

- and H. Ohta, *ibid.*, **97**, 3246 (1975), and references cited therein; (b) S. Farid, S. E. Hartman, J. C. Doty, and J. L. R. Williams, *ibid.*, **97**, 3697 (1975).
 (28) For a review see A. Lablache-Combier, *Bull. Chim. Soc. Fr.*, 4791 (1972).
 (29) H. Beens and A. Weller, *Chem. Phys. Lett.*, **2**, 140 (1968).
 (30) In the case of thiobenzophenone, triple association leads to the formation of a 2:1 adduct with acrylonitrile.^{3,16}
 (31) For instance, in enone photocycloaddition; P. de Mayo, *Acc. Chem. Res.*, **4**, 41 (1971).

- (32) For a discussion of the behavior of such radicals, see L. M. Stephenson and J. I. Brauman, *J. Am. Chem. Soc.*, **93**, 1988 (1971).
 (33) J. C. Bevington and D. E. Eaves, *Trans. Faraday Soc.*, **55**, 1777 (1959).
 (34) A. U. Blackham and N. L. Eatough, *J. Am. Chem. Soc.*, **84**, 2922 (1962).
 (35) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
 (36) E. E. Reid, "Organic Chemistry of Bivalent Sulfur", Vol. 2 Chemical Publishing Co., New York, N.Y., 1960, p 29.

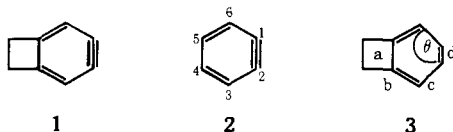
Cyclobuta[1,2-*d*]benzyne. Generation, Trapping, and Dimerization to 2,3:6,7-Dicyclobutabiphenylene

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Abstract: Cyclobuta[1,2-*d*]benzyne has been generated from 4,5-bromiodobenzocyclobutene and magnesium or butyllithium. The transient reactive species can be trapped with furan as the Diels-Alder adduct. In the absence of trapping agents dimerization occurs to 2,3:6,7-dicyclobutabiphenylene, a novel strained benzenoid hydrocarbon with distinctly olefinic properties.

Among the more interesting C₈H₆ isomers, *cis,cis*-octa-3,5-diene-1,7-diyne,¹ 1,2-dehydrocyclooctatetraene,² tri-pentafulvalene,^{3,4} pentalene,^{4,5} and benzocyclobutadiene⁶ have received considerable attention. We now wish to add another unusual member to this illustrious family by the synthesis of cyclobuta[1,2-*d*]benzyne (**1**), the reactivity of which is of in-

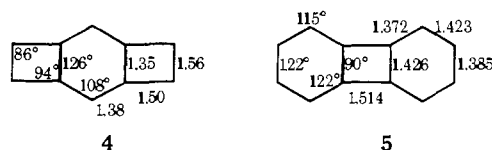


terest in comparison with *o*-benzyne. Dimerization provides access to a hitherto unknown⁷ hydrocarbon system, 2,3:6,7-dicyclobutabiphenylene (**10**), formed by linear fusion of three alternating four-membered rings and two benzene rings.

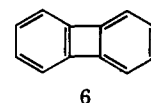
Numerous theoretical investigations⁸ of *o*-benzyne (**2**) have indicated a distorted geometry of the six-carbon framework characterized by a short 1,2 bond, a relatively long 4,5 bond, and bond angle increases at $\angle C_{123}$ and $\angle C_{345}$. It seems reasonable to assume that a chemical modification of the *o*-benzyne nucleus which leads to augmentation of this structural distortion will result in increased stability of the strained triple bond.⁹ One such modification could be fusion to strained rings, for instance, as in benzocyclobutenes. Benzocyclobutenes have also been the subject of theoretical calculations,¹⁰ and the fused ring leads to changes in the benzene nucleus best described by (accentuated) structure **3** in which bond *a* is elongated, bond *d* shortened when compared with benzene, and angle θ is increased. The notion thus seemed attractive, that stabilization of the *o*-benzyne nucleus might be achieved by fusion to a four-membered ring at the 4,5 positions leading to cyclobuta-benzyne **1**. The added stability of this species might then manifest itself in its relatively greater ease of formation when compared with model compounds. In addition, we hoped that **1** would provide synthetic entry into the unknown ring system **10**, which could then be subjected to physical and chemical investigation. Our interest in dimer **10** stemmed from its anticipated strain-related and potentially antiaromatic properties. Thus, 1,2:4,5-dicyclobutabenzene (**4**), the closest known analogue of **5** reveals its increased strain in the electronic spec-

trum with bathochromic shifts of ca. 10 nm in comparison with durene.¹¹

Examination of x-ray crystallographic data on **4**¹² and biphenylene **5**¹³ (bond angles and bond lengths (Å) as shown) indicate that **10** should be much more strained than either model. For instance, fusing a benzene ring to **4** might be ex-

