A Study of the Syntheses and Properties of $[2_2](1,6)$Cyclooctatetraenyl(1,4)cyclophane and $[2_4](1,2,5,6)$Cyclooctatetraenyl(1,2,4,5)cyclophane

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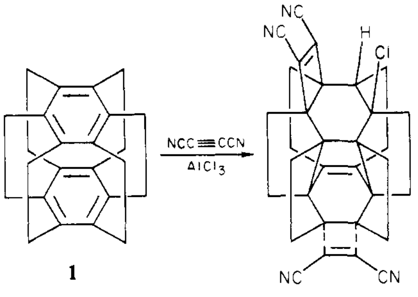
Received May 9, 1983

Abstract: Although studies of the π-electron interactions in cyclophanes having decks with $(4n + 2)$ π-electrons are quite extensive, very little is known about cyclophanes with decks of $4n$ π-electrons or the forced interactions of $4n$ with $4n$ or $4n$ with $(4n + 2)$ π-electron systems. Syntheses of the title compounds, **8** and **15**, the first cyclophanes containing one cyclooctatetraene deck, are described. Single-crystal X-ray analyses show the cyclooctatetraene decks in each of these molecules to be tub shaped. This geometry prevents π-electron delocalization in the cyclooctatetraene ring and, as evidenced from the photoelectron and ultraviolet spectral properties of **8** and **15**, the only interaction observed is that between the π-electron systems of the benzene deck and an isolated carbon–carbon double bond of the cyclooctatetraene deck. Reduction of the cyclooctatetraene ring of **8** can be accomplished either electrochemically or by lithium metal to give the dianion **25**, which, in turn, reacts with uranium tetrachloride to give uranocene, **26**. Likewise, ruthenium complexation of the benzene deck of **8** occurs readily to give **27**.

Although much data have been acquired regarding the properties of $[2_n]$cyclophanes having decks of $(4n + 2)$ π-electrons, and photoelectron spectral studies,[1-3] in particular, provide convincing evidence of π-electron delocalization in these molecules, no comparable studies have been made with cyclophanes having decks of $4n$ π-electrons or a combination of decks with $4n$ and $(4n + 2)$ π-electrons. A simple Hückel analysis suggests that the interaction of cyclophane decks having $4n$ π-electrons, or a combination of decks with $4n$ and $(4n + 2)$ π-electrons, should be quite different from the known examples where both decks have $(4n + 2)$ π-electrons. The present study was undertaken, therefore, to explore this area, and we now report the preparation of the title compounds, where in each case one deck has a cyclooctatetraene ring and the other deck has a benzene ring.

In considering approaches to the synthesis of cyclophanes having cyclooctatetraene decks, we were much influenced by the fact that all of the possible $[2_n]$cyclophanes are now known and a variety of methods for their syntheses have been developed.[3] Thus, methods providing for the ring expansion of benzene decks to cyclooctatetraene decks would allow the use of known $[2_n]$-cyclophanes as starting materials and might also permit a series of cyclooctatetraene–cyclophanes to be prepared in which a variety of bridging patterns would be present.

For many $[2_n]$cyclophanes, participation of the benzene decks as a diene in the Diels–Alder reaction relieves strain, and so addition of dienophiles to $[2_n]$cyclophanes to give barrelene derivatives is a common phenomenon.[4-7] In the case of $[2_6]$-(1,2,3,4,5,6)cyclophane (**1**, superphane), formation of a barrelene-type adduct increases, rather than relieves, strain, and as a consequence superphane is inert toward dienophiles under the standard conditions. However, when **1** was treated with dicyanoacetylene in the presence of aluminum chloride in an attempt to force the addition, a remarkable reaction occurred to give **2**.[8] The most likely explanation for this transformation requires, as a first step, the 1,2-addition of dicyanoacetylene to each of the benzene decks. Thus, in principle, this remarkable reaction might provide a one-step conversion of a benzene deck to a cyclooctatetraene deck.



