate freely, resonate as an unresolved singlet at δ 7.51.

1,2,5,6-Tetrakis(dibromomethyl)naphthalene (**8**) was isolated as a complex mixture of isomers, as previously observed for the 1,2-bis(dibromomethyl) analogue,[4] contaminated with hepta- and nona-bromo derivatives. The crude octabromide was used directly without purification for the debromination step.

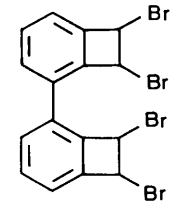
Photobromination of 2,3,5,6-tetramethylpyrazine with *N*-bromosuccinimide gave the octabromide (**9**) in high yield, but attempts to prepare 3,4,5,6-tetrakis(dibromomethyl)pyridazine by this method failed. It was hoped that replacement of ring

Table 1.

Precursor	Reaction temp. (°C)	Reaction time	Product	Yield (%)
(1)	120	3 min	(13)	6
			(14)	2
(2)	110	2 min	(15a)	61
			(16)	13
(5)	100	15 min	(17)	90—100
			(19)	0
(6)	120	2 min	(21)	1
(7)	65—70	4 h	(22)	42
(8)	70—80	3 h	(23)	37
(11)	105	1 min	(24)	11
(12)	105	2 min	(25)	27

C–H by nitrogen would reduce the hindrance to bromination shown by (2); however, the bromomethylpyridazines appear particularly susceptible to decomposition *via* intermolecular quaternisation.[1,9] A reaction under high-dilution conditions gave a low yield of the tetrabromide (10); this compound polymerises rapidly when concentrated and was identified on the basis of its n.m.r. and mass spectra.

Reaction of the Bromides with Sodium Iodide.—Debromination of the bromides (1), (2), (5)—(9), (11),[10] and (12)[11] with sodium iodide in DMF at 65—120 °C gave the cyclobutarenes and/or quinodimethanes (13)—(17), (21)—(25). The reaction conditions and products are listed in Table 1 and are discussed in detail below. The cyclisation temperatures and times quoted are those giving optimum yields of cyclobutarene products; prolonged heating at the higher temperatures resulted in decomposition. Traces of iodocyclobutarenes, when formed, were removed by the procedure of McOmie *et. al.*,[12] but treatment of the cyclobutabiphenylenes (24) and (25) under these conditions gave addition products.[13]



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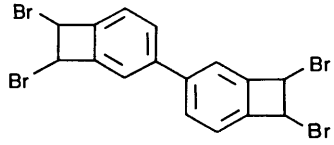

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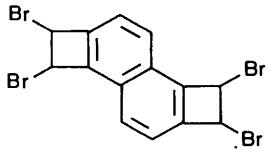
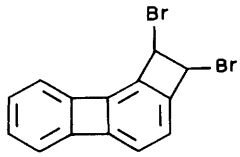
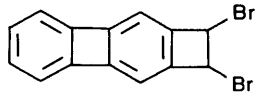


(23) a; *trans,trans*
b; *cis , trans*

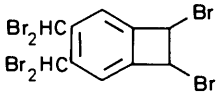


(24) a ; *trans*
b ; *cis*



(25) a; *trans*
b; *cis*

1,2,4,5-tetrahydrobenzo[*a,d*]dicyclobutene (14). No *cis*-isomers could be detected, as evidenced by low-field signals for the cyclobutene ring protons,[14] but this is not surprising considering the low overall yield of the reaction. The competing decomposition of (1) may take place *via* the initial generation of the *p*-quinodimethane (26). If this is the case, then the main constraint on the yield lies in formation of the first four-membered ring, and in support of this, cyclisation of the hexabromide (13) at 120 °C gave a 29% yield of (14). Debromination of the hexabromide (13) with zinc generates the



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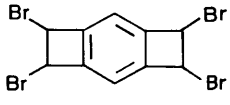

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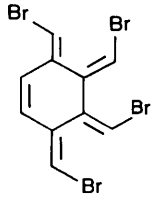
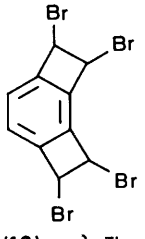
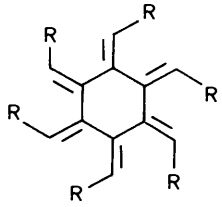


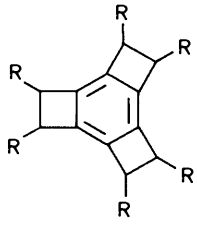
(15) a; the *E,E,Z,Z* – isomer
b; the *Z,E,Z,Z*,– isomer



(16) a ; b ; The two *trans,trans*- isomers

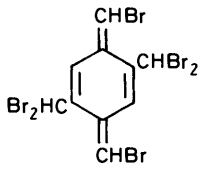


(17) a ; R = Br
b ; the *E,E,E, Z,Z,Z*- isomer
(18) R = H



(19) R = Br
(20) R = H

Cyclisation of 1,2,4,5-tetrakis(dibromomethyl)benzene (1) did not take place below 110 °C, but a reaction at 120 °C gave the *trans*-dibromomonocyclobuta derivative (13) and predominantly one isomer of *trans,trans*-1,2,4,5-tetrabromo-reactive ene–diene intermediate (27); its chemistry is under investigation. Diaza analogues of (13) and (14) could not be prepared from the octabromopyrazine (9), the products (if formed) presumably polymerise under the reaction conditions.[1]



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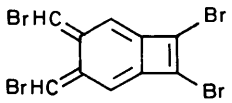
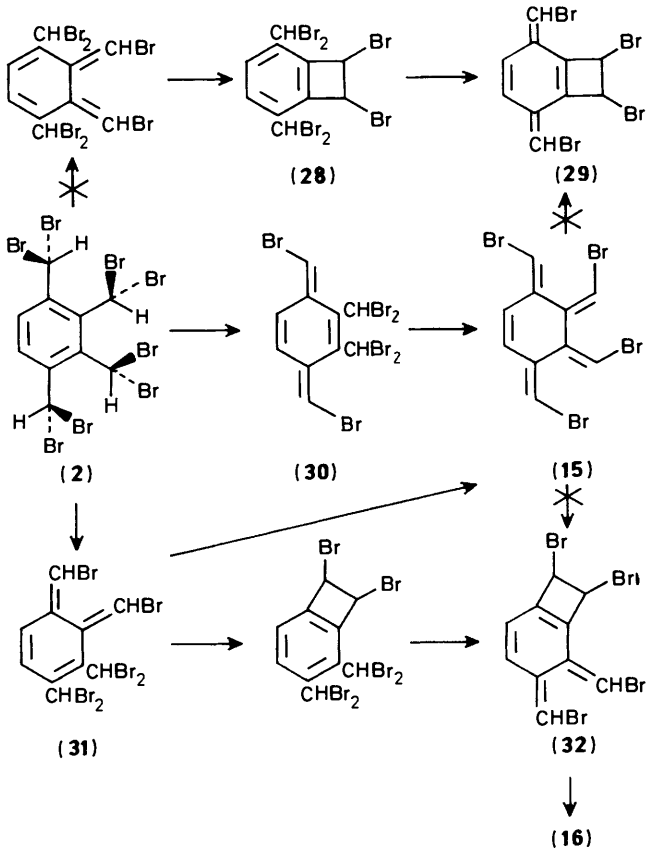


