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(45) The minor component was due to the presence of several percent of the isomeric 1-methoxypropene in the reaction mixture.
(46) Both compounds were isomerically pure by GC, but apparently contained impurities acquired during their separation.

Cyclophanes. 8.[1] [2.2](1,4)Tropylioparacyclophane Tetrafluoroborate. Synthesis and Charge-Transfer Interaction‡

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Abstract: The synthesis of [2.2](1,4)tropylioparacyclophane tetrafluoroborate (**1**) is described. It is prepared from [2.2]paracyclophane (**4**) in six steps in 27% overall yield. Reduction of **4** with Na/NH_3 affords the tetrahydro derivative tricyclo[8.2.2.$2^{4,7}$]hexadeca-1(12),4,7(15),10(13)-tetraene (**5**). Treatment of **5** with KO-*t*-Bu/$CHBr_3$ at 0 °C gives a 4:1 mixture of mono- and dicarbene adducts 11,11-dibromotetracyclo[8.3.2.$2^{4,7}$.$0^{10,12}$]heptadeca-1(14),4,7(17)-triene (**6a**) and 11,11,14,14-tetrabromopentacyclo[8.3.3.2.$0^{4,15}$.$0^{10,12}$]octadeca-1(17),6-diene (**6b**), respectively. Monocarbene adduct **6a** is treated with DDQ and the resulting 11,11-dibromotetracyclo[8.3.2.$2^{4,7}$.$0^{10,12}$]heptadeca-1(14),4,6,16-tetraene (**7**), dehydrobrominated with pyridine to give 11-bromotricyclo[8.3.2.$2^{4,7}$]heptadeca-1(14),4,6,10(15),11,16-hexaene (**8**). Bromide **8** is reduced with *tert*-butyllithium giving tricyclo[8.3.2.$2^{4,7}$]heptadeca-1(14),4,6,10(15),11,16-hexaene (**9**). Treatment of **9** with trityl fluoroborate affords the title compound, **1**. Characterization and spectral comparisons of the above compounds are described. Cyclophane **1** exhibits a broad band at 323 nm in its electronic spectrum indicative of an intramolecular charge-transfer interaction between the neutral and charged aromatic rings.

Charge-transfer complexes have been observed and studied in a wide variety of chemical and biological systems.[2] Interest in these complexes stems from the fact that many molecular interactions are potentially charge transfer in nature. Examples of how complexes have been used to better understand interacting molecular systems can be found in the theory of activated complexes of chemical reactions[3] and the binding of substrate molecules to enzyme sites in biochemical reactions.[4] Most recently, charge-transfer complexes have been the focus of purely applied research in which their semi-, photoconductive and other electrical properties are being tested.[5] Due to the above and the ever growing interest in charge-transfer complexes and charge-transfer interaction, it is important to continuously refine the qualitative and quantitative descriptions that define charge-transfer interaction.

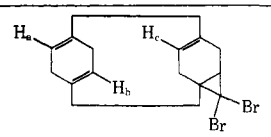
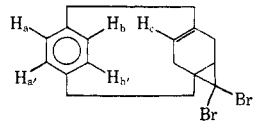
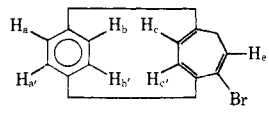
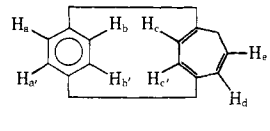
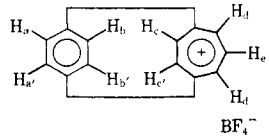
Several groups have investigated model chemical systems for the study of intramolecular charge-transfer interaction. Some have connected donor and acceptor with saturated hydrocarbon chains[6] while others have incorporated the interacting groups within an inflexible framework.[7] Along with other investigators, we recognized that the cyclophane macrocycle offers a unique model system for the study of charge-transfer complexation. Some advantages which the cyclophane macrocycle offers are the following: (a) the effective distance between the interacting groups can be changed synthetically by the variation of the number of atoms in the chains bridging the donor–acceptor pair; (b) for the [*m.n*] cyclophane, where *m* and *n* are not greater than four, the structural features of the cyclophane macrocycle forces a nearly parallel orientation of the interacting groups; (c) it is possible to incorporate a large number of donor–acceptor pairs into the cyclophane structure by practical synthetic methods.