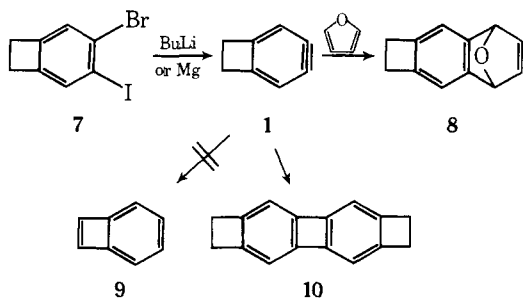


pected to cause an unfavorable shortening of the cyclobutane bond to which the benzene ring is being fused by ca. 0.14 Å. Alternatively, fusing four-membered rings to biphenylene as in **10** should cause a contraction of its cyclobutene bonds by ca. 0.08 Å, increasing unfavorable cyclobutadienoid¹⁴ overlap. We therefore expected dimer **10** to be a molecule with unusual chemical and physical properties, possibly too unstable to be formed and/or too reactive to be isolable. It became an even greater synthetic challenge after publication of a report⁷ that described the generation and trapping of 2,3-dehydrobiphenylene (**6**), a benzo derivative of **1**, and the unsuccessful attempts to obtain dimers from this species.



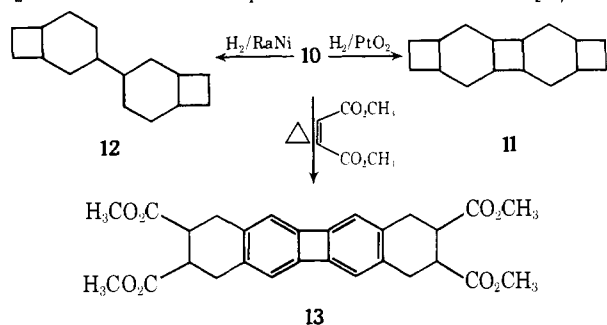
Generation, Trapping, and Dimerization of Cyclobuta[1,2-*d*]benzyne (1**).** 4,5-Bromiodobenzocyclobutene (**7**)¹⁵ was chosen as a suitable precursor to **1**.

Compound **1** can be efficiently generated by the action^{2,16} of ca. 2 M *n*-butyllithium in hexane on **7** and trapped as the furan adduct **8**¹⁷ (70%; mp 83–84 °C; *m/e* 170.0759; calcd 170.0756). The NMR spectrum (CCl₄) of **8** shows signals at τ 3.12 (t, *I* \approx 0.5 Hz, 2 H, vinyls), 3.15 (s, 2 H, benzenic), 4.52 (bs, 2 H, bridgehead), and 7.02 (s, 4 H, cyclobutene). The vinylic and bridgehead protons absorb at unusually low field as observed in related compounds.¹⁸ Alternatively, treatment of **7** with 1 equiv of magnesium in the presence of furan leads to



the same cycloadduct **8**. Cyclobutabenzynes **1** could formally rearrange via two mechanistically interesting, though unlikely, 1,5-hydrogen shifts to benzocyclobutadiene **9**. Indeed, careful examination of the reaction mixture did not reveal the presence of even traces of the furan adduct of benzocyclobutadiene.¹⁹ Similarly, without trapping agent present, no benzocyclobutadiene dimer¹⁹ was detected. In this case, however, repeated preparative thin-layer chromatography, followed by fractional crystallization led to the desired (2 + 2) dimer **10** of cyclobutabenzynes **1** in 4% yield as pale-yellow crystals (mp 225–226 °C dec).¹⁷ The structural assignment is based on the spectral and chemical properties. The mass spectrum parent ion was at m/e 204.0936 (calcd 204.0939); the NMR spectrum^{32a} (CDCl₃) had signals at τ 3.72 (s, 4 H) and 7.10 (s, 8 H). The electronic spectrum is depicted in Figure 1 and compared with model compounds (vide infra). The formation of **10** is accompanied by a mixture of 2,2'-dibromo- and bromoiodobisbenzocyclobutenyl as evidenced by NMR and mass spectral data (see Experimental Section). Dicyclobutabiphenylene **10** is apparently decomposed by the butyllithium used in its synthesis, and a better method of preparation is found in the reaction of **7** with magnesium (12%).²⁰ NMR analysis of the crude product mixture reveals an almost identical composition in both cases except for the difference in the yields of **10**.