(27)

The reaction of the octabromide (**2**) at temperatures above 100 °C gave a 1:1 mixture of the two isomers of *trans,trans*-1,2,3,4-tetrabromo-1,2,3,4-tetrahydrobenzo[*a,c*]dicyclobutene (**16**) in 13% yield, traces of *cis,trans*-isomers could also be detected in some experiments. The major product from this reaction (*ca.* 60%), and the only product formed below 100 °C, was a single isomer of 3,4,5,6-tetrakis(bromomethylene)cyclohexene (**15a**). Debromination of (**2**) with zinc at 25 °C gave (**15a**) in 85—90% yield. The cyclohexene (**15a**) is an air-sensitive colourless solid which decomposes after several hours at 25 °C, but can be stored for several months at −10 °C. Models indicate that this molecule is unlikely to be planar. The available n.m.r. data does not permit an unambiguous distinction between (**15a,b**), but the difference in chemical shifts of the cyclohexene protons, which resonate as doublets at δ 6.66 (1-H) and 6.80 (2-H), *J* 10.25 Hz, lend support to the *E,E,Z,Z*-isomer (**15a**). Further support comes from consideration of the 'locked' conformation of the octabromo precursor (**2**), which should undergo facile 1,6-elimination of bromine resulting in initial formation of the (*E,Z*)-*p*-quinodimethane (**30**). The cyclohexene (**15a**) decomposed on heating in DMF in the presence or absence of sodium iodide and no cyclised products were formed. Photoirradiation of (**15a**) in CCl_4 and other solvents, under conditions used to form 1,2-dibromo-1,2-dihydrocyclobuta-[1]phenanthrene from the respective (*E,Z*)-quinodimethane,[4] also proved unsuccessful. Since the driving force for such reactions is the formation of a low-energy (aromatic) product from a high-energy (quinodimethane) precursor, it is not surprising that a substantial energy barrier prevents the cyclisation of (**15a**) to either of the high-energy species (**29**) or (**32**). Clearly if the cyclohexene (**15a**) is not a precursor to (**16**) then at least two pathways are operative in this case (Scheme 1). The absence of the monocyclobuta derivatives (**28**) and (**29**) amongst the reaction products suggests initial attack by sodium iodide at the least hindered 1- (or 4-) dibromomethyl group of the octabromide (**2**). The subsequent course of the reaction may be determined by competition between quinodimethane formation and an anionic cyclisation,[4] or may simply reflect the relative distribution of the debromination products (**30**) and (**31**) at 110 °C. The ratio of ring-opened and cyclised products observed in this reaction is very similar to those obtained from high-temperature flash-thermolytic experiments.[15] The two four-membered rings are formed sequentially, and the first step dictates the overall yield.

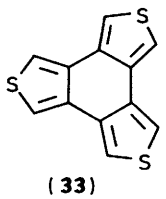
The reaction of the dodecabromide (**5**) with sodium iodide in the temperature range 80—150 °C gave a complex mixture of bromo- and iodo-hexakis(methylene)cyclohexane (hexaradialene) derivatives. Signals at δ 5.6—5.7 in the ^{1}H n.m.r. spectrum indicated trace formation of the cyclobutene derivatives in some experiments, but the desired 1,2,3,4,5,6-hexabromo-1,2,3,4,5,6-hexahydrobenzo[*a,c,e*]tricyclobutene (**19**) could not be detected. This further emphasises the crucial role of the initial cyclisation step(s). Attempts to prepare the parent hydrocarbon (**20**) by thermolysis of hexamethylbenzene derivatives gave hexaradialene (**18**) as the sole product,[16,17] but thermolysis of a dicyclobutabenzene derivative under similar conditions gave (**20**) in 53% yield, uncontaminated by isomer (**18**).[18] Debromination of the dodecabromide (**5**) with zinc at 100 °C gave the (all-*E*)-hexaradialene (**17a**) as air-stable colourless crystals



Scheme 1.

which only decomposed when heated to above 100 °C. Low yields of an unstable isomer, probably (**17b**), also formed in this reaction. The ^{1}H n.m.r. spectrum of (**17a**) shows a singlet at δ 6.81, whereas that of (**17b**) shows three singlets of equal intensity at δ 6.51, 6.56, and 6.75. The six-membered rings in (**17a, b**) are expected to be strongly puckered to minimise steric interactions between the bromomethylene groups.[19] Attempts to cyclise (**17a, b**) to the tricyclobutabenzene (**19**) under the conditions described for (**15a**) above were unsuccessful. A reaction of the dodecabromide (**5**) with sodium sulphide gave benzo[1,2-*c*:3,4-*c'*:5,6-*c''*]trithiophene (**33**) in 83% yield, the applications of this and related reactions will be described at a later date.

The relative yields of the cyclobutabiphenylenes (**24**) and (**25**) appear to reflect the stabilities of the respective quinodimethane precursors (**34**) and (**35**). The annellated benzocyclobuta groups should destabilise (**34**) and stabilise (**35**) in comparison with 5,6-bis(bromomethylene)cyclohexa-1,3-diene: decomposition of the cyclobutadienoid intermediate (**34**) may compete significantly with cyclisation to the product (**24**). Both cyclobutabiphenylenes are decomposed rapidly under the reaction conditions, and a rapid work-up, particularly for (**24**), is essential for isolation of products. 1,2-Dibromo-1,2-dihydrocyclobuta[*b*]biphenylene (**25**) reacted with nonacarbonyldi-iron to give the tricarbonyliron complex (**36**) in 91% yield. The isomer (**24**) was decomposed by nonacarbonyldi-iron, and 1,2-dibromo-1,2-dihydrobenzocyclobutene gives poor yields of η^4-benzocyclobutenetricarbonyliron (**37**) under these conditions.[20,21] The preferred bond structure adopted by the biphenylene (**25**), to minimise anti-aromatic effects,[22] facilitates debromination to the complex (**36**). The ^{1}H coupling constants of the benzocyclobutene complex (**37**)[23] and a structural analysis of a derivative[24] reveal that the electron demand of the complexed tricarbonyliron groups lead to a reduction in delocalisation of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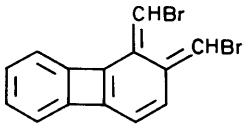
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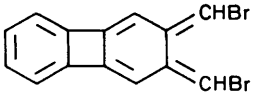
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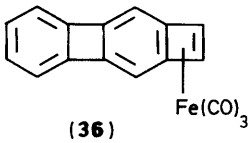
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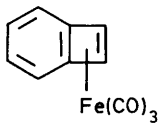
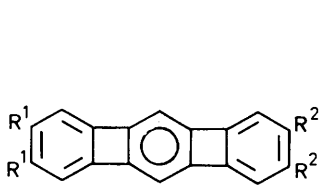
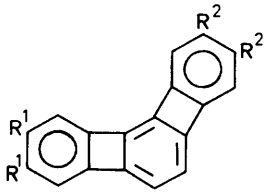