We have been interested in the potential interaction that a fully charged moiety would have on a second neutral or charged group in a rigid framework.[1] Examples of three systems which are of interest to us for charge-transfer and conductance studies are **1**, **2**, and **3** (see Figure 1). This paper describes our work on the synthesis of the first member of this series [2.2](1,4)tropylioparacyclophane tetrafluoroborate (**1**) and on the charge-transfer interaction that is present in this molecule.

Synthesis. Scheme I shows the synthetic sequence used to obtain cyclophane **1**. Birch reduction of [2.2]paracyclophane by the method of Marshall and Folsom[8a] affords the tetrahydro derivative **5** in 96% yield. When **5** is treated with bromoform and potassium *tert*-butoxide in benzene:*tert*-butyl alcohol solution at 0 °C, starting material **5** and a mixture of the mono- and dicarbene adducts **6a** and **6b**[9] are obtained in yields of 46, 42, and 10%, respectively, after chromatography on silica gel. Monocarbene adduct **6a** is then treated with dichlorodicyanobenzoquinone (DDQ) at room temperature in benzene and is quantitatively converted to dibromide **7**. Dehydrobromination of **7** in refluxing pyridine affords bromide **8** in 81%

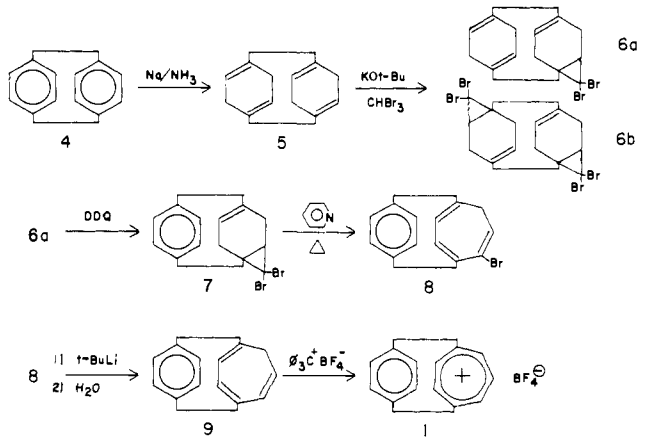
‡ Dedicated to Professor Robert Burns Woodward on the occasion of his 60th birthday.

Table I. Physical and Spectral Properties of **6a**, 7, 8, 9, and 1

	Structure	Melting point,[a] °C	NMR,[b] δ	IR,[c] cm^{-1}	UV,[d] λ, nm (ε)	MS,[e] *m/e*
6a			2.34 (m, 17 H) 5.20 (m, 1 H) 5.69 (m, 2 H)			383.989 13 303.064 95 222.141 37 196.997 33 104.059 26
7		117–119	1.28–3.41 (m, 13 H) 4.56 (m, 1 H) 7.00 (m, 4 H)	2840–3020 1665, 1425 1435, 755	226 sh (1.03 × 10^4) 238 sh (7.10 × 10^3) 282 (5.73 × 10^2)	381.972 68 301.059 54 222.140 32 196.996 78 104.061 56
8		87–88	2.08–3.28 (m, 10 H) 4.91 (t, J = 7 Hz, 1 H) 5.50 (ABq, J = 11.5 Hz, 2 H) 6.83 (ABq, J = 8 Hz, 2 H) 6.97 (broad s, 2 H)	2800–3020 1615, 1600 1520, 1505	220 sh (1.84 × 10^4) 238 sh (6.37 × 10^3) 283 (2.69 × 10^3)	301.057 32 221.133 15 195.989 93 104.061 56
9		163–164.5	1.25–3.28 (m. 10 H) 4.88 (m, 2 H) 5.55 (broad s, 2 H) 6.54 (m, 2 H) 6.91 (m, 2 H)	2800–3020 1620, 1605 1500, 1425 1415	220 sh (1.31 × 10^4) 238 sh (4.90 × 10^3) 280 (1.50 × 10^3)	222.139 65 221.132 90 118.078 78 104.061 02
1		133–135 dec	3.21–3.98 (m, 8 H) 6.00 (m, 2 H) 7.19 (m, 2 H) 7.76 (m, 2 H) 8.49 (m, 3 H)	2840–3080 1585, 1545 1485, 1415 1090, 1050	238 sh (7.98 × 10^3) 278 (2.16 × 10^3) 295.5 (3.20 × 10^3) 323 (2.23 × 10^3) 353 (1.59 × 10^3) 400 sh (5.24 × 10^2)	221.131 70 117.070 92 104.061 39