Exposure of **10** to PtO₂/H₂ led to fast uptake of 6 moles of H₂ and formation of compound **11**¹⁷ as a colorless oil [m/e 216;



NMR spectrum (CCl₄) τ 7.7–8.9 (m)]. Under the same conditions 4,5-diphenylbenzocyclobutene was recovered unchanged from the hydrogenation mixture containing completely hydrogenated **11**. Similar hydrogenation of **10** with Raney nickel resulted in the rupture of what is presumably the central four-membered ring to give **12**. This assignment is tentative and is based on the known propensity of biphenylene to cleave the central ring in the presence of Raney nickel,⁶ the mass spectrum which shows a parent ion at m/e 218, and the NMR spectrum [(CCl₄) τ 7.6–8.9].

Oxidation of **10** proceeded slowly in air and rapidly on treatment with 1 equiv of *m*-chloroperbenzoic acid to give unidentified products.

When **10** was heated with dimethyl maleate in a sealed tube (175 °C, 20 h) the yellow bis-adduct **13** was obtained¹⁷ [mp 250–260 °C, presumably a mixture of isomers; m/e 492; NMR spectrum (CDCl₃) τ 3.60 (bs, 4 H), 6.30 (bs, 12 H), 7.00 (m, 12 H); uv spectrum λ_{max} (Et₂O) 247, 257, 270, 279, 296, 309, 324 sh, 354, 374, 397; ir spectrum ν_{CO} 1725 cm⁻¹].

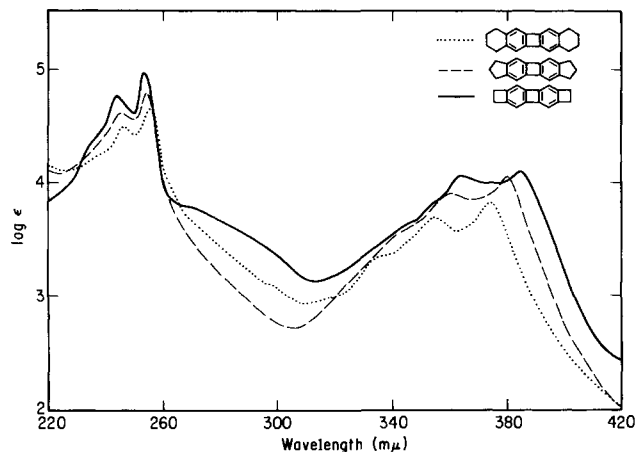
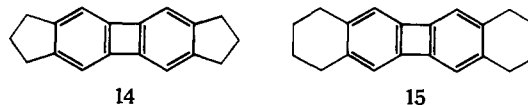


Figure 1. Electronic spectra of biphenylenes **10**, **14**, and **15** in 95% ethanol.

For comparison purposes, other less strained analogues of **10** were synthesized. Thus, 5,6-bistrimethylsilylindane and 6,7-bistrimethylsilyltetralin were converted in three steps²² via indan-5,6-yne and tetralin-6,7-yne (Mg method) to biphenylenes **14** and **15** in low yield (4 and 2.5%, respectively, in the last step).¹⁷



Compounds **14** and **15** were characterized by their typical spectral properties. The indanyne dimer **14** forms very pale-yellow crystals (mp 197–200 °C) and has a molecular ion at m/e 232.1250 (calcd 232.1252). The NMR spectrum (CDCl₃) shows peaks at τ 3.50 (s, 4 H), 7.25 (m, 8 H), and 7.87 (m, 4 H). The tetralinyne dimer **15** forms colorless crystals (mp 195–198 °C) and has a molecular ion at m/e 260.1600 (calcd 260.1597). The NMR spectrum (CDCl₃) shows absorptions at τ 3.67 (s, 4 H), 7.33 (m, 8 H), and 8.22 (m, 8 H). The electronic spectra of both **14** and **15** are depicted in Figure 1. Compound **15** has been claimed in the literature²³ to be formed in the pyrolysis of 6,6'-bistetralinyl-7,7'-iodonium iodide, and its structure was assigned on the basis of the electronic spectrum. This claim seems in error, since the spectral characteristics of **15** are at odds with the reported data.