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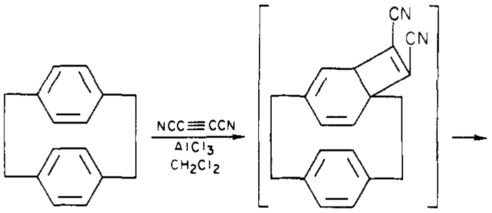
Investigation of this reaction with a range of other $[2_n]$-cyclophanes showed that it was not general. However, treatment of a solution of $[2_2](1,4)$cyclophane (**3**) in dichloromethane with



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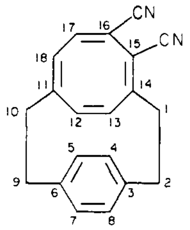

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dicyanoacetylene in the presence of aluminum chloride afforded 15,16-dicyano$[2_2](1,6)$cyclooctatetraenyl(1,4)cyclophane (**5**) in 33% yield.

Ciganek first showed that dicyanoacetylene can be added to benzene in a 1,4 Diels–Alder fashion and that this addition is strongly catalyzed by aluminum chloride.[4] He also showed that dicyanoacetylene adds to $[2_2](1,4)$cyclophane to give barrelene-type derivatives.[4] However, the present example is apparently the first instance showing that the reaction of an arene deck of a cyclophane with dicyanoacetylene in the presence of aluminum chloride leads to 1,2-addition followed by ring expansion to give cyclooctatetraene derivatives. Presumably, the reaction occurs via **4** as an intermediate. Other catalysts, such as diethylaluminum

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[1] Kovač, B.; Mohraz, M.; Heilbronner, E.; Boekelheide, V.; Hopf, H. *J. Am. Chem. Soc.* **1980**, *102*, 4314-4324.

[2] Heilbronner, E.; Yang, Z-z.; *Top. Curr. Chem.* **1983**, *115*, 1-55.

[3] Boekelheide, V. *Top. Curr. Chem.* **1983**, *113*, 87-145.

[4] Ciganek, E. *Tetrahedron Lett.* **1967**, 3321-3325.

[5] Truesdale, E. A.; Cram, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 5825-5827.

[6] Gray, R.; Boekelheide, V. *J. Am. Chem. Soc.* **1979**, *101*, 2128-2136.

[7] Murad, F.; Kleinschroth, J.; Hopf, H. *Angew. Chem.* **1980**, *92*, 388-389. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 389-390.

[8] Sekine, Y.; Boekelheide, V. *J. Am. Chem. Soc.* **1981**, *103*, 1777-1785.

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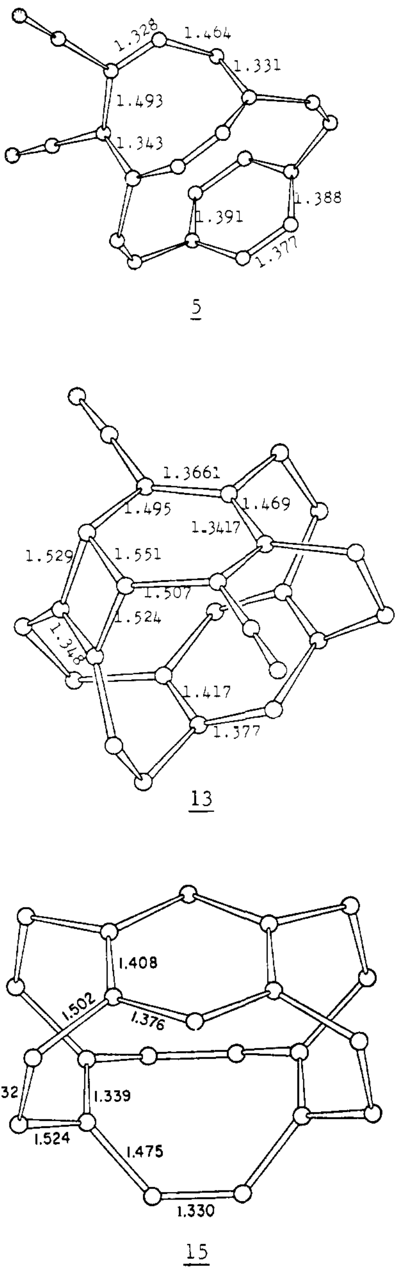
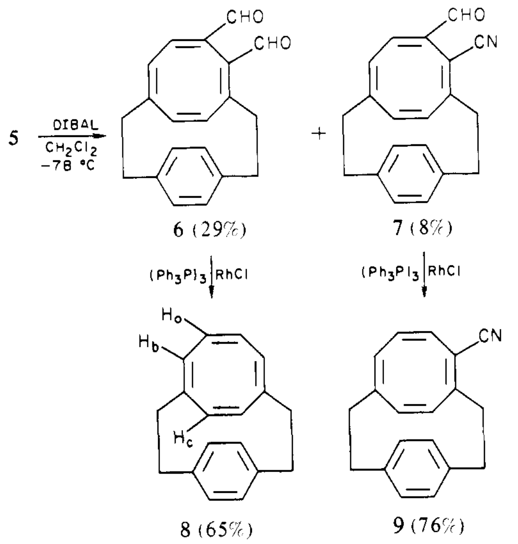