(37)

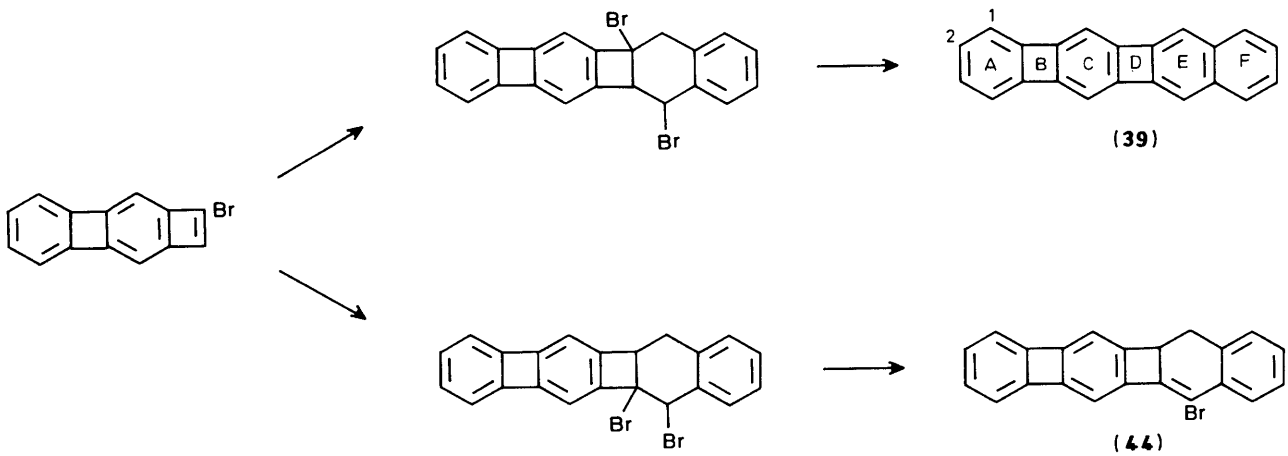
the benzene rings. This effect is enhanced in the central benzenoid ring of the complex (**36**), enabling the system to maximise aromatic character at the expense of anti-aromatic character.[25] The ^{1}H n.m.r. spectrum of the complex (**36**) consists of three singlets, at δ 4.10 (2 H, 1-, 2-H), 6.26 (2 H, 3-, 8-H), and 7.05 (4 H, 4- to 7-H). In comparison with the spectrum of the *trans*-dibromide (**25**), 3- and 8-H are shielded (Δδ, +0.18 p.p.m.) by bond localisation, and 4- to 7-H are deshielded (Δδ, −0.28 p.p.m.) due to the associated reduction of the paratropic ring current. The ^{13}C spectrum of (**36**) shows signals at δ 55.2 (C-1, -2), 88.9 (C-2a, -8a), 109.9 (C-3, -8), 119.7 (C-4, -7), 129.9 (C-5, -6), 146.1, 148.7 (C-3a, -3b, -7a, 7b), and 214.6 (carbonyl carbons), and resembles that of (**37**) (previously unreported): 52.4 (C-1, -2), 96.1 (C-2a, -6a), 124.2 (C-3, -6), 127.4 (C-4, -5), and 214.7 (carbonyl carbons). The chemical shifts of the benzenoid carbons probably reflect strain rather than ring-current effects,[26] but those of the carbonyl carbons suggest that the electron demand of the tricarbonyliron group is similar in both cases. On this evidence, the electron density of the complexed rings in (**36**) and (**37**) is intermediate between that of the equivalent cyclobutene[20,27] and cyclobuta[*f*]phenanthrene complexes.[28]

Benzocyclobutabiphenylene Derivatives.—The structures and properties of the linear and angular benzocyclobutabiphenylenes (**38**) and (**41**) are attracting renewed interest following the discovery by Vollhardt *et al.* that both compounds are readily accessible by cobalt-catalysed yne–diyne cycloadditions.[29,30] *X*-Ray structural data for (**41**) and a silylated derivative of (**38**) indicate that these compounds are best represented by the structures illustrated, both systems adopt electronic structures which maximise aromatic and minimise anti-aromatic ring currents. In the ^{1}H n.m.r. spectrum of (**41**)[31] the central ring protons 5- and 6-H resonate in the vinylic region, and the terminal ring protons at lower field than in biphenylene itself, indicating a reduced paramagnetic contribution from the four-membered rings.[32] The high-field shift of the terminal ring protons in the linear isomer (**38**) with respect to biphenylene[29,33] is consistent with a reduction in diamagnetic current coupled with an enhanced paramagnetic contribution from the cyclobutadienoid rings, and this second effect is reinforced at the central ring, which remains largely delocalised.[29]


(**38**) R^1 = R^2 = H
(**39**) R^1 = H, R^2 = Benzo
(**40**) R^1, R^2 = Benzo


(**41**) R^1, R^2 = H
(**42**) R^1 = H, R^2 = Benzo
(**43**) R^1, R^2 = Benzo

To obtain a further insight into the factors influencing these electronic effects, the syntheses of benzo- and dibenzo- derivatives of (**38**) and (**41**) were attempted using the 'crossed' cycloaddition method developed by Barton *et al.*[10] 1,1,2,2-Tetrabromo-1,2-dihydrobenzocyclobutene reacts with 1,2-bis(dibromomethyl)benzene in the presence of zinc to give benzo[*b*]biphenylene, but benzo[1″,2″:3,4:4″,5″:3′,4′]dicyclobuta[1,2-*b*:1′,2′-*b*′]dinaphthalene (**40**) could not be prepared because of the insolubility of the octabromodicyclobutabenzene precursor under the conditions used. In order to circumvent the need to prepare tetrabromobenzocyclobutene derivatives, the reaction between 1,2-dibromo-1,2-dihydrobenzocyclobutene and 1,2-bis(bromomethyl)benzene in the presence of base was investigated. An experiment at 25 °C in THF using potassium t-butoxide as the base gave primarily 5-bromobenzo[*a*]biphenylene,[34] but at 60 °C gave the crossed cycloaddition product, benzo[*b*]biphenylene in 40—50% yield. Under these conditions the dibromide (**25**) gave the bromobiphenylene (**44**) (45%) and naphtho[2′,3′:3,4]cyclobuta[1,2-*b*]biphenylene (**39**) (32%) (Scheme 2). The similarity in yields of (**39**) and (**44**) suggests that the initial cycloaddition step shows little stereospecificity and



Scheme 2.