[a] Uncorrected. [b] **6a**, 7, 8, 9 in $CDCl_3$, 1 in CD_3NO_2. [c] KBr. [d] **6a**, 7, 8, 9 in EtOH (abs), 1 in CH_3CN. [e] High resolution.

Scheme I



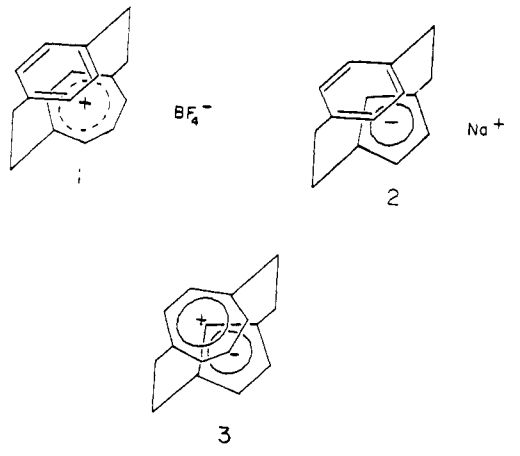


Figure 1.

yield after chromatography on silica gel. Reduction of the C–Br bond in **8** with *tert*-butyllithium at −78 °C, followed by quenching of the lithio intermediate with water, affords cyclophane **9** in 82% yield after crystallization. Conversion of **9** to [2.2](1,4)tropylioparacyclophane tetrafluoroborate (**1**) is effected by treatment with trityl tetrafluoroborate, prepared in situ, and is isolated in 51% yield by precipitation from anhydrous ether as pale-yellow needles. The overall yield of **1** from [2.2]paracyclophane is 27%.

Structural Assignments. The physical and spectroscopic properties used to assign structures to **6a**, **7**, **8**, **9**, and **1** are incorporated in Table I. The monocarbene adduct **6a**, though chromatographically pure, was obtained as an oil and could not be crystallized. NMR and mass spectral data were, however, consistent with the structure proposed. Specifically, the mass spectrum of **6a** showed an accurate molecular ion for $C_{17}H_{20}Br_2$ and other prominent fragments at $M^+ - H_2$, $M^+ - Br$ and $M^+ - Br_2$. In addition, the typical fragmentation of [2.2]phanes,[10] i.e., cleavage of the two ethylene bridges, giving rise to fragment ions of each half of the original cyclophane structure, is observed. The mass spectral behavior of compounds **7**, **8**, **9**, and **1** are also all consistent with a cyclophane structure. Each exhibits an accurate molecular ion as well as the appropriate fragment ions from cleavage of the ethylene bridges.

The infrared spectra of these compounds are all relatively simple, and the expected absorption in the 3100–2800 cm^{-1} and 1600–1400 cm^{-1} regions is present in all the compounds. In addition, the presence of the prominent band at 1090–1050 cm^{-1} in the infrared spectrum of **1** confirms the presence of the tetrafluoroborate anion in this compound.

