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SYNTHESIS AND REACTIONS OF 5,6,11,12-TETRADEHYDRODIBENZO[*a,e*]CYCLOOCTENE AND 5,6-DIDEHYDRODIBENZO[*a,e*]CYCLOOCTENE†[1,2]

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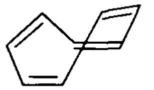
Abstract—Syntheses of 5,6,11,12-tetradehydrodibenzo[*a,e*]-cyclooctene (**5**) and 5,6-didehydrodibenzo[*a,e*]cyclooctene (**6**) by dehydrobromination with potassum *t*-butoxide of 5,6,11,12-tetrabromo-5,6,11,12-tetrahydrodibenzo[*a,e*]cyclooctene (**9**) and 5,6-dibromo-5,6-dihydrodibenzo[*a,e*]cyclooctene (**8**), respectively, are described. Compounds **5** and **6** are unusual, essentially planar, conjugated anti-aromatic 8-membered ring systems, the reactions of which have been studied. The diacetylene **5** readily underwent Diels–Alder reaction with 1,3-diphenylisobenzofuran and furan to give the bis-adducts **13** and **14**, respectively. [2+2]Cycloaddition between **5** and dichloroketene and subsequent hydrolysis of the gem-dichloride yielded 2,3,6,7-dibenzobicyclo[6.2.0]deca-2,6,8-trien-4-yne-9,10-dione (**21**). The monoacetylene **6** readily underwent Diels-Alder reaction with 1,3-diphenylisobenzofuran and furan to give the mono-adducts **24** (*endo* and *exo* isomers) and **25**, respectively. 1,3-Dipolar cycloaddition of phenylazide to **6** led to the 1-phenyl-1H-triazole derivative **27**, whereas [2+2]cycloaddition between **6** and dichloroketene and hydrolysis yielded 2,3,6,7-dibenzobicyclo[6.2.0]deca-2,4,6,8-tetraene-9,10-dione (**30**). Spectral, as well as chemical and electrochemical reductions, of **5** and **6** have been studied. For instance, treatment of the monoacetylene **6** with a potassium mirror gave the aromatic 10π-electron dianion **34**.

The work described in this paper arose from our interest in the synthesis and study of planar conjugated 8-membered ring compounds, which were expected to be anti-aromatic $4n$ π-electron systems. Unfortunately, cycloocta-1,3,5,7-tetraene (**1**), itself exists in the strainless nonplanar D_{2d} "tub" conformation **1**, due to the strain inherent in a planar structure.[4]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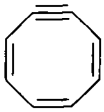
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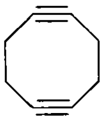
A possible way to modify cyclooctatetraene so as to make it planar is to replace one or more of the double bonds by an acetylene,[5] and Krebs and Byrd[6] have attempted to prepare such a molecule, cycloocta-1,3,5-trien-7-yne (**2**), by dehydrobromination of 1-bromocycloocta-1,3,5,7-tetraene with potassium t-butoxide. However, it was not possible to isolate **2** due to its reactivity, and its existence as a transient intermediate could only be inferred from its transformation products.[6]

Shortly before we started our work in this field, the rather surprising finding was announced by Kloster-Jensen and Wirz[7] that cycloocta-1,5-diyne (**3**), containing two highly strained acetylenic bonds, could be isolated as a relatively stable crystalline compound.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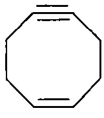
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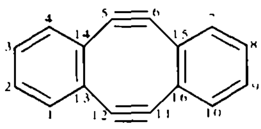
Subsequently, Leupin and Wirz[8] succeeded in isolating the less stable cyclooct-1-en-5-yne (**4**). In view of the isolation of **3**, we considered that it might be possible to prepare the related 5,6,11,12-tetradehydrodibenzo[*a,e*]cyclooctene (**5**), a conjugated cycloocta-1,5-diyne containing two annelated benzene rings. We also decided to investigate the synthesis of 5,6-didehydrodibenzo[*a,e*]cyclooctene (**6**), a conjugated dibenzanneleted cyclooct-1-en-5-yne derivative, formally related to **4**. We chose first to work in the dibenz[*a,e*]cyclooctene series, since the presence of the fused benzene rings was expected to stabilize the molecules, and to prevent the formation of cumulene linkages by base treatment of suitable precursors. We now report the synthesis and study of compounds **5** and **6**, which could be isolated as crystalline compounds.[9,10,11]



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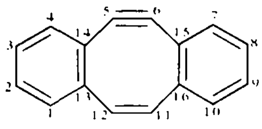

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SYNTHESIS AND REACTIONS OF 5,6,11,12-TETRADEHYDRODIBENZO[*a,e*]CYCLOOCTENE (5)

The starting material for the synthesis of 5,6,11,12-tetradehydrodibenzo [*a,e*]cyclooctene (**5**) was 5,6,

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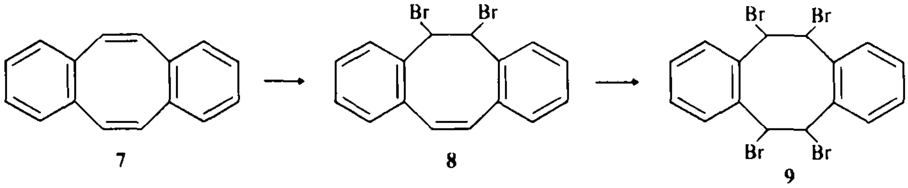
†This paper is dedicated to the memory of the late Prof. R. B. Woodward.



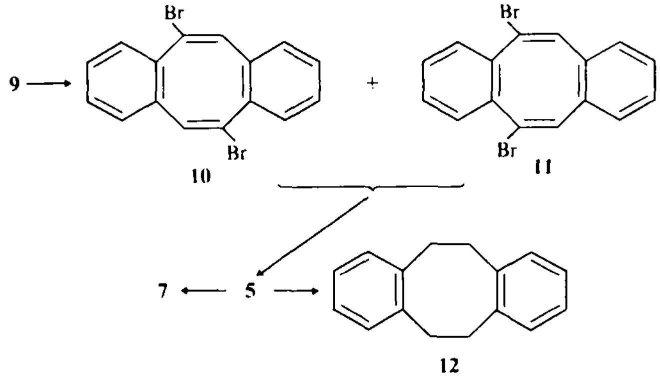
11,12-tetrabromo-5,6,11,12-tetrahydrodibenzo-[*a*,*e*]cyclooctene (**9**), which had been prepared a number of years ago by the addition of bromine[12] to dibenzo[*a*,*e*]cyclooctene (7).[13,14] It is of interest that the conversion of **7** to the dibromide **8** proceeds readily in dichloromethane or chloroform at 0–5°,[12] whereas addition of the second molecule of bromine is a much less facile process (requiring irradiation of a carbon tetrachloride solution with an ultraviolet lamp at 60° or higher[12]) presumably for steric reasons. Only one stereoisomer of the tetrabromide **9** (m.p. 191–193°) appears to be formed, but its stereochemistry has not been determined.

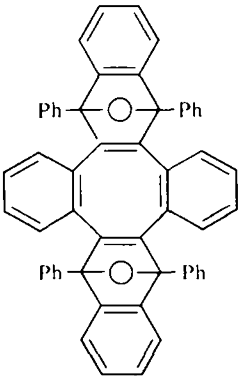
Dehydrobromination of the tetrabromide **9** with an excess of 1,5-diazabicyclo[4.3.0]non-5-ene in boiling benzene resulted in the loss of only one molecule of hydrogen bromide from each of the two 1,2-dibromo groupings, and led to 81 % of a mixture of the divinyl dibromides **10** and **11** as an apparently homogeneous crystalline product, m.p. 137–138°. The gross structure of the mixture of **10** and **11** was established by the elemental analysis, the mass spectrum, and by hydrogenation in ethanol over a Pd–C catalyst to give 5,6,11,12-tetrahydrodibenzo[*a*,*e*]cyclooctene (**12**),[15] identical to a sample obtained by similar hydrogenation of dibenzo[*a*,*e*]cyclooctene (7). That the dibromides, which could not be separated, were a mixture of **10** and **11** was shown by the presence of two singlets at δ 7.34 and 7.30 in the 220 MHz ^{1}H NMR spectrum.