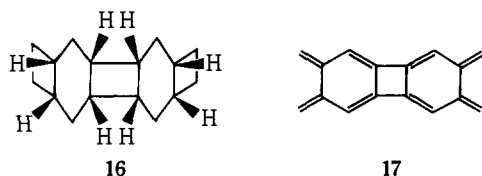
Discussion

Although the products derived from the treatment of bromoiodide **7** with Mg or butyllithium could be derived directly from organometallic intermediates, their formation in rather similar ratios regardless of the precursor strongly argues for the generation of benzyne intermediate **1**. Moreover, efficient trapping with furan is characteristic and diagnostic for a dehydrobenzene derivative.⁹ The formation of dimer **10** could in principle arise via Wurtz–Fittig type coupling of 2,2'-dihalobisbenzocyclobutenyls, which constitute some of the side products isolated from the reaction mixture. However, this reaction pathway seems highly improbable in view of the well established^{6,9,31} reluctance of 2,2'-dihalobiphenyls to form organometallic reagents and the extreme inefficiency of biphenylene formation by this method. Indeed, reexposure of the halobenzenes formed in the generation of **7** with magnesium to the reaction and even more drastic conditions (excess magnesium, iodine activation, heat) did not result in the formation of dimer **10**. Nevertheless, synthesis of **10** via reaction of cyclobutabenzynes **1** with an organometallic reagent derived from bromoiodide **7**, followed by subsequent coupling, cannot be rigorously excluded in our system. By analogy with the

parent compound **5**, however, we feel that formation of **10** occurs, at least predominantly, via direct dimerization of benzyne **1**.

With regards to the anticipated reactivity of **1**, it is interesting to compare the respective yields of dimer formation (under identical conditions) in the reactions leading to **10**, **14**, and **15**. It seems that, as the ring fused to the benzyne becomes more strained, dimerization becomes more efficient, the greatest change occurring when going from **14** to **10**. It is quite logical that good yields of biphenylene can only be obtained when the stationary concentration of dehydrobenzene is high, while at the same time that of the dehydrobenzene precursor or of any other species which might interact with the dehydrobenzene is low.⁹ The obtained results indicate that the triple bond in compound **1** is formed more readily than that of its higher homologues, allowing higher concentrations of benzyne to be built up either freely in solution or near the metal surface in the case of magnesium. More efficient dimerization is the result. More definitive probes of the reactivity of **1**, for instance its discriminative potential in competition reactions with nucleophiles,²⁴ will have to await further studies.

2,3:6,7-Dicyclobutabiphenylene (**10**) is an unusual novel hydrocarbon, the physical and chemical properties of which reflect the increased strain in the molecule when compared with suitable model compounds. The ease of hydrogenation is remarkable and unlike benzocyclobutene or biphenylene.⁶ This seems to indicate that **10** has considerable cyclohexatriene character, a property that is usually detected chemically by hydrogenation experiments.²⁵ The exact stereochemistry of hydrogenation product **11** is not known but it is a fair assumption that all hydrogens will be delivered from the same side of the molecule leading to a basket-type structure **16**.



Dimer **10** is also considerably more sensitive to oxidation than benzocyclobutene, biphenylene, or **14** and **15**, a further indication of its unusual reactivity.

As might be expected, reaction with dimethylmaleate occurs, presumably stepwise, at both ends of the molecule to give **13**. However, cycloaddition to dienophiles could in principle occur via the bis-*o*-xylylene **17** with concomitant optimal strain release, and attempts to distinguish between this and a stepwise process in the formation of **13** are in progress.