The NMR spectra of these compounds are most instructive for structural assignment. Thus, the two hydrogen multiplet at δ 5.69 for the H_a and H_b protons in **6a** is lost when **6a** is converted to **7**. The absorption for the now deshielded benzenoid protons (H_a, $H_{a'}$, H_b, and $H_{b'}$) in **7** appears at δ 7.00. On the other hand, the single vinylic proton H_c which appears at δ 5.20 in **6a** is shifted upfield by 0.64 ppm to δ 4.56 when **6a** is

converted to **7**. This upfield shift is consistent with the rearomatization of the noncarbene-substituted ring, since the H_c proton now is shielded by the anisotropic influence of that ring.

Upon dehydrobromination of **7** compound **8** is formed in which the least-squares planes of the six- and seven-membered rings are parallel. Because of the presence of the bromine atom and the dissymmetry of the halo-substituted seven-membered ring relative to the six-membered ring, both H_a and both H_b protons in **8** experience a greater difference in magnetic environments than the corresponding protons in **7**. In addition, since the $H_{b'}$ proton is situated almost directly over the bromine atom, its chemical shift is expected to be quite different from the H_b proton. Thus, the H_a and $H_{a'}$ protons in **8** appear as a broad singlet at δ 6.97 while the H_b and $H_{b'}$ protons appear as an AB quartet (J = 8 Hz) centered at δ 6.83. The two H_c protons also appear as an AB pattern centered at δ 5.50 (J = 11.5 Hz) due to their different environments relative to the bromine atom. The H_e proton appears as a broadened triplet at δ 4.91 (J = 7 Hz) due to the adjacent nonequivalent methylene protons. All the vinylic protons on the seven-membered ring are shifted upfield relative to their normal chemical shift in cycloheptatriene as would be expected from the shielding influence of the proximate benzene ring. Thus, the H_e proton is shifted upfield by 0.37 ppm, the H_c proton by 0.69 ppm, and the $H_{c'}$ proton by 0.91 ppm. Consistent with the structure proposed for **8**, the H_e proton experiences the smallest shielding influence because of its greater distance from the shielding region of the aromatic ring.

Reduction of **8** yields **9**, and the absence of the bromine atom causes the AB nature of the two H_b and the two H_c protons in **8** to have more AA′ character in **9**. Thus both H_a and both H_b protons appear as an AA′BB′ multiplet centered at δ 6.78 (δ 6.54, H_b and δ 6.91, H_a) while the two H_c protons appear as a broad singlet at δ 5.55. As expected the H_d and H_e protons appear as a multiplet at δ 4.88 due to allylic coupling with the adjacent methylene protons on the seven-membered ring.

Finally, in **1**, the effect of the newly developed tropylium ring on the benzenoid protons causes a 0.54 ppm upfield shift for the two H_b protons and a downfield shift of 0.28 ppm for the two H_a protons relative to the positions of the same protons in **9**. It would be expected that both H_b protons (δ 6.00) appear more highly shielded than the H_a protons because they experience the central core of the shielding cone of the aromatic seven-membered ring. The slight downfield shift of the two H_a protons (δ 7.19) indicates that these protons experience a lower shielding influence or perhaps a deshielding influence. This suggests that the two aromatic rings are off-centered such that both H_a protons are out of the shielding cone, while the two H_b protons are centrally located in the shielding cone. The effect of aromatization of the seven-membered ring on the H_c, H_d, and H_e protons is more pronounced. Relative to the same protons in **9** these protons are shifted downfield approximately 2.86 ppm, to a position which is in accord with the chemical shift for the protons in tropylium ion itself (δ 9.28).[11] The H_c protons are found as a multiplet centered at δ 7.76 while the H_d and H_e protons are found as a multiplet centered at δ 8.49. The usual upshield shift caused by a shielding nucleus within the cyclophane structure is similarly observed for the tropylium protons in **1** relative to the parent tropylium ion. Specifically, the H_c protons are shifted upfield by 1.5 ppm and the H_d and H_e protons by 0.82 ppm. This difference in the shielding influence of the benzenoid ring on the H_c, H_d, and H_e protons is consistent with the nonsymmetrical nature of the tropylium ring in **1** and the off-centering of the two aromatic rings. The two H_c protons experience the greatest upfield shift due to their presence in the central shielding region of the benzene ring. In contrast, the H_d and H_e protons are on the periphery of that region and are less shielded.