Dehydrobromination of the tetrabromide **9** with a stronger base (potassium t-butoxide) in tetrahydrofuran at room temperature resulted in the loss of four molecules of hydrogen bromide, and gave the diacetylene **5** as pale yellow crystals in 70 % yield, which could also be obtained (in 28 % yield) under similar conditions from the divinyldibromides **10** and **11**. The structure of the diacetylene **5** was confirmed by the IR spectrum ($C\equiv C$ stretching band at 2180 cm^{-1}), the mass spectrum (M^+ at *m/e* 200), and by hydrogenation experiments. Dibenzo[*a*,*e*]cyclooctene (**7**) was obtained in 31 % yield when a solution of **5** in ethyl acetate in the presence of a Pt catalyst was allowed to absorb *ca* 2 molar equivalents of hydrogen, whereas 5,6,11,12-tetrahydrodibenzo[*a*,*e*]cyclooctene (**12**)[15] was formed when the hydrogenation of **5** under these conditions was allowed to proceed to completion. Rather surprisingly, the diacetylene **5** proved to be a comparatively stable compound, although some decomposition was observed after several days when the solid was allowed to stand at room temperature without protection from light or air.

The acetylenic bonds in the diacetylene **5** are considerably strained, and this is shown by their enhanced reactivity. Thus, compound **5** (formed *in situ* from **10**, **11**, and potassium t-butoxide) underwent ready Diels–Alder reaction with 1,3-diphenylisobenzofuran at room temperature. The bis-adduct **13**, isolated in 57 % yield, formed pale pink crystals, m.p. 274–275°. It appeared to be a mixture of the *endo* and *exo* isomers, but separation could not be achieved. Similarly, Diels–Alder reaction of **5** with furan at room temperature afforded the bis-adduct **14**. This substance was not isolated, but was converted by catalytic hydrogenation in ethyl acetate over Pt to the corresponding tetrahydro-compound, which was then dehydrated to tetraphenylene (**15**)[17] (16 % yield based on **5**) by means of phosphorus pentoxide in orthophosphoric acid.[16] 5,6,11,12-Tetrahydrodibenzo[*a*,*e*]cyclooctene (**12**), derived from unchanged **5**, was also isolated in 9 % yield.

The strain of the acetylenes in **5** was also indicated by the [2+2]cycloaddition between **5** and dichloroketene[18,19] (generated *in situ* from dichloroacetyl chloride and triethylamine),[20] which led to 28 % (42 % based on converted **5**) of the red mono-adduct **16**, m.p.





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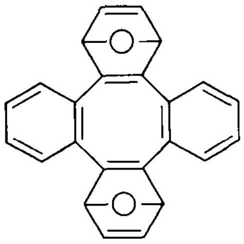

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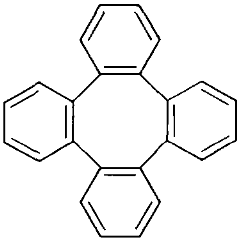


15

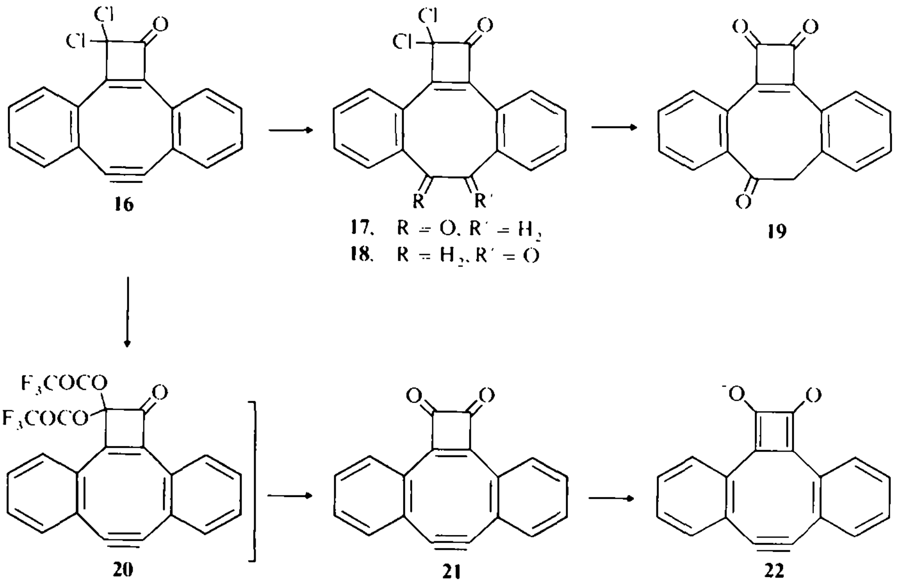
144–145° dec.[21,22] It was of interest to convert the dichloroketone **16** to the annelated cyclobutene-1,2-dione **21**. In practice, attempted hydrolysis of **16** to **21** with concentrated sulphuric acid[23] at 65° for 2 hours resulted also in hydration of the acetylene, and gave the yellow trione **19**, m.p. 173–174°, in 70% yield. Unfortunately, hydration of the strained acetylenic bond in **16** appears to take place prior to hydrolysis of the gem-dichloride, since treatment of **16** with concentrated sulphuric acid under milder conditions (20° for 10 seconds) led to a mixture of the hydrated products **17** and **18**, m.p. 123–125°.

After some experimentation, it was found that the desired diketone **21** could be obtained conveniently by treatment of the dichloroketone **16** with silver trifluoroacetate[24] in boiling benzene, followed by hydrolysis of the presumed intermediate gem-bis-(trifluoroacetate) **20** with water.[21] The diketone **21**, an interesting compound consisting of a cyclobutene-1,2-dione ("cyclobutadienequinone") annelated to a presumably planar conjugated 8-membered ring (see below), was obtained as an unstable red crystalline solid. Although the yield was good, the exact yield could not be determined due to the instability of the substance.

The electrochemical reduction of the quinone **21** to the radical anion, and then to the dianion **22**, has been studied (for details, see Ref. 21). The interesting observation was made that the reduction of **21** is relatively facile, suggesting that the fusion of two planar anti-aromatic $4n$ π-electron rings in **22**, the core of which is a $(4n + 2)$ π-electron cyclobutadienocyclooctatetraene system, has resulted in aromatic stabilization.

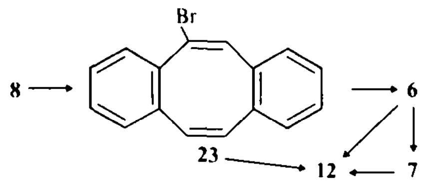
SYNTHESIS AND REACTIONS OF 5,6-DIDEHYDRODIBENZO[*a,e*]CYCLOOCTENE (6)

The starting material for the synthesis of 5,6-didehydrodibenzo[*a,e*]cyclooctene (**6**) was the previously mentioned 5,6-dibromo-5,6-dihydrodibenzo[*a,e*]cyclooctene (**8**), readily obtained in 85% yield by bromination[12] of dibenzo[*a,e*]cyclooctene (**7**). Dehydrobromination of **8** with 1,5-diazabicyclo-[4.3.0]non-5-ene in boiling benzene gave 80% of the



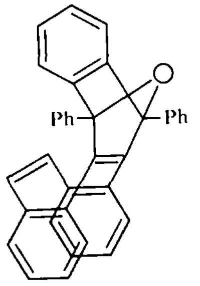
16 **17**, $R = O, R' = H_2$ **18**, $R = H_2, R' = O$ **19**

20 **21** **22**

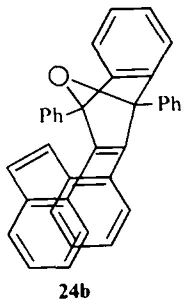


vinyl bromide **23**, m.p. 76–78°. Dehydrobromination of either the dibromide **8** or the monobromide **23** with potassium t-butoxide in tetrahydrofuran at room temperature for 1–2 min led to the monoacetylene **6** (34% yield from **8**, 24% yield from **23**) as golden yellow crystals, which proved to be very unstable. Thus, it decomposed after being allowed to stand for a few min at room temperature without protection from light or air, and was generally prepared immediately before it was required for the various measurements and reactions described subsequently.[25] It was found important that the dehydrobromination of **8** or **23** with potassium t-butoxide was allowed to proceed for only a short time, since longer reaction times resulted in drastic reductions in the yield of **6**. Catalytic hydrogenation of **6** in ethyl acetate over a Pt catalyst yielded dibenzo[*a,e*]cyclooctene (**7**) in 14% yield when *ca* 1 molar equivalent of hydrogen was allowed to be absorbed, whereas 5,6,11,12-tetrahydrodibenzo-[*a,e*]cyclooctene (**12**) was obtained when the hydrogenation of **6** under these conditions was allowed to proceed to completion. Compound **12** was also obtained by catalytic hydrogenation of the vinyl bromide **23** in ethanol over a Pd–C catalyst.