The spectral data on **10** are not as easily interpreted as its chemical behavior. While the increasing strain is clearly evidenced in the electronic spectra of the series **15**, **14**, **10** (see Figure 1) with incremental bathochromic shifts of the highest wavelength band in the order of 5–6 nm,²⁶ the NMR spectra^{32a} in the series do not allow a clear cut distinction between **10** and its homologues to be made. However, this finding does not seem too surprising in view of the various factors expected to contribute to the chemical shifts of biphenylenes **10**, **14**, and **15**. These compounds might be considered tetrasubstituted benzenes, but comparison of their NMR spectra with that of durenene²⁷ (τ_{arom} 3.19) indicates substantial high-field shifts of the absorptions due to the aromatic protons of the biphenylenes. These high-field shifts could be due to the cyclobutadienoid character of the central four-membered ring leading to partial paratropism in the system¹⁴ or, in the case of **10** (and to a lesser extent in **14**), to partial bond fixation leading to partially decreased diatropism. Counteracting the trend to higher field absorption will be the hybridization effects invoked by Streitwieser et al.²⁸ to explain the increased acidity of aryl

positions adjacent to fused strained rings. In this theory, rehybridization of the carbons at the site of fusion is postulated such as to increase the p character of the orbitals used to construct the strained ring, hence leading to increased s character in the remaining orbital to which the carbon α to the ring is bound. The resulting decrease in electron density at this carbon should lead to deshielding of the aromatic protons. To what extent each of the above factors contributes to the observed chemical shifts must await the synthesis of other systems designed to probe these effects.²⁹

Current efforts focus on the reduction of **10** to the corresponding radical ion and dianion, the acidity of the arylhydrogens, the stereochemistry of the cycloaddition products, the heat of hydrogenation, the stereochemistry of **11**, and the search for the trimer of **1**, 2,3:6,7:10,11-tricyclobutatriphenylene.^{32b}

Experimental Section

Generation of Cyclobuta[1,2-*d*]benzyne (1**) in Furan. Synthesis of Adduct **8**.** To a solution of 4,5-bromiodobenzocyclobutene (**7**, 100 mg, 0.32 mmol) in furan (5 ml) was added 2.4 M *n*-butyllithium in hexane (0.135 ml, 0.32 mmol) with magnetic stirring under nitrogen at -75°C . The mixture was warmed to room temperature, quenched with water (50 ml), and extracted with ether (50 ml); the ether layer was washed with water (3×50 ml) and dried (Na_2SO_4). Preparative TLC on silica, eluting with ether–petroleum ether $30\text{--}60^\circ\text{C}$ (5:95), gave two bands. The first band (15 mg) consisted of a mixture of starting material, 2,2'-bromiodobisbenzocyclobutenyl [*m/e* 412, 410 (1:1)] and other bromides as evidenced by the mass spectrum. The second band gave colorless crystals of adduct **8** (39 mg, 70%), crystallized from methanol–ether at -20°C : mass³⁰ *m/e* 170 (M^+ , 39%), 142 (52%), 141 (100%), 115 (75%); ir (neat) ν_{max} 2880, 1430, 1320, 1270, 1195, 1005, 863, 848, 788, 687 cm^{-1} ; for high resolution mass, NMR, and uv spectra, see text.

Compound **8** could also be generated from **7** (100 mg), magnesium (12 mg) in furan solvent, and the presence of a trace amount of iodine. The Grignard reaction stopped, however, after ca. 10% conversion leading to recovery of starting material (90%) and a small amount of cycloadduct **8** (~6%). No improvement on the efficiency of this step could be achieved.

2,3:6,7-Dicyclobutabiphenylene (10**). A. Butyllithium Method.** To a solution of 4,5-bromiodobenzocyclobutene (**7**, 100 mg, 0.32 mmol) in ether–tetrahydrofuran (1 ml, 1:1) was added 2.4 M *n*-butyllithium in hexane (0.135 ml, 0.32 mmol) with magnetic stirring under nitrogen at -75°C . The solution rapidly turned yellow, was warmed to room temperature, worked up with water–ether, and dried (Na_2SO_4). An NMR spectrum (CCl_4) of the crude mixture showed multiplets at τ 2.7–3.5 and 6.8 (relative intensity ratio 1:2) in addition to the singlets assigned to dimer **10**. Preparative TLC followed by crystallization as described in B) furnished yellow crystals of **10** (1.3 mg, 4%).