The ultraviolet spectra of **7**, **8**, **9**, and **1** are in accord with the assigned structures. Typically, [2.2]cyclophanes exhibit broad absorptions which are reduced in intensity relative to a single chromophore unit, and the bands associated with the aromatic groups are bathochromically shifted.[12] In addition, a band which is indicative of transannular π–π interaction is usually observed.[13a,b] All the above compounds exhibit the bathochromically shifted absorption for the benzenoid ring at 282, 283, 280, and 278 nm for **7**, **8**, **9**, and **1**, respectively. (The corresponding absorption for [2.2]paracyclophane is found at 282 nm and for [8]paracyclophane at 275 nm.)[13c] The overall blue shift in this band as one progresses from **7** → **8** → **9** → **1** indicates that the benzenoid ring is less distorted in **1** than in **7**, **8**, or **9**.

The presence of the cycloheptatriene ring in **8** and **9** is indicated by the absorption and intensity at 283 nm (ϵ 2690) and 280 nm (ϵ 1500), respectively. Cycloheptatriene itself absorbs at 262.5 nm (ϵ 2870), and thus the absorption for the cycloheptatriene chromophore in **8** and **9** is 21 and 18 nm, respectively, red-shifted. This is to be expected by analogy with the 20-nm bathochromic shift observed for [2.2]paracyclophane [282 nm (ϵ 236)] relative to *p*-xylene [262 nm (ϵ 300)]. The intensity of the 280-nm absorptions in both **8** and **9** also indicates that the cycloheptatriene chromophore is absorbing in this region because it would be difficult to rationalize that this intensity is due solely to a benzene chromophore.

The band associated with transannular π–π interaction in cyclophanes is present in **1** at 238 nm as would be expected for the interaction between the two aromatic nuclei. This band is also present as an inflection in **7**, **8**, and **9** at 238 nm which suggests some transannular interaction between the benzenoid ring and the π systems in these compounds.

Compound **1** exhibits a λ_{max} at 295.5 nm (ϵ 3200) which is attributable to the tropylium absorption. Tropylium tetrafluoroborate has a λ_{max} at 273.5 nm (ϵ 4350),[14] and as would be expected, **1** exhibits the characteristic bathochromic shift for the tropylium chromophore. This 22-nm shift compares favorably with the 20-nm bathochromic shift observed for [2.2]paracyclophane relative to *p*-xylene.

Charge-Transfer Interaction. Of particular interest in the electronic spectrum of **1** (see Figure 2) are the bands observed at 323, 353, and 400 nm. Winstein and Feldman[15] have prepared complexes of tropylium ion with various donors and found that with *p*-xylene a charge-transfer band is observed at 323 nm. This is exactly the position of one of the bands in the spectrum of **1**, and we attribute it to an intramolecular charge-transfer interaction between the six- and seven-membered aromatic rings. Presumably, the additional long wavelength bands result from new interactions created by the rigid structural framework.[16]

Intramolecular charge-transfer bands in cyclophanes have been documented by Cram[17] and Misumi[18] for various phanes containing neutral donor and acceptor groups. Other studies have focused on increasing the intramolecular interaction in phanes by adding electron-donating and -withdrawing groups to the aromatic rings.[19] [2.2](1,4)Tropylioparacyclophane tetrafluoroborate (**1**) represents the first example of a charge-transfer interaction in a cyclophane in which a fully developed positive charge on a carbonaceous framework acts as an acceptor. It will be of interest to see whether a charge-transfer interaction exists in **2** where the normal donor properties of the benzenoid ring may have to be reversed. In view of the fact that donor capacity is usually dependent on electron density and acceptor capacity on electron deficiency, compound **3** may prove to be the most interesting of the group.