As in the diacetylene **5**, the acetylenic bond in the monoacetylene **6** is strained, and this is shown by its enhanced reactivity. For instance, Diels–Alder reaction of **6** (formed *in situ* from **8** and potassium *tert*-butoxide) with 1,3-diphenylisobenzofuran at room temperature led to 25% of the *endo* adduct **24a**, m.p. 282–285°, and 4.5% of the *exo* adduct **24b** m.p. 268–270°. Unlike in the case of the *endo* and *exo* adducts **13**, separation between **24a** and **24b** could be achieved simply by preparative layer chromatography. The stereochemical assignments are based on ^{1}H NMR spectrometry. The olefinic protons in the isomer m.p. 282–285° resonate at considerably higher field (δ6.14) than in the isomer m.p. 268–270° (δ6.70 or at lower field). Since the olefinic protons are expected to be shielded by the dihydroisobenzofuran ring in the *endo* adduct **24a**, but not in the *exo* adduct **24b**, the higher melting isomer is assigned the *endo* structure **24a**, and the lower melting isomer the *exo* structure **24b**.

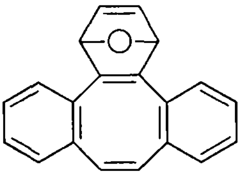


24a



24b

Similarly, Diels–Alder reaction of **6** with furan at room temperature gave 51% of the adduct **25**, m.p. 182–183°, which on catalytic hydrogenation in ethyl acetate over Pd–C and subsequent dehydration of the resulting dihydro-compound with phosphorus pentoxide in orthophosphoric acid[16] led to 13,14-dihydrotribenzo[*a,c,e*]cyclooctene (**26**)[26] in 27% yield.



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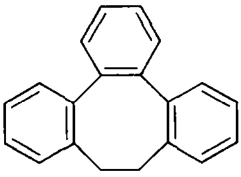

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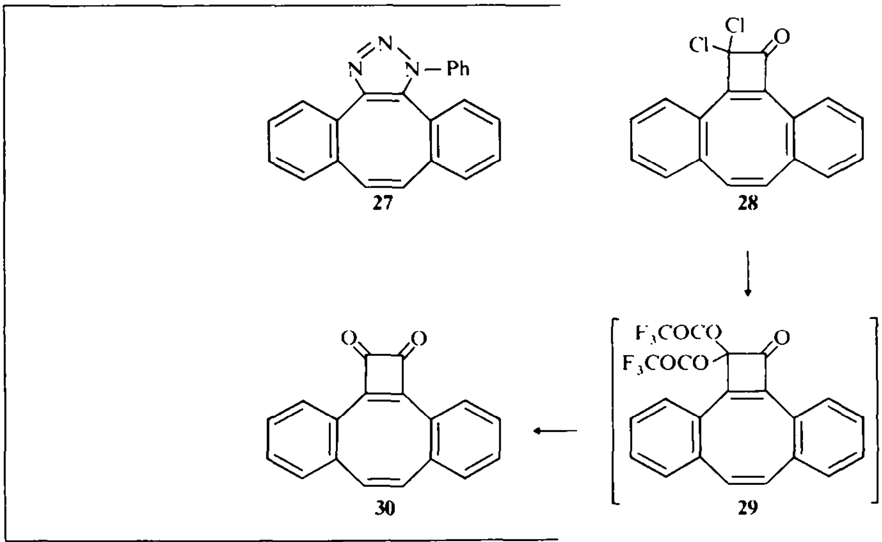
An example of a 1,3-dipolar cycloaddition to the acetylene in **6** was provided by the reaction with phenylazide[27] in ether at room temperature, whereby the annelated 1-phenyl-1H-triazole derivative **27**, m.p. 223–224°, was obtained in 66% yield. In the same way as the diacetylene **5**, the monoacetylene **6** underwent smooth [2+2]cycloaddition with dichloroketene

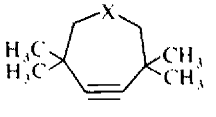


(generated *in situ* from dichloroacetyl chloride and triethylamine),[20] whereby the yellow dichloroketone **28** m.p. 158–160°, was obtained in 17% yield.[21] Treatment of **28** with silver trifluoroacetate in boiling benzene, followed by hydrolysis of the resulting gem-bis(trifluoroacetate) **29** with water, then led in low yield to the relatively stable compound **30**, consisting of a cyclobutene-1,2-dione ("cyclobutadienequinone") annelated to cyclooctatetraene, as pale yellow crystals, m.p. 198–199°.[21]

SPECTRAL AND OTHER PROPERTIES OF 5,6,11,12-TETRADEHYDRODIBENZO[*a,e*]CYCLOOCTENE (5) and 5,6-DIDEHYDRODIBENZO[*a,e*]CYCLOOCTENE (6)

A number of spectral and other properties of **5** and **6**, not previously mentioned in this paper, have been investigated. Much of this work has already been published elsewhere, and this and the next section will therefore be confined mainly to a description of previously unpublished material, as well as drawing attention to the published work.

X-Ray crystallographic analyses of the diacetylene **5**[28] and the monoacetylene **6**[29] have been carried out. As expected, the eight-membered ring in **5** was found to be essentially coplanar, and the acetylenic bonds are highly strained (average angular deformation, 24.2°).[28] The monoacetylene **6** crystallized as two different molecules (molecules A and B).[29] The 8-membered ring in molecule A is also essentially coplanar, but a significant deviation from coplanarity was observed in molecule B.[29] The average deviation of the acetylenic bond from the normal value in compound **6**, molecule A, was 24.5°, and in **6**, molecule B, it was 27.5°.[29] There is only one report of a more highly strained cyclic acetylene, namely 3,3,6,6-tetramethyl-1-thiacycloheptyne (**31**), in which the deformation of the acetylene was found to be 34.2° by an electron diffraction study of the molecule in the gas phase.[30]



31. X = S
32. X = CH_2

The strain of the acetylenes in the cyclic acetylenes **5** and **6** was also demonstrated by the ^{13}C NMR spectra (Table 1). Compared with an unstrained acetylene, such as 2,2,5,5-tetramethylhex-3-yne, the ^{13}C resonances have shifted to much lower field, the value being similar to that of the highly strained cycloheptyne derivatives **31**[31] and **32**.[32]

Since compounds **5** and **6** contain essentially coplanar conjugated 8-membered rings, their ^1H NMR spectra were expected to show them to be paratropic ("antiaromatic"). Preliminary ^1H NMR spectral results, reported in 1974,[9] confirmed this expectation. More recently, a complete analysis of the ^1H NMR spectrum of the diacetylene **5** has been carried out by Günther *et al.*[33] This gave definite support for the antiaromaticity of the 8-membered ring of **5**, a fact demonstrated most convincingly by the Q-value method.[33]

A well-resolved ^1H NMR spectrum of the monoacetylene **6** has recently been carried out by Günther *et al.* at 400 MHz.[34] This spectrum (in acetone-d_6) appears as a 4 H multiplet at δ 6.86 (H(2), H(3), H(8), H(9)), a 2 H doublet at δ 6.67 (H(4), H(7) or H(1), H(10)), a 2 H doublet at δ 6.51 (H(1), H(10) or H(4), H(7)), and a 2 H singlet at δ 5.45 (H(11), H(12)). By comparison, in the ^1H NMR spectrum of dibenzo[*a,e*]cyclooctene (**7**)[35] containing an atropic nonplanar 8-membered ring,[35] the benzenoid protons (in $CDCl_3$) resonate at δ 7.11 (H(2), H(3), H(8), H(9)) and 7.02 (H(1), H(4), H(7), H(10)), and the olefinic protons at δ 6.71. The relatively high-field resonance of the benzenoid protons of **6**, and especially the high-field resonance of the 8-membered ring olefinic protons as compared with those of **7**, clearly indicates the existence of a paramagnetic ring current in the 8-membered ring of **6**.