B. Magnesium Method. A solution of bromiodide **7** (250 mg, 0.81 mmol) in ether (1 ml) was stirred in the presence of magnesium (20 mg, 0.82 mmol) at room temperature under nitrogen. After ca. 2 h the solution had turned yellow and was stirred for an additional 22 h. The mixture was added to an aqueous solution of ammonium chloride, extracted with ether, and dried (Na_2SO_4). An NMR spectrum (CCl_4) of the crude mixture looked almost identical with the NMR spectrum obtained on the crude product of method A except that the singlets assigned to **10** were considerably stronger. Preparative TLC on silica, eluting with ether–pentane (3:97), gave a prominent yellow band in addition to other unidentified bands. Repeated preparative TLC, using a continuous plate development technique in which the top (ca. 1 in.) of the plate is allowed to be exposed to the atmosphere enabling continuous solvent evaporation, for 6 h (silica, eluting with pentane), gave two overlapping bands. The first band was enriched in **10**. Crystallization from ether, followed by recrystallization from ether–methanol, gave pure **10**. The mother liquors and the second band were reexposed to preparative TLC and the crystallization treatment, to optimize the yield of dicyclobutabiphenylene **10** (10 mg, 12%): mass³⁰ *m/e* 204 (M^+ , 100%), 203 (21%), 202 (52%), 201 (11%), 200 (9%), 189 (13%), 176 (12%); ir (KBr) ν_{max} 2870, 1415, 1230, 860 cm^{-1} ; for high resolution mass, NMR, and uv spectra, see text.

The mother liquors (140 mg, crude) were reexposed to preparative TLC, but the mixture could only be separated partially into two main components. NMR spectra (CCl₄) of these mixtures reveal absorptions at τ 2.21 (bs), 3.03 (m), 6.72 (s), 6.77 (s), 6.82 (bs). Mass spectra indicate the presence of at least two compounds, 2,2'-bromiodobis-benzocyclobutenyl [*m/e* 412, 410, (1:1, M⁺), 331 (M⁺ - Br)] and 2,2'-dibromobisbenzocyclobutenyl [*m/e* 366, 364, 362 (1:2:1, M⁺), 295, 283 (1:1, M⁺ - Br)].

Hydrogenation of Dicyclobutabiphenylene 10 with PtO₂ Catalyst. Dimer **10** (5 mg) was hydrogenated over prerduced PtO₂ in ethanol (5 ml) for 10 min. The yellow color of the solution disappeared rapidly during the first few minutes of hydrogenation. The mixture was filtered and the solvent evaporated to give a colorless oil of hydrocarbon **11** (5 mg): mass³⁰ *m/e* 216 (M⁺, 4%), 188 (7%), 108 (M/2, 20%), 80 (100%); for the NMR spectrum, see text.

Similar hydrogenation of **10** (5 mg) in the presence of 4,5-diphenylbenzocyclobutene (5 mg) led to quantitative recovery of the latter.

Hydrogenation of Dicyclobutabiphenylene 10 with Raney Nickel Catalyst. Raney nickel (100 mg) was placed in ethanol (5 ml) and hydrogenated to saturation. Subsequently, **10** was added (5 mg) and the mixture stirred at room temperature. After a few minutes the yellow solution had decolorized. The mixture was filtered, the solvent evaporated, and the resulting colorless oil analyzed by mass spectrometry:³⁰ *m/e* 218 (M⁺, 1%), 217 (4%), 215 (2%), 214 (2%), 213 (13%), 188 (11%), 80 (100%); for the NMR spectrum, see text.

Cycloaddition of Dimethyl Maleate to 10. Synthesis of Bis-Adduct 13. Dimer **10** (5 mg, 0.025 mmol) and dimethyl maleate (6.2 μ l, 0.05 mmol) were heated in an evacuated tube to 175 °C for 20 h. The crude product was subjected to preparative TLC on silica, eluting with ether-pentane (1:1), to give seven bands. The second band gave an unidentified yellow oil (5 mg): mass³⁰ *m/e* 494 (28%), 493 (2%), 492 (9%), 434 (31%), 375 (15%), 374 (13%), 315 (15%), 255 (70%); NMR (CDCl₃) τ 3.59 (rel intensity 12), 6.22, 6.25, 6.27 (all s, 75), 6.90 (m, 90); uv spectrum λ_{\max} (Et₂O) 248, 257, 267 sh, 275 sh, 294 sh, 308, 328, 350 sh, 372, 397 nm. This compound appears to be a hydrogenated bis-adduct of **10**, but the exact structure is unknown.