In addition to the above, placement of a charge on a carbonaceous framework in close proximity to charged or other interacting groups may potentially impart semi- or photoconductive properties to these systems. The conductive properties

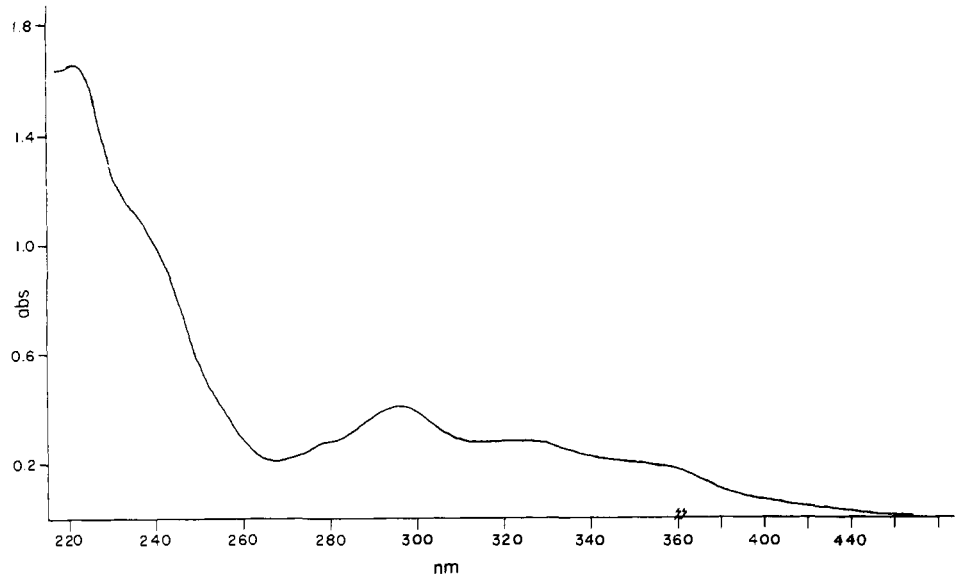


Figure 2. The electronic spectrum of [2.2](1,4)tropylioparacyclophane tetrafluoroborate (1) in CH_3CN.

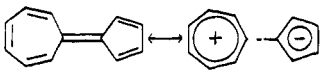


Figure 3.

of **1**, as well as **2** and **3**, will be of interest in this regard. Compound **3** is of particular significance since the charges are thoroughly stabilized in the five- and seven-membered aromatic rings. Quenching of the charges by bond formation between the rings is prohibited due to the structural requirement of the cyclophane macrocycle. This is not the case with sesquifulvalene[20] in which resonance contributions of the dipolar forms are nil (see Figure 3).[21] It seems possible that compound **3**, a solely carbonaceous compound, may possess significant ionic character and important conductive properties. We are progressing toward the synthesis of **2** and **3** and will be constructing and studying similar systems for charge-transfer and conduction studies.[22]

Experimental Section

General. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 567 grating spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian Model A-60A. Chemical shifts are reported in δ units, using Me_4Si as an internal standard. Ultraviolet spectra were recorded on a Perkin-Elmer Model 323 spectrophotometer. High resolution mass spectra were kindly supplied by Dr. Catherine E. Costello of Massachusetts Institute of Technology. Microanalyses for some compounds were determined by Galbraith Laboratories, Knoxville, Tenn.

Tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,7(15),10(13)-tetraene (5).[8] Compound **5** was prepared in 96% yield by the method of Marshall and Song,[8b] and its physical properties were identical with those described previously.