The electronic spectra of 5,6,11,12-tetradehydrodibenzo[*a,e*]cyclooctene (**5**) and 5,6-didehydrodibenzo[*a,e*]cyclooctene (**6**), which proved to be quite complex, are given in Figs. 1 and 2, respectively, as well as in Table 2. The main maxima are at 271 and 275 nm, respectively, with high molecular extinction coefficients (179,800 and 119,400,[36] respectively). These characteristics, the complexity of the spectra, as well as the fine structure in the *ca* 315–460 nm region (Figs. 1 and 2), must be due to the essentially planar conjugated 8-membered rings in **5** and **6**. By

Table 1. ^{13}C NMR spectral resonances of cyclic acetylenes (in ppm downfield from internal tetramethylsilane)

Compound	Solvent	δ
2,2,5,5-Tetramethylhex-3-yne [a]	CCl_4	87.0
3,3,8,8-Tetramethylcyclo-1-octyne [a]	CCl_4	97.6
3,3,6,6-Tetramethyl-1-thiacyclohept-4-yne (**31**) [a]	CCl_4	108.5
5,6,11,12-Tetradehydrodibenzo[*a,e*]cyclooctene (**5**) [b]	CCl_4	109.3
5,6-Didehydrodibenzo[*a,e*]cyclooctene (**6**) [b]	CCl_4	108.5
3,3,7,7-Tetramethylcyclohept-1-yne (**32**) [c]	$CDCl_3$	109.8

[a] Reference 31; [b] H. Günther, private communication; [c] reference 32.

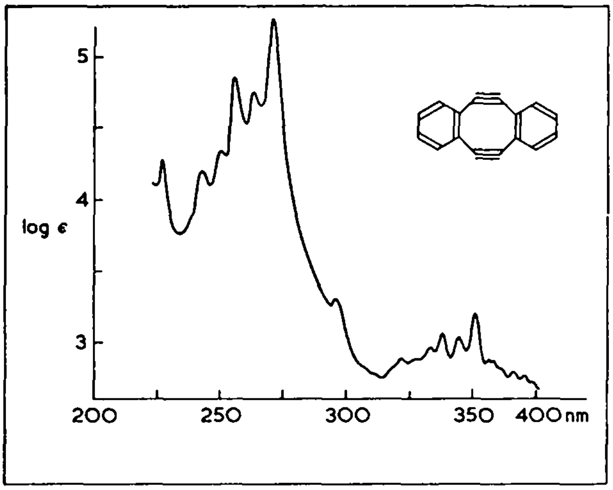
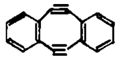
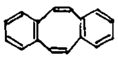
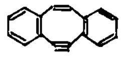
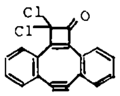
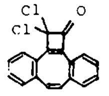
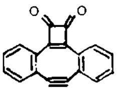
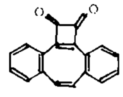


Fig. 1. Electronic absorption spectrum of 5,6,11,12-tetradehydrodibenzo[*a,e*]cyclooctene (**5**), in hexane.

Table 2. Main electronic absorption maxima of compounds **5**, **6**, **7**, **16**, **21**, **28**, and **30** (ε values and solvents in parentheses)

Essentially planar 8-ring		Nonplanar 8-ring	
 **5**	271 nm (179,800, hexane)	 **7**	242 nm (25,200, hexane)
 **6**	275 nm (119,400,[a] hexane)		
 **16**	283 nm (97,300, cyclohexane)	 **28**	259 nm (33,900, cyclohexane)
 **21**	282 nm (31,700,[a] ethanol)	 **30**	265 nm (13,700, ethanol)

[a] The ε value is a minimum one, due to the instability of the compound.

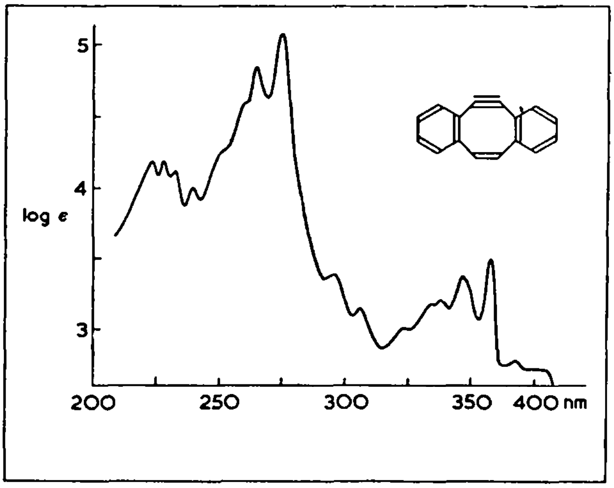


Fig. 2. Electronic absorption spectrum of 5,6-didehydrodibenzo[*a,e*]cyclooctene (**6**), in hexane.

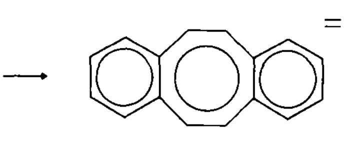
comparison, the electronic spectrum of the nonplanar dibenzo[*a,e*]cyclooctene (**7**) shows a single maximum at 242 nm (ε 25,200), without fine structure. The considerable bathochromic shift and increase in the ε value in **5** and **6** as compared to **7** is also apparent in the presumably planar 5,6-didehydrodibenzo[*a,e*]-cyclooctene-derivatives **16** and **21**, as compared with the corresponding nonplanar dibenzo[*a,e*]cyclo-octene-derivatives **28** and **30** (see Table 2).

CHEMICAL AND ELECTROCHEMICAL REDUCTIONS OF 5,6,11,12-TETRADEHYDRODIBENZO[*a,e*]CYCLOOCTENE (5) AND 5,6-DIDEHYDRODIBENZO[*a,e*]CYCLOOCTENE (6)

It has been shown that treatment of dibenzo[*a,e*]-cyclooctene (**7**), containing a nonplanar atropic 8-membered ring, with an alkali metal, leads to the dianion **33** in which the 8-membered ring is now a planar 10π-electron system.[37] It was to be expected that the dehydro derivatives **5** and **6** of **7**, containing essentially planar paratropic 8-membered rings, could also be converted to 10π-dianions corresponding to **33** by treatment with an alkali metal.[38]

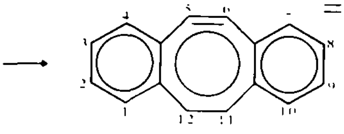
In practice treatment of the diacetylene **5** in tetrahydrofuran-d_8 with a potassium mirror at −20° resulted in polymerization, perhaps because the presence of two acetylenes promotes anion polymerization.[39] On the other hand, similar treatment of the monoacetylene **6** with a potassium mirror led to a deep green solution of the di-potassium salt of the dianion 34.[9,40] Comparison of the ^{1}H NMR spectrum of the dianion **34** (100 MHz, −40°) with that of the precursor **6** shows that the H(2), H(3), H(8), and H(9) benzenoid proton resonances have shifted upfield from δ 6.86 to 6.2, the H(1), H(4), H(7), and H(10) benzenoid proton resonances have shifted downfield from δ 6.51 and 6.67 to 7.75, and the olefinic proton resonances have shifted downfield from δ 5.45 to 6.67. The observed downfield shift by *ca* 1.2 ppm of the olefinic 8-membered ring proton resonances, as well as those of the benzenoid protons adjacent to the 8-membered ring (despite the introduction of two negative charges), is fully in accord with the conversion of a paratropic to a diatropic system, by formation of the dianion.