Table 2. ^{1}H N.m.r. spectra of the benzocyclobutabiphenylenes (**38**)—(**43**)

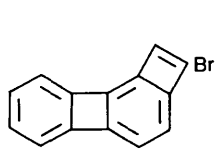
	δ_H (Multiplicity)				
	Compd.				
^{1}H Nucleus	(**38**)	(**39**)	(**41**)	(**42**)	(**43**)
1	6.42 (m)	6.57 (m)			7.20 (s)
2	} 6.63 (m)	} 6.71 (m)	} 6.95 (m)	} 6.91 (m)	7.59 (m)
3					} 7.34 (m)
4	6.42 (m)	6.57 (m)		6.80 (m)	
5	6.24 (s)	6.46 (s)	} 6.12 (s)	6.29 (d)[a]	7.59 (m)
6	6.42 (m)	6.67 (s)		6.39 (d)[a]	7.10 (s)[b]
7	} 6.63 (m)	7.38 (m)	} 6.95 (m)	7.14 (s)	} 6.58 (s)
8		} 7.18 (m)		7.60 (m)	
9	6.42 (m)			} 7.34 (m)	7.10 (s)
10	6.24 (s)	7.38 (m)			7.59 (m)
11		6.67 (s)		7.60 (m)	} 7.34 (m)
12		6.46 (s)		7.21 (s)	
13					7.59 (m)
14					7.20 (s)

[a] $J_{5,6}$ 6.78 Hz. [b] Identified by n.O.e. enhancement on irradiation of 7-, 8-H. Data for compounds (**38**) and (**41**) is taken from the literature.[32]

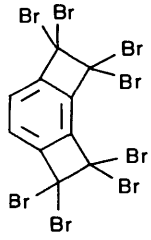
that the subsequent dehydrohalogenation steps occur exocyclic to the cyclobutene ring. ^{1}H N.m.r. data for (**38**), (**41**), and derivatives prepared in this paper are collated in Table 2. The biphenylene (**39**) forms highly insoluble bright orange microcrystals, stable indefinitely in the solid state or in dilute solution. Benzo[3,4]cyclobuta[1,2-*b*]biphenylene (**38**) decomposes when allowed to stand overnight in chlorinated solvents,[29] linear benzannulation thus stabilises the system. A comparison of the n.m.r. spectra of (**38**) and (**39**) is instructive. The biphenylene (**39**) maximises aromatic character at the cost of localisation of the 5b(6) and 11(11a) carbon–carbon double bonds (the E ring); the A ring is more delocalised than in (**38**), and the paramagnetic character of the B and D rings is reduced. Hydrogens at positions 5,12, and 1—4 are deshielded with respect to (**38**), and the difference in chemical shifts between 1-H and 2-H is reduced from 0.21 (**38**) to 0.14 p.p.m. (**39**). The F ring should not be significantly perturbed by paramagnetic currents,[35] thus the high-field shifts of 7—10-H also support an extreme degree of localisation in the E ring. Lesser effects of this type can be seen in the spectra of benzo[*b*]biphenylene[32] and 6,11-methanobenzo-[3,4]cyclobuta[1,2]cyclodecene.[5,36]

Dehydrobromination of a mixture of the tetrabromide (**14**) and 1,2-bis(bromomethyl)benzene gave a mixture of insoluble mono- and di-bromo products analogous to (**44**), the biphenylene (**40**) could not be detected. However, the dibromide (**24**) reacted under these conditions to give naphtho[2′,3′:3,4]cyclobuta[1,2-*a*]biphenylene (**42**) (45%) as pale yellow crystals, uncontaminated by the isomer(s) of (**44**). An inspection of the main resonance contributors to the initial deprotonated intermediate indicates that the reactive species in this case is likely to be 2-bromocyclobuta[*a*]biphenylene (**45**). Following the failure to prepare (**40**) above no attempt was made to dehydrobrominate (**16**), but zinc-debromination of the octabromide (**46**) and 1,2-bis(dibromomethyl)benzene gave benzo-[1″,2″:3,4:3″,4″:3′,4′]dicyclobuta[1,2-*b*:1′,2′-*b*′]dinaphthalene (**43**) (51%). Debromination of (**46**) probably occurs stepwise, attempts to isolate the dicyclobutene (**47**), formally a 10π-electron system, were unsuccessful.

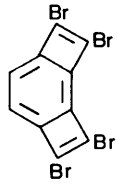
The most striking feature of the n.m.r. spectra of these compounds is a pronounced shift to low field of the central ring protons, from δ 6.12 to 6.58 along the series (**41**)—(**43**). This suggests an increasing degree of delocalisation in the central benzenoid ring, and is supported by the coupling constants $J_{5,6}$ for (**41**)[29] and (**42**) of 6.42 and 6.78 Hz, respectively.



(**45**)



(**46**)



(**47**)

However, the remaining benzenoid protons do not experience a marked high-field shift as a result of increasing bond localisation and/or paramagnetic shielding; the cyclobutanaphthalene proton shifts, in particular, are virtually identical in (**42**) and (**43**). On this evidence these rings are more localised than in 1,2-dihydrocyclobuta[*b*]naphthalene,[37,38] but are considerably more delocalised than in benzo[*b*]biphenylene.[32] The central rings still retain substantial cyclohexatriene character.

Experimental

Unless stated otherwise the following conditions apply: organic extracts were dried over sodium sulphate or magnesium sulphate, and light petroleum refers to the fraction b.p. 40—60 °C. N.m.r. spectra were recorded for solutions in deuteriochloroform containing tetramethylsilane as an internal standard. Other general details and instrumentation have been previously described.[1] The following compounds were prepared by literature methods: 2,2′,3,3′-tetramethylbiphenyl,[39] 3,3′4,4′-tetramethylbiphenyl,[40] 1,2-bis(dibromomethyl)biphenylene,[10] 2,3-bis(dibromomethyl)biphenylene,[11] and benzocyclobutene-tricarbonyliron.[20]

1,2,4,5-*Tetramethylnaphthalene*.—A solution of 2,5-dimethylnaphthalene (3.8 g) and *N*-bromosuccinimide (12.5 g) in dimethylformamide (DMF) (50 ml) was stirred at 70—80 °C for 24 h, cooled and poured onto ice. The product was filtered, dried, and recrystallised from EtOH to give 1,4-dibromo-2,5-dimethylnaphthalene (5.43 g, 71%), m.p. 157—158 °C (lit.,[41] m.p. 160—161 °C). A suspension of the dibromide (5.0 g) in tetrahydrofuran (THF) (60 ml) was stirred at 20 °C and a solution of methyl-lithium in ether (1.4M; 30 ml) was added

Table 3.