11,11-Dibromotetracyclo[8.3.2.2^{4,7}.0^{10,12}]heptadeca-1(14),4,7-(17)-triene (6a). Tetrahydroparacyclophane (**5**) (1.20 g, 5.66 mmol) was dissolved in 25 ml of benzene. After the addition of *tert*-butanol (15 ml), potassium *tert*-butoxide (1.27 g, 11.33 mmol) was dissolved and the mixture cooled to 0 °C. A solution of bromoform (2.86 g, 11.33 mmol) in benzene (15 ml) was added dropwise to the stirring solution over a 45-min period. Additional stirring was continued for an hour. Solvent was removed from the reaction mixture by rotoevaporation, leaving a yellow oil which was partitioned in 20 ml of anhydrous ether and 20 ml of water. The aqueous layer was extracted twice with 20 ml of ether. The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated. Separation of the resulting oily mixture was effected on silica gel plates in hexane. The highest R_f fraction was recovered starting material (0.55 g, 45.6%). The following fraction was the desired monocarbene adduct **6a** (0.91 g, 41.7%), which was a clear oil requiring no further purification. The lowest R_f fraction was the dicarbene adduct **6b** (0.32 g, 10.3%). **6a** NMR ($CDCl_3$) 2.34 (m, 17 H), 5.20 (m, 1 H), 5.69 (m, 2 H); MS *m/e* 383.989 13 (obsd), 383.914 73 (calcd), 301, 222, 197, 104. **6b** NMR ($CDCl_3$) 1.20–2.78 (m, 18 H), 5.40 (m, 2 H).

11,11-Dibromotetracyclo[8.3.2.2^{4,7}.0^{10,12}]heptadeca-1(14),4,6,-16-tetraene (7). 11,11-Dibromotetracyclo[8.3.2.2.^{4,7}0^{10,12}]heptadeca-1(14),4,7(17)-triene (**6a**) (1.96 g, 5.0 mmol) was dissolved in benzene (25 ml). 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) (1.4 g, 6.25 mmol) was added and stirring continued for 1 h. The reaction mixture was filtered through a celite layer, followed by rapid chromatography through neutral alumina using benzene as an eluent. Removal of the benzene afforded white crystalline **7** in quantitative yield. Recrystallization from ethanol afforded white crystalline plates: mp 117–19 °C; NMR ($CDCl_3$) 1.28–3.41 (m, 13 H), 4.56 (m, 1 H), 7.00 (m, 4 H); IR (KBr) cm^{-1} 2840–3020, 1665, 1425, 1435, 755; UV (EtOH) λ nm (ϵ) 226 sh (1.03×10^4), 238 sh (7.10×10^3), 282 (5.73×10^2); MS *m/e* 381.972 68 (obsd), 381.975 47 (calcd), 301, 222, 197, 104.

Anal. Calcd for $C_{17}H_{18}Br_2$ (mol wt 381.97): C, 53.41; H, 4.75; Br, 41.83. Found: C, 53.47; H, 4.80; Br, 41.93.

11-Bromotricyclo[8.3.2.2^{4,7}]heptadeca-1(14),4,6,10(15),11,16-hexaene (8). 11,11-Dibromotetracyclo[8.3.3.3^{4,7}.0^{10,12}]heptadeca-1(14),4,6,16-tetraene (**7**) (1.2 g, 3. 2 mmol) was refluxed for 24 h in pyridine under nitrogen. After removal of solvent, the desired 11-bromotricyclo[8.3.2.2^{4,7}]heptadeca-1(14),4,6,10(15),11,16-hexaene (**8**) was chromatographed on silica gel using hexane as the eluent, affording 0.76 g (81%). Recrystallization from ethanol yielded a white granular solid: mp 87–8 °C; NMR ($CDCl_3$) 2.08–3.28 (m, 10 H), 4.91 (t, J = 7 Hz, 1 H), 5.50 (ABq, J = 11.5 Hz, 2 H), 6.83 (ABq, J = 8 Hz, 2 H), 6.97 (broad s, 2 H); IR (KBr) cm^{-1} 2800–3020, 1615, 1600, 1520, 1505; UV (EtOH) λ nm (ϵ) 220 sh (1.84×10^4), 238 sh (6.37×10^3), 283 (2.69×10^3); MS *m/e* 301.057 32 (obsd), 301.05918 (calcd) 221, 196, 104.