7



33

6



34

The conversion of dibenzo[*a,e*]cyclooctene (**7**) to the corresponding radical anion, and the study of its structure by ESR spectrometry, have been described.[37,41,42] The preparation and the study of the structures of the radical anions of **5** and **6** by ESR spectrometry have been reported subsequently.[42] In connection with this work, the catalytic deuteration of 5,6,11,12-tetradehydrodibenzo[*a,e*]cyclooctene (**5**) to 5,6,11,12-tetradeuteriodibenzo[*a,e*]cyclooctene (**7**-d_4) was carried out, followed by bromination to the corresponding 5,6-dibromide (**8**-d_4), and dehydrobromination to 5,6-didehydro-11,12-dideuteriodibenzo[*a,e*]cyclooctene (**6**-d_2).[42]

The electrochemical reduction of the three dibenzo[*a,e*]cycloctene derivatives **5**–**7** has been studied, and the results have been published.[43]

EXPERIMENTAL

Microanalyses were carried out by the microanalytical section of the Chemistry Department, University College London. M.ps were determined on a Kofler hot-stage microscope apparatus, and are uncorrected. B.ps are also uncorrected. The electronic spectra were determined on a Unican SP 800 recording spectrophotometer. IR spectra were recorded on a Unican SP 200 spectrophotometer. ^{1}H NMR spectra were determined on a Varian HA-100 or T-60 spectrometer in $CDCl_3$, unless stated otherwise, and the chemical shifts are reported as δ values in ppm downfield from $SiMe_4$ as internal standard. High resolution mass spectra were recorded on an AEI MS9 mass spectrometer at 70 eV. Tlc plates were prepared with Merck Kieselgel HF_{254}, or were obtained commercially (pre-coated Merck Kieselgel 60 F_{254} plates, layer thickness, 0.25 mm). Al_2O_3 for column chromatography was Woelm neutral grade III. KO^{t}Bu was obtained from Fluka Chemicals Ltd., and was used without purification unless stated otherwise. Solvents were purified and dried by standard methods. All solvents were removed under reduced pressure.

Dibenzo[a,e]cyclooctene (**7**). Dibenzobicyclo-[2.2.2]octatriene was prepared by addition of an excess of *cis*-1,2-dichloroethylene to anthracene in a sealed tube at 250° for 24 hr to give 70% of *cis*-2,3-dichlorodibenzobicyclo-[2.2.2]octatriene,[44] from which the chloro groups were reduced in 90% yield by reduction with sodium in boiling n-amyl alcohol.[44,45] A soln of dibenzobicyclo[2.2.2]octatriene (1 g) in dry THF (250 ml) was irradiated[14] with a medium pressure UV lamp (Hanovia, 125 W) for 24 hr under N_2. The solvent was evaporated, the residue was extracted with petroleum ether (b.p. 40–60°), and decanted from insoluble material. Evaporation and crystallization from EtOH gave **7** (0.75 g, 75%), colourless crystals, m.p. 105–106° (lit[46] m.p. 106.2–106.9°); ^{1}H NMR δ 7.09 (m, AA′,BB′, 8 H), 6.75 (s, 4 H); UV λ_{max} (hexane) 242 nm (ε 25,200).

5,6,11,12-*Tetrabromo*-5,6,11,12-*tetrahydrodibenzo*[a,e]-*cyclooctene* (**9**).[12] A soln of Br_2 (0.78 g, 4.88 mmol) in CCl_4 (5 ml) was added dropwise to a soln of **7** (0.5 g, 2.45 mmol) in CCl_4 (5 ml). The soln was heated to 75° and irradiated with a medium pressure UV lamp (Hanovia, 125 W) until the soln became light yellow. Evaporation of solvent and crystallization from cyclohexane gave **9** (0.80 g, 62%), colourless crystals, m.p. 191–193° (lit[12] m.p. 195–197°, 202°); ^{1}H NMR δ 7.80–6.62 (m, 8 H), 5.28, 6.29 (ABq, 4 H, J = 10 Hz).

5,11-*Dibromodibenzo*[a,e]*cyclooctene* (**10**) *and* 5,12-*dibromodibenzo*[a,e]*cyclooctene* (**11**). A soln of **9** (500 mg, 0.95 mmol) and 1,5-diazabicyclo[4.3.0]non-5-ene (1.3 g, 10.5 mmol) in benzene (4 ml) was boiled under reflux under N_2 for 2 hr. The soln was cooled and then washed with 2N H_2SO_4aq and H_2O. The benzene layer was dried ($MgSO_4$) and evaporated. Crystallization from EtOH gave **10** and **11** (280 mg, 81%), which could not be separated by column chromatography on Al_2O_3 or SiO_2, colourless crystals, m.p. 137–138°; ^{1}H NMR δ (220 MH) 7.42–6.98 (m, 10 H), including singlets at δ 7.34, 7.30 (total 2 H); MS measured M$^+$ 359.9156. Calc. for $C_{16}H_{10}{}^{79}Br_2$: 359.9150 (Found: C, 52.86; H, 2.67; Br, 44.34. $C_{16}H_{10}Br_2$ requires: C, 53.04; H, 2.77; Br, 44.19%).

5,6,11,12-*Tetradehydrodibenzo*[a,e]*cyclooctene* (5)

(a) *By dehydrobromination of* **9** *with* KO^{t}Bu. A soln of **9** (206 mg, 0.39 mmol) in dry THF (3 ml) was added dropwise during 1 min to a stirred soln of KO^{t}Bu (400 mg, 3.57 mmol; purified by sublimation) in dry THF (20 ml) at room temp under N_2, and the soln was then stirred for 10 min. 2N HCl aq was added, followed by extraction with ether. The organic layer was washed with H_2O, and dried ($MgSO_4$). Evaporation, chromatography on Al_2O_3, and elution with pentane, gave **5** (55 mg, 70%), pale yellow plates which decomposed at *ca* 110° on attempted m.p. determination; δ ^{1}H NMR δ 7.24–6.36 (AA′BB′) (for complete analysis see ref. 33); ^{13}C NMR (CCl_4, see Table 1 and Ref. 34a) δ 133.2 (C(13), C(14), C(15), C(16)), 128.3, 126.3 (C(1), C(2), C(3), C(4), C(7), C(8), C(9), C(10)), 109.3 (C(5), C(6), C(11), C(12)); UV (hexane) (see Fig. 1, Table 2) λ_{max} 227 nm (ε 18,000), 243 (15,700), 249 (21,300), 256 (69,700), 263 (56,200), 271 (179,800), 296 (1900), with a weak broad band between *ca* 315 and 430 nm showing considerable fine structure (maximum ε 1570 at 352 nm); IR (KBr) ν_{max} 2180 cm^{-1} (w); measured M$^+$ 200.0632, Calc. for $C_{16}H_8$: 200.0626. (Found: C, 95.91; H, 4.02. $C_{16}H_8$ requires: C, 95.97; H, 4.03%).

(b) *By dehydrobromination of* **10** *and* **11** *with* KO^{t}Bu *in THF*. A mixture of **10** and **11** (200 mg, 0.55 mmol) in dry THF (2.5 ml) was added dropwise during 3 min to a stirred soln of KO^{t}Bu (365 mg, 3.26 mmol) in dry THF (200 ml) at room temp. under N_2, and the soln was then stirred for 30 min. 2N HCl aq was added, followed by extraction with ether. The organic layer was washed with H_2O and dried ($MgSO_4$). Evaporation, chromatography on Al_2O_3, and elution with pentane, gave **5** (30.5 mg, 28%), identical in all respects with the material obtained by method (a). The yield of **5** from **10** and **11** was 24% when the dehydrobromination was carried out with KO^{t}Bu in benzene at 65°.