Precursor	Method	Reaction time (h)	Product	Yield (%)	Found C	Found H	Found Br	Found N	Requires C	Requires H	Requires Br	Requires N
1,2,4,5-Tetramethylbenzene	A	8	(1)[a]	97								
1,2,3,4-Tetramethylbenzene	A	1	(3)	90	19.8	1.2	79.0		19.7	1.3	78.9	
(3)	A[b]	40—50	(2)	50—60	15.7	0.9	83.5		15.7	0.8	83.6	
			(4)	20—30	14.4	0.7	85.2		14.2	0.6	85.2	
Hexamethylbenzene	A[c]	400—500	(5)	100	13.0	0.5	86.3		13.0	0.5	86.5	
2,2′,3,3′-Tetramethylbiphenyl	A	12	(6)	88	22.9	1.4	75.8		22.8	1.2	76.0	
	B	16		94								
3,3′,4,4′-Tetramethylbiphenyl	A	3	(7)	90	22.8	1.2	76.0		22.8	1.2	76.0	
	B	6		95								
1,2,5,6-Tetramethylnaphthalene	A	48	(8)[d]	*ca.* 90	20.9	1.1	78.1		20.6	1.0	78.4	
1,2,4,5-Tetramethylpyrazine	B	18	(9)[e]	70	12.5	0.7	83.2	3.5	12.5	0.5	83.3	3.6
3,4,5,6-Tetramethylpyridazine	B	0.5	(10)[f]	*ca.* 10								

[a] M.p. 304—306 °C (from $CHCl_3$) (lit.,[6] 305 °C). [b] Photobromination on the above scale proceeded very slowly after formation of the hexabromide (3). The quoted reaction time is for bromination of a 0.025M-solution of the isolated hexabromide (3), formation of (2) was readily monitored by n.m.r. spectroscopy (see text). Recrystallisation of the crude product gave (2), the nonabromide (4) was purified by evaporation of the filtrate, followed by column chromatography on silica using light petroleum as the eluant. [c] Hexakis(bromomethyl)benzene[8] precipitates after 20—30 min and severe 'bumping' is unavoidable. The insolubility of the higher bromides serves to maintain a very low concentration of bromomethyl derivatives in solution, the reaction was not appreciably faster at higher dilution. [d] The crude product (8) consists of a mixture of isomers, contaminated with traces of the hepta- and nona-bromide (on the evidence of the mass spectrum). An analytical sample was obtained after repeated washing of this product with CH_2Cl_2. [e] Succinimide residues were removed from the insoluble octabromide (9) by washing with MeCN. [f] Solution concentration 10^{-3}M. The product (10) decomposed on attempted purification, and an analytical sample could not be obtained.

dropwise (exothermic for the first 15 ml of addition). The resulting solution was stirred at 30 °C for 2 h, during which time the colour changed progressively from pale yellow to deep purple, green, and finally to pale brown. The solution was cooled, the excess of methyl-lithium was destroyed by addition of EtOH, and the mixture poured into ether. After having been washed with water, the organic phase was dried and evaporated to give the title compound (2.9 g, 99%) m.p 115—117 °C (from EtOH) (lit.,[42] m.p. 114—115 °C).

3,4,5,6-*Tetramethylpyridazine*.—A solution of hydrazine hydrate (3.0 g) in ethanol (5 ml) was added over a period of 5 min to a stirred solution of 3,4-dimethylhexane-2,5-dione[43] (8.0 g) in ethanol (50 ml) at 10 °C. The solution was stirred at 25 °C for 1 h, and then lead(IV) oxide (15 g) added. This suspension was stirred at 60 °C for 3 h, during which time the colour changed from black to yellow, and was then cooled and filtered. The filtrate was evaporated and the residue distilled to give the title compound (5.0 g, 65%), m.p. 65—67 °C [lit.,[44] m.p. 69 °C (decomp.)].

General Procedure for the Preparation of the Bromomethyl Derivatives (**1**)—(**10**).—These reactions were performed with bromine (method A) or *N*-bromosuccinimide (method B) in carbon tetrachloride using a 200 W sunlamp as the heat and photochemical source. Reactions using method A proceed more rapidly if the bromine addition is regulated such that the free concentration in the refluxing solution is low. For Method B reactions were performed using an excess of one equivalent of *N*-bromosuccinimide, and on completion the solutions were filtered to remove succinimide and *N*-bromosuccinimide residues while hot to prevent crystallisation of products. The rate of bromination is markedly affected by the concentration of the precursor, and at high concentration often stops at an intermediate stage. Unless stated otherwise, in the reactions described in this paper, 150 ml of a 0.1M-solution of the respective methyl compounds were used. On completion, the product was either filtered directly, or (if still in solution) the carbon tetrachloride was evaporated without washing and the solid product so obtained was recrystallised from an appropriate solvent. For microanalytical and other data, see Table 3.

Properties of the bromides (**2**)—(**10**). (Compound, crystallisation solvent, m.p., spectra). The mass spectra of the bromides (**2**)—(**10**) and other compounds prepared below show sequential loss of bromine from the molecular ion; only the highest *m/z* value and the most prominent fragmentation peaks are given.

1,2,3,4-*Tetrakis(dibromomethyl)benzene* (**2**) ($CHCl_3$–EtOH), m.p. 235—236 °C; δ 6.72 (1 H, s, 1α-H), 7.41 (1 H, s), 7.80 (1 H, s), 7.87 (1 H, s), (2α-, 3α-, or 4α-H, unassigned), and 8.06 and 8.07 (2 H, d, 5-, 6-H); *m/z* 687 and 685 (M^+ − Br, 11%) and 126 (M^+ − 8Br, 100).

2,3-*Bis(bromomethyl)*-1,4-*bis(dibromomethyl)benzene* (**3**) ($CHCl_3$), m.p. 182—183 °C; δ 4.48 (4 H, s, 2 × CH_2Br), 6.12 (2 H, s, 2 × $CHBr_2$), and 7.97 (2 H, s, 5-, 6-H); *m/z* 608 (M^+, 32%) and 128 (M^+ − 6Br, 100).

1,2,3-*Tris(dibromomethyl)*-4-*tribromomethylbenzene* (**4**) (EtOH), m.p. 205—207 °C; δ 7.90 (1 H, s), 8.07 (1 H, s), 8.18 (1 H, s) (1α-, 2α-, or 3α-H, unassigned), 8.16 (1 H, d), and 8.30 (1 H, d) (5-, 6-H, unassigned, $J_{5,6}$ 8.79 Hz); *m/z* 686 and 684 (M^+ − 2Br, 4.6%), 445 (M^+ − 5Br, 100), and 125 (M^+ − 9Br, 40).

Hexakis(dibromomethyl)benzene (**5**) (insoluble in organic solvents), decomp. >305 °C; $\nu_{max.}$(KCl disc) 1 130 and 898 cm^{-1}; *m/z* 1 031 and 1 029 (M^+ − Br, 3%), 551 and 549 (M^+ − 7Br, 100), and 150 (M^+ − 12Br, 76).

2,2′,3,3′-*Tetrakis(dibromomethyl)biphenyl* (**6**) ($CHCl_3$–EtOH), m.p. 248—251 °C; δ_H see text; *m/z* 682 (M^+ − 2Br, 8%) and 202 (M^+ − 8Br, 100).

3,3′,4,4′-*Tetrakis(dibromomethyl)biphenyl* (**7**) (Me_2SO), m.p. 221—222 °C; δ 7.51 (4 H, s, 4 × $CHBr_2$) and 7.55—7.90 (6 H, m, ArH); *m/z* 763 and 761 (M^+ − Br, 11%), 443 and 441 (M^+ − 5Br, 100), and 202 (M^+ − 8Br, 41).

1,2,5,6-*Tetrakis(dibromomethyl)naphthalene* (**8**), m.p. 175—245 °C (mixture of isomers, see text); δ 6.85—8.45 (complex system of multiplets); *m/z* 496 (M^+ − 4Br, 0.32%), 176 (M^+ − 8Br, 43), and 83 (100).