Figure 1. Depiction of geometry and key bond lengths as determined by X-ray crystallographic analysis for **5**,[9] **13**,[12] and **15**.[18]

chloride and ethylaluminum chloride, are also effective, but aluminum chloride appears to be most satisfactory. Attempts to effect a second addition of dicyanoacetylene to **5**, either of the Diels–Alder type or by 1,2-addition followed by ring expansion, were unsuccessful.

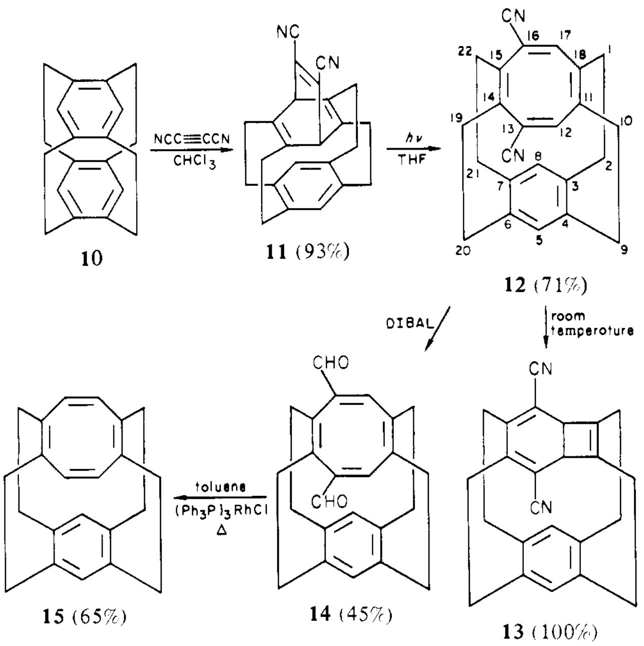
Although the composition and spectral properties of **5** were in accord with its assigned structure, absolute proof of structure was obtained by an X-ray crystallographic analysis.[9] As shown in Figure 1, the cyclooctatetraene ring is tub shaped, the carbon–carbon double bonds are localized in accord with structure **5**, and the cyano groups are twisted out of conjugation with each other.

Reduction of **5** with diisobutylaluminum hydride(DIBAL) in dichloromethane gave two products, principally the dialdehyde **6** plus some of the monoaldehyde **7**. The correct choice of structure between the two possibilities for the monoaldehyde cannot be made with certainty, but the assignment of **7** is based on the presumption that the cyano group at the 15-position is more sterically hindered than that at the 16-position and so will be reduced more slowly. When a solution of **6** in toluene containing



chlorotris(triphenylphosphine)rhodium was boiled under reflux, carbon monoxide was ejected and the desired $[2_2]$(1,6)-cyclooctatetraenyl(1,4)cyclophane (**8**) was formed in 65% yield. A similar treatment of the monoaldehyde **7** gave the 15-cyano derivative **9** in 76% yield.

To provide an addition example of a cyclophane with a cyclooctatetraene deck $[2_4]$(1,2,4,5)cyclophane (**10**) was chosen as



the starting material. $[2_4]$(1,2,4,5)Cyclophane reacts rapidly with dicyanoacetylene to give the normal barrelene-type adduct **11**, and the nature of the product is not changed by the presence of aluminum chloride. Fortunately, though, the photochemical rearrangement of barrelene derivatives to give cyclooctatetraene derivatives is well-known[10] and proceeds well in the case of **11**.[11] Thus, irradiation of a solution of **11** in tetrahydrofuran gave the dicyanocyclooctatetraene derivative **12** in 71% yield. However, **12** proved to be thermally unstable and, on standing in solution at room temperature, underwent electrocyclic ring closure to afford the bicyclo[4.2.0]octatriene derivative **13**.