Dibenzo[*a,e*]*cyclooctene* (7) *from* **5**. A soln of **5** (42 mg, 0.21 mmol) in EtOAc (5 ml) was added to pre-hydrogenated $PtO_2.H_2O$ (5 mg) in EtOAc (10 ml), and the mixture was stirred vigorously in H_2 at room temp and atmospheric pressure until 10.2 ml of H_2 had been absorbed (theoretical uptake, 9.5 ml, 0.42 mmol). Removal of the catalyst, evaporation of the solvent, PLC on Merck Kieselgel 60 PF_{254} (pentane-ether, 10:1), and crystallization from EtOH, yielded **7** (13.2 mg, 31%), colourless crystals, m.p. 102–104°, identical with an authentic sample.

5,6,11,12-*Tetrahydrodibenzo*[a,e]*cyclooctene* (12).

(a) *By hydrogenation of* **7**. A soln **7** (20 mg, 0.098 mmol) in EtOH (2 ml) was shaken in H_2 over a 10% Pd–C catalyst (10 mg) at room temp and atmospheric pressure for *ca* 90 min. The catalyst was removed, the solvent was evaporated, and the residue was extracted with CCl_4. Evaporation of the solvent and crystallization from MeOH gave **12** as colourless crystals, m.p. 109–110° (lit[15] m.p. 109.4–109.9°); ^{1}H NMR δ 6.99 (s, 8 H), 3.10 (s, 8 H).

(b) *By hydrogenation of* **10** *and* **11**. A soln of **10** and **11** (103 mg, 0.28 mmol) in 95% EtOH (4 ml) was stirred in H_2 over a 10% Pd–C catalyst (14 mg) at room temp and atmospheric pressure for *ca* 5 hr. The catalyst was removed, the solvent was evaporated, and the residue was extracted with CCl_4. Evaporation of the solvent and crystallization from EtOH gave **12** as colourless crystals, m.p. 109–110°, undepressed on admixture with a sample prepared by method (a).

(c) *By hydrogenation of* **5**. A soln of **5** (11 mg, 0.055 mmol) in EtOAc (4 ml), added to pre-hydrogenated $PtO_2.H_2O$ (4 mg) in EtOAc (10 ml), and the mixture was stirred vigorously in H_2 at room temp and atmospheric pressure until no further absorption occurred (uptake of H_2, 5.0 ml, *ca* 0.23 mmol). Removal of the catalyst, evaporation of the solvent, and crystallization from MeOH yielded **12** as colourless crystals, m.p. 108–109°, identical with that prepared by methods (a) and (b).

Bis-adduct **13**. A mixture of **10** and **11** (362 mg, 1 mmol), KO^{t}Bu (682 mg, 6.1 mmol), and 1,3-diphenylisobenzofuran (542 mg, 2 mmol) in ether (25 ml) was stirred at room temp for 80 hr. H_2O was added, the mixture was filtered, and the solid was combined with the residue obtained by evaporation of the dried ($MgSO_4$) filtrate. Repeated crystallization of the combined solids from CCl_4–EtOH yielded **13** (422 mg, 57%), presumably a mixture of *endo* and *exo* isomers, as pale pink crystals, m.p. 274–275°; ^{1}H NMR δ 7.90–7.10 (m, 26 H), 7.10–6.50 (m, 8 H), 6.50–6.15 (m, 2 H); MS measured M$^+$ 740.2648, Calc. for $C_{56}H_{36}O_2$: 740.2715. (Found: C, 90.46; H, 4.89. $C_{56}H_{36}O_2$ requires: C, 90.81; H, 4.86%).

Tetraphenylene (**15**). A soln of **5** (90 mg, 0.45 mmol) in furan (10 ml) was stirred for *ca* 100 hr. The excess furan was evaporated from the resulting **14**, the residue was dissolved in EtOAc (9 ml), added to pre-hydrogenated $PtO_2.H_2O$ (15 mg) in EtOAc (10 ml) and shaken in H_2 at room temp and atmospheric pressure. The uptake of H_2 was 22 ml (*ca* 0.98 mmol). The catalyst was removed, the solvent was evaporated, and P_2O_5 (7 g) and orthophosphoric acid (8 ml) were added to the mixture. The mixture was heated at 140° for 2 hr,[16] cooled, and poured into ice–water (50 ml). Ether was added, the organic extract was washed with H_2O, dried (Na_2SO_4), and evaporated. Plc of the residue on Merck

Kieselgel 60 PF_{254} (pentane–ether, 10:1) yielded two products. The less polar compound was **12** (8.2 mg, 9%), identified with an authentic sample. The more polar compound on crystallization from EtOH proved to be **15** (21.7 mg, 16%), colourless crystals, m.p. 239–240° (lit[17] m.p. 233°); ^{1}H NMR δ 7.26 (br s); MS measured M^+ 304.1271, calc. for $C_{24}H_{16}$: 304.1252.

9,9-*Dichloro*-2,3,6,7-*dibenzobicyclo*[6.2.0]*deca*-2,6,8-*trien*-4-*yn*-10-*one* (**16**). A soln of dichloroacetyl chloride (60 mg, 0.41 mmol) in pentane (10 ml) was added dropwise during 1 hr to a stirred soln of **5** (35 mg, 0.18 mmol) and NEt_3 (60 mg, 0.59 mmol) in pentane (10 ml) at room temp, and the mixture was stirred for *ca* 12 hr. The mixture was washed with 10% $NaHCO_3$ aq and then with H_2O. The organic layer was dried (Na_2SO_4) and evaporated. Plc of the residue on Merck Kieselgel 60 PF_{254} (pentane–ether, 10:1) yielded two products. The less polar compound (12 mg, 34%) proved to be unchanged **5** The more polar compound on crystallization from EtOH proved to be **16** (15 mg, 28%, 42% based on converted **5**), red crystals m.p. 144–145° dec.; ^{1}H NMR δ 8.16–7.80 (m, 2 H) 7.26–6.88 (m, 4 H), 6.80–6.60 (m, 2 H); UV (cyclohexane) (see Table 2) λ_{max} 250 nm (ε 32,500), 275 (80,000), 283 (97,300), 310 (2740), 326 (2200), 362 (6970), 382 (7800); IR (KBr) ν_{max} 1760 cm^{-1} (s); MS measured M^+ 309.9953. Calc. for $C_{18}H_8{}^{35}Cl_2O$: 309.9935. (Found: C, 69.51; H, 2.73; Cl, 23.15. $C_{18}H_8Cl_2O$ requires: C, 69.45; H, 2.57, Cl, 22.83%).

9,9-*Dichloro*-2,3,6,7-*dibenzobicyclo*[6.2.0]*deca*-2,6,8-*triene*-4,10-*dione* (**17**) *and* 9,9-*dichloro*-2,3,6,7-*dibenzobicyclo*-[6.2.0]*deca*-2,6,8-*triene*-5,10-*dione* (**18**). Compound **16** (4.5 mg, 0.015 mmol) was stirred in conc H_2SO_4 (1 ml) until all the red crystals had disappeared (*ca* 10 sec). The soln was immediately poured into ice, and ether was added. The ether extract was washed with 10% $NaHCO_3$ aq and H_2O, and was then dried (Na_2SO_4) and evaporated. Plc on Merck Kieselgel 60 PF_{254} (pentane-ether, 10:1) yielded unchanged **16** and then a mixture of **17** and **18**, pale yellow crystals, m.p. 124°, from ether–pentane. Analytical tlc showed two proximate spots, indicating the presence of both possible isomers; MS measured M^+ 328.0032, Calc. for $C_{18}H_{10}{}^{35}Cl_2O_2$: 328.0058.