The third band gave yellow crystals of the bis-adduct **13** (6.2 mg, 50%) recrystallized from ether-pentane: mass³⁰ *m/e* 492 (M⁺, 5%), 432 (1%), 255 (2%), 254 (1.5%), 253 (6.5%), 252 (2%), 205 (3%), 43 (100%); ir (neat) ν_{\max} 2910, 1725, 1255, 1200, 1090, 800, 735 cm⁻¹; for NMR and uv spectrum, see text. The other bands were discarded.

2,3,6,7-Dicyclopentenobiphenylene (14). A solution of 5,6-bromiodoindan²² (260 mg, 0.81 mmol) in ether (1 ml) was stirred in the presence of magnesium (20 mg, 0.82 mmol) at room temperature under nitrogen. After 24 h the mixture was added to an aqueous ammonium chloride solution, extracted with ether, and dried (Na₂SO₄). Repeated preparative TLC, as described for the synthesis of **10**, followed by crystallization (methanol-ether), gave biphenylene **14** (3.8 mg, 4%): mass³⁰ *m/e* 232 (M⁺, 100%), 231 (28%), 216 (12%), 215 (14%), 205 (11%), 204 (11%), 203 (20%), 202 (27%), 115 (13%); for high resolution mass, NMR, and uv spectra, see text.

The mother liquors (145 mg) contained a mixture of dihalides as indicated by NMR and mass spectral analysis. This mixture was not investigated further.

2,3,6,7-Dicyclohexenobiphenylene 15. 6,7-Bromiodotetralin²² (270 mg, 0.81 mmol) was allowed to react using identical conditions with the synthesis of **14**. Workup and separation of the product from the contaminating mixture of dihalides also proceeded quite analogously to give biphenylene **15** (2.7 mg, 2.5%) recrystallized from methanol-ether: mass³⁰ *m/e* 260 (M⁺, 96%), 232 (52%), 219 (14%), 217 (16%), 215 (23%), 204 (35%), 202 (35%), 43 (100%); for high resolution mass, NMR, and uv spectra, see text.