Anal. Calcd for $C_{17}H_{17}Br$ (mol wt 301.06): C, 67.77; H, 5.69; Br, 26.54. Found: C, 67.52; H, 5.68; Br, 26.46.

Tricyclo[8.3.2.2^{4,7}]heptadeca-1(14),4,6,10(15),11,16-hexaene (9). 11-Bromotricyclo[8.3.2.2^{4,7}]heptadeca-1(14),4,6,10(15),11,16-hexaene (**8**) (170 mg, 0.55 mmol) was dissolved in tetrahydrofuran (25 ml), freshly distilled from lithium aluminum hydride. The flask was previously flame dried and supplied with a magnetic stirrer, dropping funnel, nitrogen inlet, and septum inlet. The solution was cooled to −78 °C and then 5 ml of a 0.95 M *tert*-butyllithium in pentane solution was syringed into the flask. (The *tert*-butyllithium solution should be standardized before use.) Stirring was continued for 1 h, during which time a granular precipitate of LiBr formed. The reaction mixture was quenched with 20 ml of wet tetrahydrofuran (10% water). The milky precipitate was filtered off through a celite

layer, and solvent was removed. Recrystallization of the crude reaction product from ethanol afforded 88 mg (80%) of tricyclo[8.3.2.2^{4,7}]heptadeca-1(14),4,6,10(15),11,16-hexaene (**9**): mp 163–164.5 °C; NMR ($CDCl_3$) 1.25–3.28 (m, 10 H), 4.88 (m, 2 H), 5.55 (s, 2 H), 6.54 (m, 2 H), 6.91 (m, 2 H); IR (KBr) cm^{-1} 2800–3020, 1620, 1605, 1500, 1425, 1415; UV (EtOH) λ nm (ε) 220 sh (1.31×10^4), 238 sh (4.90×10^3) 280 (1.50×10^3); MS *m/e*, 222.139 65 (obsd), 222.140 85 (calcd), 221, 118, 104.

Anal. Calcd for $C_{17}H_{18}$ (mol wt 222.16): C, 91.83; H, 8.16. Found: C, 91.99; H, 8.11.

[2.2](1,4)Tropylioparacyclophane Tetrafluoroborate (1). Tricyclo[8.3.2.2^{4,7}]heptadeca-1(14),4,6,10(15),11,16-hexaene (**9**) (55 mg, 0.25 mol) was dissolved in a minimum amount of acetic anhydride (10 ml) and cooled in an ice bath. A solution of acetic anhydride (5 ml) containing triphenylcarbinol (65.2 mg, 0.25 mmol) and fluoroboric acid (22 mg, 0.25 mmol) was prepared[14] and added dropwise at 0 °C. Stirring was continued for 1 h. The solution was poured quickly into 200 ml of freshly distilled ether (from sodium). Within minutes a cloudy precipitate appeared and slowly, fine pale-yellow needles formed. The precipitate was filtered to yield [2.2](1,4)tropylioparacyclophane tetrafluoroborate (**1**) (58 mg, 51%): mp 133–35 °C dec; NMR (CD_3NO_2) 3.21–3.98 (m, 8 H), 6.00 (m, 2 H), 7.19 (m, 2 H), 7.76 (m, 2 H), 8.49 (m, 2 H); IR (KBr) cm^{-1} 2840–3080, 1585, 1545, 1485, 1415, 1090, 1050; UV (CH_3CN) λ nm (ε) 238 sh (7.98×10^3), 278 (2.16×10^3), 295.5 (3.20×10^3), 323 (2.23×10^3), 353 (1.59×10^3), 400 sh (5.24×10^2); MS *m/e*, 221.131 70 (obsd), 221.133 02 (calcd), 222, 117, 104.

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References and Notes

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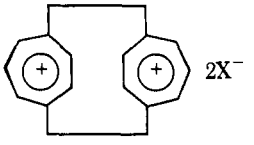

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