2,3,6,7-*Dibenzobicyclo*[6.2.0]*deca*-2,6,8-*triene*-4,9,10-*trione* (**19**). Compound **16** (30 mg, 0.1 mmol) and conc H_2SO_4 (7 ml) were heated at 65° for 2 hr. The soln was cooled, poured into ice, and ether was added. The ether extract was washed with 10% $NaHCO_3$ aq and H_2O, and was then dried (Na_2SO_4) and evaporated. Crystallization from EtOH gave **19** (18.5 mg, 70%) as pale yellow crystals, m.p. 173–174°; ^{1}H NMR δ 9.16–9.00 (m, 1 H), 8.30–8.04 (m, 2 H), 7.96–7.42 (m, 5 H), 3.95 (s, 2 H); IR (KBr) ν_{max} 1760 (s), 1690 cm^{-1} (m); MS measured M^+ 274.0641, Calc. for $C_{18}H_{10}O_3$: 274.0631. (Found: C, 78.14; H, 3.67. $C_{18}H_{10}O_3$ requires: C, 78.82; H, 3.68).

2,3,6,7-*Dibenzobicyclo*[6.2.0]*deca*-2,6,8-*trien*-4-*yne*-9,10-*dione* (**21**). Silver trifluoroacetate (25.8 mg, 0.12 mmol) in benzene (2 ml) was added to **16** (6.2 mg, 0.02 mmol) in benzene (2 ml), and the soln was boiled under reflux for 1 hr under N_2. The precipitated AgCl was removed by filtration, washed with benzene, and the resulting soln of **20** was hydrolyzed by being shaken vigorously several times with 250 ml portions of H_2O. The organic extract was dried (Na_2SO_4) and evaporated. The resulting **21** was separated from insoluble polymeric material by extraction with an appropriate solvent (EtOH, $CHCl_3$, ether, etc.), depending on which solution was required for further study. If necessary, the solvent was evaporated as quickly as possible; the resulting **21** formed orange-red crystals, which decomposed rapidly in the neat state; ^{1}H NMR δ 8.55–6.55 (complex m); UV (EtOH) (see Table 2)[36] λ_{max} 272 nm (ε 23,800), 282 (31,700), 363 (2700), 382 (2700); IR (KBr) ν_{max} 1770 (s), 1750 cm^{-1} (s); MS measured M^+ 256.0537, Calc. for $C_{18}H_8O_2$: 256.0524.

5,6-*Dibromo*-5,6-*dihydrodibenzo*[*a,e*]*cyclooctene* **8**. A soln of Br_2 (2 g, 12.5 mmol) in CH_2Cl_2 (1 ml) was added dropwise during 5 min to a soln of **7** (2 g, 9.8 ml) at 0°, and the soln was then stirred at 0° for 20 min. Evaporation of solvent and crystallization from cyclohexane–CCl_4 yielded **8** (3.03 g, 85%), colourless crystals, m.p. 157–159° (lit[12] m.p. 157°, 162–163°); ^{1}H NMR δ 7.70–6.90 (m, 10 H), 5.83 (s, 2 H).

5-*Bromodibenzo*[a,e]*cyclooctene* (**23**). A soln of **8** (100 mg, 0.275 mmol) and 1,5-diazabicyclo[4.3.0]non-5-ene (0.35 g, 0.28 mmol) in benzene (2 ml) was boiled under reflux under N_2 for 2 hr. The soln was cooled and then washed with 2N H_2SO_4 aq and H_2O. The benzene layer was dried ($MgSO_4$) and evaporated. Slow crystallization from EtOH gave **23** (62.5 mg, 80%), colourless crystals, m.p. 76–78°; ^{1}H NMR δ 7.50–7.10 (m, 9 H), including 7.33 (d, $J = 4$ Hz) and 7.17 (br s), 6.80 (s, 2 H); measured M^+ 282.0034, Calc. for $C_{16}H_{11}{}^{79}Br$: 282.0044. (Found: C, 67.66; H, 3.78; Br, 28.33. $C_{16}H_{11}Br$ requires: C, 67.84; H, 3.89; Br. 28.27%).

5,6-*Didehydrodibenzo*[a,e]*cyclooctene* (**6**)

(a) *By dehydrobromination of* **8** *with* KO^{t}Bu. A soln of **8** (204 mg, 0.56 mmol) in dry THF (2.5 ml) was added dropwise during 1 min to a stirred soln of KO^{t}Bu (200 mg, 1.78 mmol; purified by sublimation) in dry THF (20 ml) at room temp under N_2, and the soln was then stirred for 1 min. 2N HCl aq was added, followed by extraction with ether. The ether extract was washed with H_2O, dried ($MgSO_4$), and evaporated. Chromatography of the residue on Al_2O_3 and elution with pentane yielded **6** (38.5 mg, 34%) as unstable golden yellow crystals, which decomposed at *ca* 85° on attempted m.p. determination (rapid heating); ^{1}H NMR δ 7.0–6.5 (m, 8 H), 5.50 (s, 2 H), and Discussion Section (Ref. 34) ^{13}C NMR (CCl_4, see Table 1 and ref. 34a) δ 134.9, 132.0, 129.5, 129.0, 125.8 (C(1), C(2), C(3), C(4), C(11)), 146.7, 123.0 (C(13), C(14)), 108.5 (C(5), C(6)); UV (hexane) (see Fig. 2, Table 2)[36] λ_{max} 224 nm (ε 15,100), 228 (15,500), 233 sh (13,100), 240 (10,000), 252sh (18,000), 260 (39,500), 265 (68,200), 275 (119,400), 296 (2500), 306 (1400), with a weak broad band between *ca* 315 and 460 nm showing considerable fine structure (maximum ε 3100 at 365 nm); MS measured M^+ 202.0796, Calc. for $C_{16}H_{10}$: 202.0783. (Found: C, 94.67; H, 4.84. $C_{16}H_{10}$ requires: C, 95.02; H, 4.98%).

(b) *By dehydrobromination of* **23** *with* KO^{t}Bu *in THF*. A soln of **23** (203 mg, 0.72 mmol) in dry THF (2 ml) was added dropwise during 2 min to a stirred solution of KO^{t}Bu (244 mg, 218 mmol) in dry THF (20 ml) at room temp under N_2, and the soln was then stirred for 5 min. 2N HCl aq was added, followed by extraction with ether. The organic layer was washed with H_2O and dried ($MgSO_4$). Evaporation, chromatography on alumina, and elution with pentane, yielded **6** (35 mg, 24%), identical in all respects with the material obtained by method (a). The yield of **6** from **23** was 29% when the dehydrobromination was carried out with KO^{t}Bu in benzene at 65°.

Dibenzo[a,e]*cyclooctene* (**7**) *from* **6**. A soln of **6** (30 mg, 0.15 mmol) in EtOAc (10 ml) was added to pre-hydrogenated $PtO_2 \cdot H_2O$ (7 mg) in EtOAc (10 ml), and the mixture was stirred vigorously in H_2 at room temp and atmospheric pressure until 3 ml (0.14 mmol) of H_2 had been absorbed. Removal of the catalyst, evaporation of the solvent, and crystallization from EtOH yielded **7** (4.3 mg, 14%), m.p. 103–106°, identical with an authentic sample.

5,6,11,12-*Tetrahydrodibenzo*[a,e]*cyclooctene* (**12**)

(a) *By hydrogenation of* **6**. A soln of **6** (10 mg, 0.05 mmol) in EtOAc (5 ml) was added to pre-hydrogenated $PtO_2 \cdot H_2O$ (15 mg) in EtOAc (5 ml), and the mixture was stirred in H_2 at room temp and atmospheric pressure for 2 hr. Removal of the catalyst, evaporation of the solvent, and crystallization from EtOH gave **12**, m.p. 108–109°, identical with an authentic sample.

(b) *By hydrogenation of* **23**. A soln of **23** (21 mg, 0.07 mmol) in 95% EtOH (2 ml) was stirred in H_2 over a 10% Pd-C catalyst (3.5 mg) at room temp. and atmospheric pressure for *ca* 3 hr. Removal of the catalyst, evaporation of the solvent, and crystallization from MeOH gave **12**, m.p. 107–109°, identical with an authentic sample.