Immediate reduction of **12** at low temperature with DIBAL, though, proceeded smoothly to give the dialdehyde **14**. Bisdecarbonylation of **14** by means of chlorotris(triphenylphosphine)rhodium then led to the desired $[2_4]$(1,2,5,6)-

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[9] Hanson, A. W. *Cryst. Struct. Commun.* **1981**, *10*, 559–563.

[10] Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Grunewald, G. L.; Sherwin, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 3316–3323.

[11] Gray, R.; Boekelheide, V. *J. Am. Chem. Soc.* **1979**, *101*, 2128–2136.

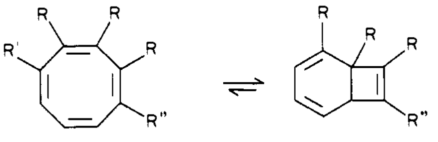
Table I. Rate Data for the Conversion of **12** to **13**

temp, K	k, min^{-1}	$t_{1/2}$, min
297	3.5×10^{-4}	1980
316	8.9×10^{-3}	78
329	2.4×10^{-2}	29

cyclooctatetraenyl(1,2,4,5)cyclophane (**15**) in 65% yield.

It is of interest that the dicyanocyclooctatetraene derivative **12** undergoes a spontaneous, thermal, valence tautomerization to the dicyanobicyclo[4.2.0]octatriene derivative **13**. This was first observed by the change in the spectral properties of **12** on standing in solution or on recrystallization. That structure **13** is indeed the correct assignment for this valence tautomer was established by a single-crystal X-ray analysis of **13**.[12]

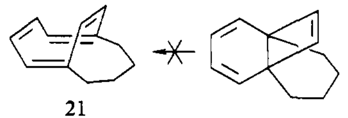
Although equilibration between cyclooctatetraene derivatives and their bicyclo[4.2.0]octatriene isomers is well-known, the equilibrium normally lies far on the side of the cyclooctatetraene isomer. Huisgen and Mietzsch first observed this equilibration for cyclooctatetraene (**16**) itself and found the equilibrium concentration of bicyclo[4.2.0]octatriene (**19**) to be only 0.01% at 100 °C.[13] Later, Vogel et al. succeeded in isolating pure bicyclo[4.2.0]octatriene (**19**) and measured the kinetic parameters (E_A = 18.7 kcal/mol; $t_{1/2}$ at 0 °C v= 14 min) for its isomerization to **16**.[14] Alkyl substitution has a strong effect on the rate of isomerization.[15,16] Quite remarkably, Paquette et al. have prepared the two bond-shift isomers, **17** and **18** and observed that **18** exists at room temperature as a 3:1 mixture of **18** and **20**.[16] On the other hand, attempts to effect isomerization of the bond-shift isomer **17** were unsuccessful.



16, R = R' = R'' = -H
17, R = R' = $-CH_3$; R'' = -H
18, R = R'' = $-CH_3$; R' = H

19, R = R'' = -H
20, R = R'' = $-CH_3$

The first example of this isomerization where the bicyclo[4.2.0]octatriene isomer is thermally stable and does not equilibrate with its valence tautomer is the propellane **22**.[17] In this case **21** is very much more strained than **22**.



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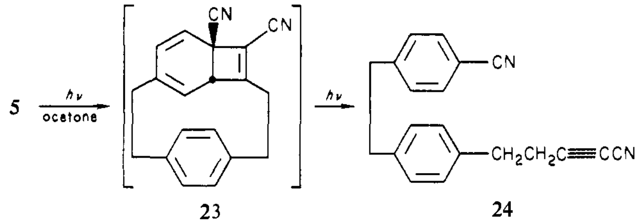
Because of the general interest in the cyclooctatetraene–bicyclo[4.2.0]octatriene isomerization, we made a kinetic study by ^{1}H NMR analysis of the valence tautomerization of **12** to **13**. The energy of activation was found to be 26.0 kcal/mol and the rate constant data are given in Table I. Within the temperature range available by this method of analysis, there was no evidence of any reverse reaction (**13** → **12**).