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References and Notes

- G. H. Mitchell and F. Sondheimer, *J. Am. Chem. Soc.*, **91**, 7520 (1969).
- H. G. Viehe, Ed., "Chemistry of Acetylenes", Marcel Dekker, New York, N.Y., 1969.
- G. J. Gleicher and J. C. Arnold, *Tetrahedron*, **29**, 513 (1973).
- (a) P. J. Garratt, "Aromaticity", McGraw-Hill, London, 1971; (b) P. Garratt and P. Vollhardt, "Aromatizität", Georg Thieme Verlag, Stuttgart, 1973.
- K. Hafner, R. Doenges, E. Goedecke, and R. Kaiser, *Angew. Chem.*, **85**, 362 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 337 (1973).
- M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds", Academic Press, New York, N.Y., 1967.
- E. N. Losey and E. LeGoff, *J. Org. Chem.*, **38**, 3812 (1973); for other unsuccessful attempts to dimerize benzyne to biphenylenes, see ref 6.
- P. Millie, L. Praud, and J. Serre, *Int. J. Quantum Chem.*, **4**, 187 (1971); D. L. Wilhite and J. L. Whitten, *J. Am. Chem. Soc.*, **93**, 2858 (1971); R. Hoffmann, A. Imanura, and W. H. Hehre, *ibid.*, **90**, 1499 (1968); R. W. Atkin and T. A. Claxton, *Trans. Faraday Soc.*, **66**, 257 (1970); M. J. S. Dewar and W.-K. Li, *J. Am. Chem. Soc.*, **96**, 5569 (1974); J. M. McKelvey and W. N. Washburn, private communication.
- R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes", Academic Press, New York, N.Y., 1967.
- See for instance: C. S. Cheung, M. A. Cooper, and S. L. Manatt, *Tetrahedron*, **27**, 701 (1971); M. Randić and Z. B. Maksić, *J. Am. Chem. Soc.*, **93**, 64 (1971); M. Randić and L. Vujisić, *J. Org. Chem.*, **37**, 4302 (1972).
- M. P. Cava, A. A. Deana, and K. Muth, *J. Am. Chem. Soc.*, **82**, 2524 (1960). For a substituted derivative, see: F. Toda and M. Ohi, *J. Chem. Soc., Chem. Commun.*, 506 (1975).
- J. L. Lawrence and S. G. G. MacDonald, *Acta Crystallogr., Sect. B*, **25**, 978 (1969).
- (a) A. Yokozeki, C. F. Wilcox, and S. H. Bauer, *J. Am. Chem. Soc.*, **96**, 1026 (1974); (b) J. K. Fawcett and J. Trotter, *Acta Crystallogr.*, **20**, 87 (1966).
- K. P. C. Vollhardt, *Top. Curr. Chem.*, **59**, 113 (1975).
- W. G. L. Aalbersberg, A. J. Barkovich, R. L. Funk, R. L. Hillard III, and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **97**, 5600 (1975).
- H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **79**, 2625 (1957).
- All new isolated crystalline compounds gave satisfactory elemental analyses and spectral data.
- See, for instance, (a) B. H. Klanderma, *J. Am. Chem. Soc.*, **87**, 4649 (1965); (b) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, New York, N.Y., 1969; (c) Varian Associates High Resolution NMR Spectra Catalog, Vol. 1, 2, 1962, 1963.
- M. P. Cava and M. J. Mitchell, *J. Am. Chem. Soc.*, **81**, 5409 (1959).
- Grignard formation in the presence of 1 equiv of trimethylsilyl chloride²¹ improved the yield of **10** only marginally (~13%).
- C. Eaborn, D. R. M. Walton, and D. J. Young, *J. Chem. Soc. B*, 15 (1969).
- R. L. Hillard III and K. P. C. Vollhardt, *Angew. Chem.*, **87**, 744 (1975); *Angew. Chem., Int. Ed. Engl.*, **14**, 712 (1975).
- E. R. Ward and B. D. Pearson, *J. Chem. Soc.*, 1676 (1959).
- R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960).
- For other "olefinic" strained benzene derivatives, see, for instance, H. Rapoport and G. Smolinsky, *J. Am. Chem. Soc.*, **82**, 1171 (1960).
- The electronic spectrum of 2,3,6,7-tetramethylbiphenylene,⁶ another suitable "strain-free" model, closely resembles that of **15**.
- E. Bullock, *Can. J. Chem.*, **41**, 711 (1963).
- A. Streitwieser, G. R. Ziegler, P. C. Mowery, A. Lewis, and R. G. Lawler, *J. Am. Chem. Soc.*, **90**, 1357 (1968).
- We and others have now been able to obtain 1,2-cyclopropa-4,5-cyclobutabenzene, the aromatic protons of which resonate at "normal" frequencies (τ 3.15): D. Davalian and P. J. Garratt, *J. Am. Chem. Soc.*, **97**, 6883 (1975); C. J. Saward and K. P. C. Vollhardt, *Tetrahedron Lett.*, 4539 (1975).
- Only the strongest and structurally most important peaks are quoted in the description of the mass spectrum.
- W. C. Lothrop, *J. Am. Chem. Soc.*, **63**, 1187 (1941); R. C. Hinton, F. G. Mann, and I. T. Millar, *J. Chem. Soc.*, 4704 (1958); H. Heaney, F. G. Mann, and I. T. Millar, *ibid.*, 3930 (1957); F. A. Hart and F. G. Mann, *ibid.*, 3939 (1957).
- NOTE ADDED IN PROOF: (a) A ¹³C NMR spectrum [δ (ppm from Me₄Si) 29.6, 113.0, 144.0, 150.1] indicates a degree of strain in **10** intermediate between that in benzocyclobutene and 1,2-cyclopropa-4,5-cyclobutabenzene.²⁹ (b) We have recently synthesized tricyclobutatriphenylene in concentrated solutions of **1**: R. L. Funk and K. P. C. Vollhardt, *Angew. Chem.*, **88**, 63 (1976); *Angew. Chem., Int. Ed. Engl.*, **15**, 53 (1976).