Adducts **24a**, **24b** (endo *and* exo *isomers*). A mixture of **8** (364 mg, 1 mmol) KO^{t}Bu (910 mg, 8.12 mmol) and 1,3-diphenylisobenzofuran (270 mg, 1 mmol) in ether (25 ml) was stirred at room temp for 100 h. H_2O was added, the mixture was filtered, and the solid was combined with the residue obtained by evaporation of the dried (Na_2SO_4) filtrate. Plc of the combined solids on Merck Kieselgel 60 $PF_{254+366}$ ($CHCl_3$–CCl_4, 1:4) gave two isomers of **24**. The more polar compound (118 mg, 25%) is the *endo* isomer **24a**, colourless crystals, m.p. 282–285°, from $CHCl_3$–EtOH; ^1H NMR δ 7.41 (s, 8 H), 7.29–6.79 (m, 12 H), 6.45–6.29 m (2 H), 6.14 (s, 2 H); MS measured M^+ 472.1842, Calc. for $C_{36}H_{24}O$: 472.1828. The less polar compound (21.7 mg, 4.6%) was the *exo* isomer **24b**, colourless crystals, m.p. 268–270°, from $CHCl_3$–EtOH; ^1H NMR δ 7.76 6.70 (m); MS measured M^+ 472.1848; Calc. for $C_{36}H_{24}O$: 472.1828. [Found (mixture of isomers): C, 91.08; H, 5.15. $C_{36}H_{24}O$ requires: C, 91.50; H, 5.12%].

5,8-*Dihydro*-5,8-*epoxytribenzo*[a,c,e]*cyclooctene* (**25**). A soln of **8** (1 g, 2.75 mmol) in THF (10 ml) was added dropwise during 10 min to a stirred soln of KO^{t}Bu (1.91 g, 17 mmol) in furan (30 ml) and THF (30 ml) at room temp under N_2. The mixture was stirred for 48 hr, and H_2O and ether were then added. The organic extract was washed with H_2O, and dried ($MgSO_4$). Evaporation and crystallization from cyclohexane yielded crude **25** (380 mg, 51%); repeated crystallization gave colourless crystals, m.p. 182–183°; ^1H NMR δ 7.41 (d, $J = 1$ Hz, 2 H), 7.23–7.07 (m, 6 H), 6.77–6.68 (m, 2 H), 6.65 (s, 2 H), 5.45 (d, $J = 1$ Hz, 2 H); MS measured M^+ 270.1042, calc. for $C_{20}H_{14}O$: 270.1044. (Found: C, 88.73; H, 5.36. $C_{20}H_{14}O$ requires: C, 88.86; H, 5.22%).

13,14-*Dihydrotribenzo*[a,c,e]*cyclooctene* (**26**). A soln of crude **25** (335 mg, 1.24 mmol) in EtOAc (10 ml) was shaken in H_2 with a 10% Pd–C catalyst (25 mg) at room temp and atmospheric pressure.[16] The uptake of H_2 was 48.7 ml (*ca.* 2.17 mmol). The catalyst was removed, the solvent was evaporated, and P_2O_5 (5 g) and orthophosphoric acid (7 ml) were added to the residue. The mixture was heated at 150° for 2 hr,[16] cooled, and poured into ice–water (20 ml). Ether was added, the organic extract was washed with H_2O, dried ($MgSO_4$), and evaporated. Plc of the residue on Merck Kieselgel 60 $PF_{254+366}$ (pentane–ether, 10:1) and crystallization from EtOH gave **26** (85 mg, 27%) as colourless crystals, m.p. 110–112° (lit[26] m.p. 111–113°); ^1H NMR δ 7.46–6.86 (m, 12 H), 3.06–2.86 (AA′BB′, 4 H); MS measured M^+ 256.1255, Calc. for $C_{20}H_{16}$: 256.1252.

4,5,8,9-*Dibenzo*-1-*phenyl*-1 H-*cyclooctatriazole* (**27**). A mixture of **8** (364 mg, 1 mmol) phenylazide (124 mg, 1.04 mmol)[27] and KO^{t}Bu (686 mg, 6.13 mmol) in ether (25 ml) were stirred at room temp for 100 hr. H_2O was added, the precipitate was collected by filtration, and added to the residue obtained by evaporation of the dried ($MgSO_4$) ethereal layer. Crystallization of the combined solids from cyclohexane–CCl_4 gave **27** (213 mg, 66%) as colourless crystals, m.p. 223–224°; ^1H NMR δ 7.72–6.90 (m, 13 H, with a sharp s at 7.38), 6.82 (s, 1 H), 6.72–6.64 (m, 1 H); MS measured M^+ 321.1273. Calc. for $C_{22}H_{15}N_3$: 321.1266. (Found: C, 82.24; H, 4.77; N, 12.99. $C_{22}H_{15}N_3$ requires: C, 82.22; H, 4.71; N, 13.08%).

9,9-*Dichloro*-2,3,6,7-*dibenzobicyclo*[6.2.0]*deca*-2,4,6,8-*tetraene*-10-*one* (**28**). Compound **6** was prepared from the dibromide **8** (200 mg, 0.55 mmol) and KO^{t}Bu as described previously. The pentane eluent from the column chromatography was concentrated to *ca* 15 ml and added to NEt_3 (210 mg, 2.08 mmol) in pentane (5 ml). Dichloroacetyl chloride (210 mg, 1.43 mmol) in pentane (10 ml) was then added dropwise over 1 hr with stirring overnight. The resulting mixture was filtered, the filtrate was washed with satd Na_2CO_3 aq, water, and dried (Na_2SO_4). Evaporation of the pentane, followed by plc of the residue on Merck Kieselgel 60 PF_{254} (pentane–ether, 8:1), and crystallization from ether EtOH yielded **28** (30 mg, 17%) as yellow crystals, m.p. 158–160°; ^1H NMR δ 8.08–7.94 (m, 1 H), 7.51–7.04 (m, 7 H), 6.55 (s, 2 H); IR (KBr) ν_{max} 1780 cm^{-1} (s). (Found: C, 68.95; H, 3.24. $C_{18}H_{10}Cl_2O$ requires: C, 69.03; H, 3.20%).

2,3,6,7-*Dibenzobicyclo*[6.2.0]*deca*-2,4,6,8-*tetraene*-9,10-*dione* (**30**). Silver trifluoroacetate (19.9 mg, 0.09 mmol) in benzene (2 ml) was added to a stirred soln of **28** (5.8 mg, 0.02 mmol) in benzene (2 ml), and the soln was boiled under reflux for 5 hr. The precipitated AgCl was removed by filtration, washed with benzene, and the resulting soln of **19** was hydrolyzed by being shaken several times vigorously with 250 ml portions of H_2O. The organic extract was dried (Na_2SO_4) and evaporated. Plc of the residue on Merck Kieselgel 60 PF_{254} (pentane ether, 7:1) and crystallization from ether pentane gave **30** (1.1 mg, 6.7%) as pale yellow crystals, m.p. 198–199°; ^1H NMR δ 7.60–7.14 (m, 8 H, incorporating a sharp s at 7.24), 6.47 (s, 2 H); UV (EtOH) (Table 2) λ_{max} 265 nm (ε 13,600), 315sh (2700); IR (KBr) 1780s, 1765sh cm^{-1} (s); MS measured M^+ 258.0683, calcd. for $C_{18}H_{10}O_2$: 258.0681.

Di-potassium salt of the dianion **34** *of* 5,6-*didehydrodibenzo*[a,e]*cyclooctene* (**6**). (Experiment carried out with Dr. P. J. Garratt). A sealed NMR tube containing a soln of **6** in THF-d_8 (dried over K on a vacuum line) and a K mirror was prepared as described by Okamura and Katz[47] and Garratt *et al.*[38] When the tube was shaken at −20°, the soln turned red and the ^1H NMR spectrum of **6** disappeared, presumably due to the formation of the radical anion.[42] Further shaking at −20° gave a deep green solution of the di-K salt of the dianion **34**, for the ^1H NMR spectrum, see Discussion.

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