An X-ray crystallographic analysis of **15** has been made and shows the cyclooctatetraene to be tub shaped but highly strained due to the forced bridging to the opposite benzene deck.[18] The geometry deduced for **15** is depicted in Figure 1. On the other hand, an X-ray analysis of **13** (geometry also presented in Figure 1) shows the molecule to be essentially strain free. Undoubtedly, relief of strain is an important factor in making the bicyclo[4.2.0]cyclooctatriene isomer **13** thermodynamically more stable than the cyclooctatetraene isomer **12**. However, since **15** is thermally stable, even though it has the same strain energy as **12**, relief of strain is not sufficient to account for the valence tautomerization of **12** to **13**. Rather, the conjugative stabilization resulting from formation of the dicyanocyclohexadiene moiety in **13** must be the determining energy term promoting the isomerization of **12** to **13**.

In contrast to the easy isomerization of **12** to **13**, 15,16-dicyano[2_2](1,6)cyclooctatetraenyl(1,4)cyclophane (**5**) is thermally stable. In an attempt to see whether **5** might undergo photochemical isomerization, a solution of **5** in acetone was irradiated by using a medium-pressure Hanovia lamp. This gave a colorless crystalline isomer **24** in 34% yield. The spectral properties of this product, though, were clearly not those of the expected bicyclo[4.2.0]octatriene **23**. Instead, the infrared, ^{1}H NMR, and ^{13}C NMR spectral data showed the presence of a disubstituted acetylene, four different methylene groups, and a simple para-disubstituted benzene ring. These data are nicely accommodated by structure **24**. Presumably, the bicyclo[4.2.0]octatriene isomer **23** is first formed but then undergoes a further photochemical cycloreversion to give **24**.



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As shown in Figure 1, X-ray analysis of **5** and **15** shows the cyclooctatetraene rings in each case to be tub shaped with localized carbon–carbon double bonds. Thus, the hoped for 8π- to 6π-electron interaction does not occur and only the interaction of a 2π-carbon–carbon double bond with the 6π-benzene ring is observed. This latter type of interaction is particularly evident in the yellow color of **8** and its ultraviolet absorption spectrum (λ_{max} 280 and 290 nm with tailing out beyond 400 nm). It is also evident from the photoelectron spectra of **8** and **15**, which are best interpreted on the basis of such a π-electron interaction.[19]

The interaction of the C_{16}–C_{17} double bond with the opposite benzene deck is also seen in the ^{1}H NMR spectrum of **8**. The signal for the H_c protons of **8** appear as a singlet at δ = 4.82, whereas the H_b and H_a protons appear as doublets at 5.19 and 5.44 ppm, respectively. The upfield shift of the H_c protons is obviously a ring current effect due to their presence over the face of the opposite benzene deck. The very small H_a–H_b coupling

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(12) Hanson, A. W. *Cryst. Struct. Commun.* **1981**, *10*, 195–200.

(13) Huisgen, R.; Mietzsch, F. *Angew. Chem.* **1964**, *76*, 36. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 83.

(14) Vogel, E.; Kiefer, H.; Roth, W. R. *Angew. Chem.* **1964**, *76*, 432. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 442.

(15) Askani, R.; Wieduwildt, M. *Chem. Ber.* **1976**, *109*, 1887–1897.

(16) Paquette, L. A.; Photis, J. M.; Ewing, G. D. *J. Am. Chem. Soc.* **1975**, *97*, 3538–3540.

(17) Paquette, L. A.; Philips, J. C.; Wingard, R. E., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 4516–4522. See also: Hanzawa, Y.; Paquette, L. A. *Ibid.* **1981**, *103*, 2269–2272.

(18) Hanson, A. W. *Cryst. Struct. Commun.* **1982**, *11*, 1401–1403.

(19) Yang, Z.; Heilbronner, E.; Boekelheide, V.; Garbe, J. *J. Mass Spectrom. Ion Phys.*, in press.

(20) Goldberg, S. Z.; Raymond, K. N.; Harmon, C. A.; Templeton, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 1348–1351.

(21) Paquette, L. A.; Gardlik, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 5016–5025.

(22) For a description of the experimental method, see: Laganis, E. D.; Voegeli, R. H.; Swann, R. T.; Finke, R. G.; Hopf, H.; Boekelheide, V. *Organometallics* **1982**, *1*, 1415–1420.

(23) Streitwieser, A., Jr.; Müller-Westerhof, U. *J. Am. Chem. Soc.* **1968**, *90*, 7364, and succeeding papers.