1,2,4,5-*Tetrakis(dibromomethyl)pyrazine* (**9**) (Me_2SO), slow decomp. >200 °C; δ[$(CD_3)_2SO$] 7.79 (s); *m/z* 768 (M^+, 1%), 689 and 687 (M^+ − Br, 100), and 128 (M^+ − 8Br, 10).

3,4,5,6-*Tetrakis(bromomethyl)pyridazine* (**10**) (unstable oil); δ

4.60 (4 H, s), and 4.74 (4 H, s) (4 × CH_2Br, unassigned); *m/z* 452 (M^+, 16%) and 132 (M^+ − 4Br, 54).

Cyclisation of Dibromomethyl Derivatives with Sodium Iodide.—The individual reaction conditions are listed in the text (Table 1). In a typical procedure, the bromide (1.0 g) was added in one portion to a stirred solution of sodium iodide (5.0 g) in DMF (40 ml) at the stated internal temperature. A slight temperature increase of 1—2 °C usually occurred, and the colour of the solution deepened with liberation of iodine. After the recommended interval, the black reaction mixture was quenched by pouring it onto ice, and then extracting it into Et_2O (300 ml). The organic phase was washed with aqueous sodium thiosulphate or metabisulphite, followed by water (3 × 50 ml), and then by saturated aqueous sodium chloride (10 ml). The solution was dried, evaporated, and the residue was chromatographed on silica or alumina to give the product. Iodo impurities were removed by standing the product in a dilute solution of bromine in carbon tetrachloride for 12—24 h,[12] followed by repurification as described above. The following precautions should be noted: The volume of DMF in large-scale reactions must be increased in order to minimise the rise in internal temperature; in general the yields obtained on large-scale reactions were considerably lower than those quoted in Table 1. A high concentration of sodium iodide relative to that of the bromide is necessary, and once the reaction is complete prolonged stirring, particularly at the higher temperatures, leads to a dramatic reduction in yields. The tetrabromodicyclobutarenes are formed as a mixture of isomers [*e.g.* two possible *trans,trans*-isomers of (**14**)]; these were not separated unless described below. The cyclobutabiphenylenes (**24**) and (**25**) were decomposed by treatment with bromine in carbon tetrachloride.

Cyclisation of (**1**). After following the procedure outlined above, chromatography of the purified product on alumina using 2% chloroform in light petroleum as the eluant gave trans,trans-1,2,4,5-*tetrabromo*-1,2,4,5-*tetrahydrobenzo*[a,d]*dicyclobutene* (**14**) as a mixture of isomers (2%). Recrystallisation gave a pure isomer, m.p. 222—223 °C (sublimed >120 °C) (from $CHCl_3$) (Found: M^+, 445.7198. $C_{10}H_6Br_4$ requires *M*, 445.7161); δ 5.42 (4 H, s, 1-, 2-, 4-, 5-H) and 7.12 (2 H, s, 3-, 6-H); δ_C 48.7 (C-1, -2, -4, -5) and 118.8 (C-3, -6); *m/z* 446 (M^+, 37%) and 126 (M^+ − 4Br, 100). This was followed by trans-1,2-*dibromo*-4,5-*bis*(*dibromomethyl*)-1,2-*dihydrobenzocyclobutene* (**13**) (6%), m.p. 165—166 °C (from $CHCl_3$–EtOH) (Found: C, 20.0; H, 1.0; Br, 78.9. $C_{10}H_6Br_6$ requires C, 19.8; H, 1.0; Br, 79.2%); δ 5.41 (2 H, s, 1-, 2-H), 7.11 (2 H, s, 4α-, 5α-H), and 7.60 (2 H, s, 3-, 6-H); δ_C 35.7 (C-4α, -5α), 48.2 (C-1, -2), and 124.4 (C-3, -6); *m/z* 606 (M^+, 0.4%) and 126 (M^+ − 6Br, 100).

Cyclisation of (**13**).—A reaction of the purified hexabromide (**13**) with sodium iodide in DMF at 120—122 °C for 10 min gave, using the work-up procedure as described above, the tetrabromide (**14**) (29%), identical with the sample described above.

Cyclisation of (**2**). Chromatography of the crude product on alumina using 2% chloroform in light petroleum as the eluant gave 3,4,5,6-*tetrakis*(*bromomethylene*)*cyclohexene*, probably the *E,E,Z,Z*-isomer (**15a**) (61%), colourless crystals, decomp. >30 °C (Found: M^+, 445.7167. $C_{10}H_6Br_4$ requires *M*, 445.7161); δ 6.47 (1 H, s), 6.56 (1 H, s), 6.65 (1 H, s), 7.11 (1 H, s) (CHBr, unassigned), and 6.66 (1 H, d, 2-H) and 6.80 (1 H, d, 1-H) ($J_{1,2}$ 10.25 Hz); *m/z* 446 (M^+, 22), 207, 205 (M^+ + 3Br, 100), and 126 (M^+ − 4Br, 73). This was followed by a 1:1 mixture of the two isomers of trans,trans-1,2,3,4-*tetrabromo*-1,2,3,4-*tetrahydrobenzo*[a,c]*dicyclobutene* (**16**) which were purified as described above (13%) (Found: C, 27.0; H, 1.3; Br 71.7. $C_{10}H_6Br_4$ requires C, 26.9; H, 1.3; Br, 71.7%). The two isomers were separated by repeated preparative t.l.c. on silica using light petroleum as the eluant. This gave (**16a**) (stereochemistry not established) as a viscous oil; δ 5.43 (4 H, s, 1-, 2-, 3-, 4-H) and 7.34 (2 H, s, 5-, 6-H); δ_C 47.0, 49.7 (C-1, -2, -3, 4, unassigned), and 126.4 (C-5, -6); *m/z* 446 (M^+, 12%) and 126 (M^+ − 4Br, 100); followed by (**16b**) (stereochemistry not established), m.p. 131—133 °C; δ 5.42 (4 H, s, 1-, 2-, 3-, 4-H) and 7.33 (2 H, s, 5-, 6-H); δ_C 47.4 and 49.6 (C-1, -2, -3, -4, unassigned) and 126.4 (C-5, -6); mass spectrum identical to that of (**16a**) above. Traces of *cis,trans*-isomers formed in some cyclisations, as evidenced by a singlet for the *cis*-ring protons at δ 5.71; these were not isolated.

Attempted cyclisation of (**5**). The crude product contained a mixture of isomers, presumably related to (**17**), which could not be separated under the conditions tried. The ^1H n.m.r. spectrum showed peaks in the range δ 6.40—6.85, and the mass spectrum indicated that the product contained both bromine and iodine.