(24) Streitwieser, A., Jr.; Dempf, D.; La Mar, G. N.; Karraker, D. G.; Edelstein, N. *J. Am. Chem. Soc.* **1971**, 7333–7334.

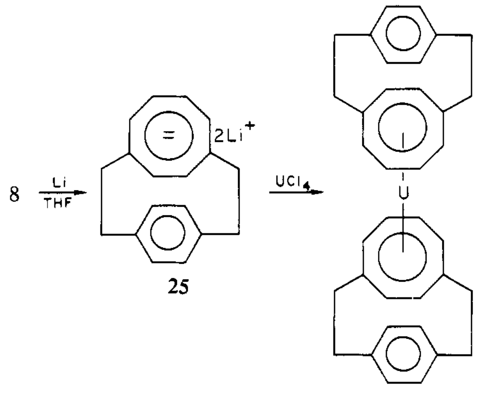
(25) Elemental and mass spectral analyses were determined by Dr. Richard Wielesek of the University of Oregon microanalytical laboratories. All of the mass spectra were taken on a CEC-21B-110 instrument set at 70 eV. Melting points were taken by using sealed, evacuated, melting point capillaries and are uncorrected. Infrared spectra were measured on a Beckman IR-7 spectrophotometer and ultraviolet spectra with a Cary-15. NMR spectra were obtained with a Varian XL-100 instrument by using deuteriochloroform as the solvent and residual chloroform (δ 7.27) as an internal standard (unless otherwise specified).

(26) Bennett, M. A.; Matheson, T. W.; Robertson, G. B.; Smith, A. K.; Tucker, P. A. *Inorg. Chem.* **1980**, *19*, 1014.

constant ($J < 1$ Hz) found for **8** is typical for cyclooctatetraene derivatives where H_a and H_b are nearly orthogonal.[27] The symmetry of **8** is likewise evident from its ^{13}C NMR spectrum, which has only nine signals, encompassing the seven different sp^2 carbons in the range of $\delta = 127.9$–140.8 and the two different sp^3 carbons at 33.2 and 37.8 ppm.

In view of the tub-shaped geometry of the cyclooctatetraene rings in **8** and **15**, it was of interest to examine their corresponding dianions. Dianions of cyclooctatetraenes are known to be planar,[20] and the ease of their reduction is related to the steric strain generated in forming the planar ring.[21] The two-electron reduction potential ($E_{1/2}$) for cyclooctatetraene itself is −1.61 V, whereas the analogous reduction potentials for **17** and **18** are −2.43 and −2.54 V, respectively.[16] Cyclic voltammetry of **8** in acetonitrile using tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte shows two, irreversible, one-electron, reduction waves at −2.36 and −2.69 V.[22] Although reduction of **8** to its dianion does occur, the high voltage required indicates that appreciable steric strain is generated during formation of the dianion. On the other hand, cyclic voltammetry of **15** showed no reduction at the highest voltage (−3.0 V) applied. Formation of a planar, eight-membered ring in **15** must incur exceptionally severe strain, and this conclusion is supported by examination of molecular models of **15** and its corresponding dianion.

Dianions of cyclooctatetraenes react readily with uranium tetrachloride to form uranocenes, a class of compounds whose synthesis and properties have been studied extensively by Streitwieser.[23] The deep red dianion **25**, formed by reaction of **8** with lithium metal in tetrahydrofuran, was treated with uranium tetrachloride and gave a deep green solid. This product was extremely sensitive, igniting spontaneously in the presence of air. Its ^{1}H NMR (360-MHz) spectrum taken in tetrahydrofuran-d_8 at room temperature showed broad resonance signals at −39.5, −33.5, and −19.0 ppm. Although the compound was too unstable to permit full characterization, its green color, sensitivity to oxygen, and its ^{1}H NMR spectrum are in accord with the uranocene structure **26**.[24]