Cyclisation of (**6**). Chromatography of the purified product on silica using 5% chloroform in light petroleum as the eluant gave trans,trans-1,1′,2,2′-*tetrabromo*-1,1′,2,2′-*tetrahydro*-3,3′-*bi*(*benzocyclobutenyl*) (**21**) (both isomers), a viscous oil (1%) (Found: C, 36.6; H, 2.1; Br, 61.5. $C_{16}H_{10}Br_4$ requires C, 36.8; H, 1.9; Br, 61.3%); δ_H 5.35—5.57 (4 H, m, 1-, 1′-, 2-, 2′-H) and 7.30—7.45 (6 H, m, ArH); δ_C 49.3, 49.8 (C-1, -1′, -2, -2′, unassigned), 122.8, 130.8, and 132.1 (C-4, -5, -6, -4′, -5′, -6′, unassigned); *m/z* 522 (M^+, 13) and 202 (M^+ − 4Br, 100).

Cyclisation of (**7**). Chromatography of the purified product, as described for (**21**) above, gave trans,trans-1,1′,2,2′-*tetrabromo*-1,1′,2,2′-*tetrahydro*-4,4′-*bi*(*benzocyclobutenyl*) (**22**) (42%) (both isomers) as a viscous oil (Found: C, 36.7; H, 2.0; Br, 61.3. $C_{16}H_{10}Br_4$ requires C, 36.8; H, 1.9; Br, 61.3%); δ_H 5.47 (4 H, s, 1-, 1′-, 2-, 2′-H), 7.29 (2 H, d, 5-, 5′-H), 7.36 (2 H, d, 3-, 3′-H), and 7.60 (2 H, dd, 6-, 6′-H); δ_C 49.37 (C-1, -1′, -2, -2′), 122.0 and 123.6 (C-3, -3′, -6, -6′, unassigned), 131.1 (C-5, -5′), and 141.9, 143.1, and 144.6 (quaternary carbons); *m/z* 522 (M^+, 97%), 443, 441 (M^+ − Br, 75), and 202 (M^+ − 4Br, 100).

Cyclisation of (**8**). Chromatography of the purified product on silica, using 25% chloroform in light petroleum as the eluant gave trans,trans-1,2,5,6-*tetrabromo*-1,2,5,6-*tetrahydrodicyclobuta*[a,f]*naphthalene* (**23a**) (35%) (both isomers), m.p. 225—227 °C (from Me_2SO) (Found: C, 34.1; H, 1.5; Br, 64.5. $C_{14}H_{10}Br_4$ requires C, 33.9; H, 1.6; Br, 64.5%); δ 5.59 (2 H, s, 2-, 6-H), 5.67 (2 H, s, 1-, 5-H), 7.45 (s H, d, 4-, 8-H), and 8.05 (2 H, d, 3-, 7-H); *m/z* 496 (M^+, 17%) and 176 (M^+ − 4Br, 100). This was followed by the cis,trans-*isomer(s)* (**23b**) (2%), m.p. 188—191 °C [microanalysis as for (**23a**) above]; δ 5.58(1 H, s, 6-H), 5.66 (1 H, s, 5-H), 5.95 (1 H, d, 2-H), 6.08 (1 H, d, 1-H), 7.44 (2 H, d, 4-, 8-H), and 8.03 (2 H, m, 3-, 7-H); δ_C 48.9, 49.7, 50.1 and 50.9 (cyclobutene C-H), 121.7, and 121.9 (C-3, -8, unassigned), and 126.6 and 127.1 (C-4, -7, unassigned); mass spectrum identical to that for (**23a**) above.

Cyclisation of (**11**). Flash chromatography of the crude product on silica using 35% chloroform in light petroleum as the eluant gave trans-1,2-*dibromo*-1,2-*dihydrocyclobuta*[a]*biphenylene* (**24**) (11%), bright yellow crystals, m.p. 80—82 °C (Found: M^+, 335.8977. $C_{14}H_8Br_2$ requires *M*, 335.8972); δ_H 5.33 (2 H, s, 1-, 2-H) and 6.55—6.80 (6 H, m, ArH); δ_C 48.8 and 51.1 (C-1, -2, unassigned), 117.8, 119.0, and 119.4 (C-4, -5, -8, unassigned), 122.3 (C-3), and 128.8 and 129.2 (C-6, -7, unassigned); *m/z* 336 (M^+, 1.5%) and 176 (M^+ − 2Br). Traces of the *cis*-isomer (**24b**), δ 5.77 (d, 1-, 2-H), were detected in the crude product, this was not isolated.

Cyclisation of (**12**). Flash chromatography of the crude product, as described for (**24**) above, gave trans-1,2-*dibromo*-1,2-*dihydrocyclobuta*[b]*biphenylene* (**25a**) (27%), pale yellow crystals, m.p. 128—131 °C (Found: C, 49.9; H, 2.3; Br, 47.8. $C_{14}H_8Br_2$ requires C, 50.0; H, 2.4; Br, 47.6%); δ_H 5.28 (2 H, s, 1-, 2-H), 6.44 (2 H, s, 3-, 8-H), 6.69 (2 H, m, 4-, 7-H), and 6.83 (2 H, m, 5-, 6-H); δ_C 50.57 (C-1, -2), 112.0 (C-3, -8), 118.3 (C-4, 7), 129.4 (C-5, -6), and 141.9, 150.0 and 154.9 (quaternary carbons);

m/z 336 (M^+, 15%) and 176 (M^+ − 2Br, 100). Traces of the *cis*-isomer (**25b**), δ 5.61 (s, 1-, 2-H), were detected in the crude product; this was not isolated.

3,4,5,6-*Tetrakis*(*bromomethylene*)*cyclohexene* (**15a**).—Debromination of a solution of the octabromide (**2**) (0.5 g) in THF (5 ml) with activated zinc[45] (*ca.* 2 g), followed by extraction of the crude product into Et_2O—H_2O, drying, filtration, and evaporation of the organic phase gave the crude product (**15**) as a colourless gum which rapidly yellowed on exposure to air. Flash chromatography of this product on silica using 2% chloroform in light petroleum as the eluant gave the title compound, probably (**15a**), as colourless crystals (0.26 g, 89%), identical to the sample prepared above.

Hexakis(*bromomethylene*)*cyclohexane* (**17**).—Zinc (*ca.* 5 g) was added in one portion to a stirred suspension of the dodecabromide (**5**) (0.5 g) in DMF (25 ml) at 100 °C. After having been stirred for 2 min the suspension was poured onto ice, and worked up as described for (**15a**) above. The crude product was chromatographed on alumina, using light petroleum as the eluant, giving the *all*-E-*isomer* of the *title compound* (**17a**) (0.19 g, 67%) as colourless crystals, slow decomp. >110 °C (Found: C, 22.8; H, 1.1; Br, 76.4. $C_{12}H_6Br_6$ requires C, 22.8, H, 1.0; Br, 76.2%); δ_H 6.81 (s); δ_C 109.6 (bromomethylene carbons) and 135.9 (quaternary carbons); *m/z* 630 (M^+, 17%), 310 (M^+ − 4Br, 41), and 150 (M^+ − 6Br, 100). Further elution gave an isomer, probably (**17b**) (4 mg, 1.4%) as a colourless oil which decomposed when allowed to stand or when dissolved in chlorinated solvents; δ_H see text; *m/z* 630 (M^+, 16%), 150 (M^+ − 6Br, 49), and 80 (100).

Benzo[1,2-c:3,4-c′:5,6-c″]*trithiophene* (**33**).—A suspension of the dodecabromide (**5**) (0.25 g) and sodium sulphide nonahydrate (3.0 g) in isopropyl alcohol (15 ml) was refluxed for 1 h. The brown suspension was poured into Et_2O, extracted with water, dried, and evaporated. The solid product was recrystallised ($CHCl_3$–hexane) to give the title compound (46 mg, 83%), m.p. 236—237 °C (lit.,[46] m.p. 236—238 °C).

Reaction of (**25**) *with Nonacarbonyldi-iron*.—A suspension of the dibromide (**25**) (0.25 g) and nonacarbonyldi-iron (1.0 g) in benzene (5 ml) was refluxed for 30 min, cooled, and chromatographed directly on silica using benzene as the eluant. This gave the *complex* (**36**) as yellow crystals (215 mg, 91%), melting range 115—125 °C (decomp.; sublimes >100 °C) (Found: M^+, 315.9846. $C_{17}H_8O_3Fe$ requires M^+, 315.9822); δ_H see text; *m/z* 316 (*M*, 21%), 260 (M^+ − 2CO, 39), 232 (M^+ − 3CO, 100), 206 (62), and 176 [M^+ − $Fe(CO)_3$, 85].

Benzo[b]*biphenylene*.—Potassium t-butoxide (4.0 g) was added in one portion to a stirred solution of 1,2-dibromo-1,2-dihydrobenzocyclobutene (1.0 g) and 1,2-bis(bromomethyl)-benzene (1.0 g) in THF (20 ml) at 60 °C. After having been stirred for 5 min the brown suspension was cooled and extracted with Et_2O–water. The organic phase was washed, dried, and evaporated to give the crude product, which on recrystallisation from $CHCl_3$–EtOH gave benzo[*b*]biphenylene (0.35 g, 45%), m.p. 242—243 °C (lit.,[47] 242.6—243.2 °C). In several runs the yield ranged from 40—50%; only traces of 5-bromobenzo[*a*]-biphenylene (1-bromobenzocyclobutene dimer) formed at this temperature.

Naphtho[2′,3′:3,4]*cyclobuta*[1,2-b]*biphenylene* (**39**).—Reaction of the dibromide (**25**) (110 mg) and 1,2-bis(bromomethyl)-benzene (100 mg) with potassium t-butoxide (1.0 g) in THF (15 ml), as described above, gave a deep yellow suspension. The solvent was evaporated, and the residue washed with several portions of water to remove inorganic salts. After having been dried, the solid was washed with dichloromethane (3 × 5 ml), leaving the highly insoluble *title compound* (**39**) as bright orange microcrystals (26 mg, 32%), m.p. >305 °C (decomp.; sublimes >250 °C) (Found: C, 95.6; H, 4.3. $C_{22}H_{12}$ requires C, 95.7; H, 4.3%); δ_H see text; *m/z* 276 (M^+, 100 %) and 138 (M^{2+}, 18). Evaporation of the dichloromethane fraction, followed by chromatography on silica using 35% dichloromethane in light petroleum as the eluant gave the *bromo derivative* (**44**) (48 mg, 45%) as yellow crystals, m.p. 169—170 °C (from $CHCl_3$–hexane) (Found: C, 73.9; H, 3.6; Br, 22.5. $C_{22}H_{13}Br$ requires C, 73.9; H, 3.6; Br, 22.4%); δ 2.93 (2 H, m, 11-H_2), 3.83 (1 H, dd, 11a-H), 6.75 (6 H, m, 1- to 5-H, 12-H), 7.28 (3 H, m, 8- to 10-H), and 7.55 (1 H, dd, 7-H); *m/z* 358 and 356 (M^+, 73%), 276 (M^+ − HBr, 100), and 138 (48).

Naphtho[2′,3′:3,4]*cyclobuta*[1,2-a]*biphenylene* (**42**).—Reaction of the dibromide (**24**) (35 mg) and 1,2-bis(bromomethyl)-benzene (30 mg) with potassium t-butoxide (0.5 g) in THF (5 ml), as described above, gave a deep brown suspension. This was diluted with water, extracted into ether, and the organic phase was dried and evaporated. The crude product was chromatographed on silica using 40% dichloromethane in light petroleum as the eluant, to give the *title compound* (**42**) (13 mg, 45%) as lemon-yellow crystals (blue fluorescence in dilute solution), m.p. 192—194 °C (sublimes >145 °C) (Found: M^+, 276.0931. $C_{22}H_{12}$ requires M, 276.0894); δ_H see text; δ_C 115.5, 115.9, 116.5, 117.1, 118.0, and 119.0 (C-1, -4—7, -12, unassigned), 126.1, 126.3, 128.3, 128.7, 128.8, 128.9, (C-2, -3, -8—11, unassigned), 134.5, 134.8, 135.8, 138.5, 145.2, 146.5, 148.7, 149.3, 150.7, and 150.8 (quaternary carbons); *m/z* 276 (M^+, 100%) and 138 (M^{2+}, 22).

1,1,2,2,3,3,4,4-*Octabromo*-1,2,3,4-*tetrahydrobenzo*[a,c]*dicyclobutene* (**46**).—A solution of the tetrabromide (**15**) (100 mg) and bromine (250 mg) in carbon tetrachloride (50 ml) was refluxed over a 200 W bulb for 8 h. The solution was cooled, evaporated, and the solid product recrystallised to give the *title compound* (**46**) (142 mg, 83%) m.p. 248—250 °C (from $CHCl_3$) (Found: C, 16.0; H, 0.3; Br, 83.9. $C_{10}H_2Br_8$ requires C, 15.7; H, 0.3; Br, 84.0); δ 7.42 (s); *m/z* 762 (M^+, 3%), 683 and 681 (M^+ − Br, 100), and 122 (M^+ − 8Br, 59).

Benzo[1″,2″:3,4:3″,4″:3′,4′]*dicyclobuta*[1,2-b:1′,2′-b′]*dinaphthalene* (**43**).—Activated zinc[45] (*ca.* 1 g) was added in one portion to a solution of the octabromide (**46**) (100 mg) and 1,2-bis(dibromomethyl)benzene (150 mg) in THF (3 ml). When the exothermic reaction had subsided, the suspension was diluted with dichloromethane, extracted with water, dried, and evaporated. The crude product was passed down a short silica column, using 50% dichloromethane in light petroleum as the eluant, to remove polymeric impurities. After the solvent had been evaporated, the yellow solid so obtained was purified by sublimation at 220 °C, and 0.1 mm Hg, to give the *title compound* (**43**) (22 mg, 51%) as pale yellow crystals (greenish fluorescence in dilute solution), m.p. 295—298 °C (sublimes >200 °C) (Found: C, 95.7; H, 4.3. $C_{26}H_{14}$ requires C, 95.7; H, 4.3%); δ_H see text; δ_C 115.8 (C-7, -8), 117.0 and 117.9 (C-1, -6, -9, -14, unassigned), and 126.3, 126.4, and 128.8 (2 C) (C-2 to -5, -10 to -13, unassigned); *m/z* 326 (M^+, 100%) and 163 (M^{2+}, 41).

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