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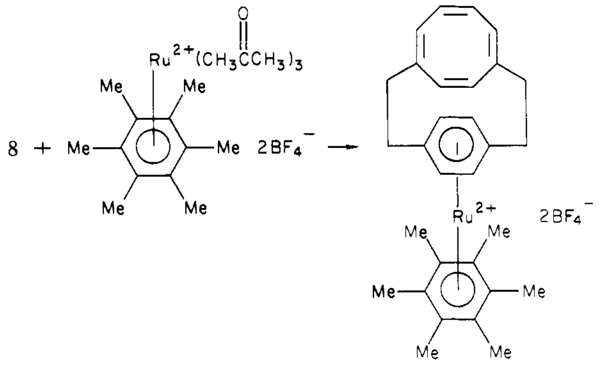
Alternatively, metal complexes can be made involving the benzene ring of **8**. Treatment of **8** with η^6-hexamethylruthenium(II) solvate, following the procedure used for ruthenium complexation of other cyclophanes,[22] readily gave the ruthenium complex **27**. Cyclic voltammetry of **27** in acetonitrile showed a reversible, two-electron, reduction wave at $E_{1/2} = 0.89$ V. This potential is very close to the value (−0.85 V) observed for the reduction of (η^6-hexamethylbenzene)(η^6-*p*-xylene)ruthenium(II)[22] and would suggest that there is very little, if any, involvement of the cyclooctatetraene ring of **27** in this electrochemical reduction.

In summary, the cyclooctatetraene–cyclophanes **8** and **15** have been prepared and have tub-shaped cyclooctatetraenyl decks. Although these molecules are not suitable for testing the interaction between 8π- and 6π-electron systems, the rigid cyclophane structure leads to unusual behavior of the cyclooctatetraene rings with regard to valence tautomerization and to dianion formation. Both the cyclooctatetraene and benzene decks remain available for metal complexation.



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Experimental Section[25]

15,16-Dicyano[2$_2$](1,6)cyclooctatetraenyl(1,4)cyclophane (5). To a solution of 1.49 g (7.16 mmol) of [2$_2$](1,4)cyclophane (**3**) in 400 mL of dichloromethane warmed up to 30 °C there was added an excess of dicyanoacetylene and 2.0 g (15 mmol) of aluminum chloride. After the mixture had been stirred for 4 days at room temperature, it was poured into an aqueous sodium bicarbonate solution and extracted with chloroform. The combined chloroform extracts were dried and concentrated, and the residual solid was chromatographed over silica gel by using chloroform for elution. The main fraction of eluate gave a solid that, after recrystallization from a chloroform–hexane mixture, afforded 295 mg of bright orange crystals. The solid residue from the filtrate was purified by thin-layer chromatography, providing an additional 389 mg of **5** (total yield, 33%) as orange crystals: mp 222–225 °C; IR 2212 and 2197 cm^{-1} (−C≡N); ^{1}H NMR δ 7.39–6.99 (4 H, m, ArH), 6.50 (1 H, d, vinyl-H), 5.37 (1 H, d, vinyl-H), 5.09 (2 H, s, vinyl-H), 3.51–1.69 (8 H, m, −CH$_2$−); ^{13}C NMR δ 163.0, 149.5, 145.8, 138.4, 137.3, 136.2, 131.9, 129.2, 128.1, 126.3, 39.5, 38.4, 32.8, 30.7; UV λ_{max} 320 nm (sh, ϵ 405); mass spectrum m/e 284, 268, 256, 243; molecular weight calcd for $C_{20}H_{16}N_2$ 284.131, found (high-resolution mass spectrum) 284.132. Anal. ($C_{20}H_{16}N_2$) C, H, N.

DIBAL Reduction of 5 To Give 6 and 7. To a solution of 236 mg (0.831 mmol) of 15,16-dicyano[2$_2$](1,6)cyclooctatetraenyl(1,4)-cyclophane (**5**) in 75 mL of dichloromethane cooled to −78 °C was added 2.7 mmol of diisobutylaluminum hydride (Aldrich, 1 M DIBAL in hexane) dropwise with stirring. After the mixture had been stirred for 5 h, it was warmed to 0 °C, 10 mL of a saturated aqueous ammonium chloride solution was added, and the mixture was extracted with chloroform. Concentration of the extract followed by chromatography of the residue over silica gel using chloroform for eluation gave two products.

The **main product 6** was recrystallized from a dichloromethane–hexane mixture to give 70.3 mg (29%) of red-orange needles: mp 195–198 °C; IR ν_{max} 1686, 1666 cm^{-1} (−HC=O); ^{1}H NMR δ 9.92 (1 H, s, −CH=O), 9.32 (1 H, s, −CH=O), 7.15–6.85 (4 H, m, ArH), 6.73 (1 H, d, vinyl-H), 5.75 (1 H, d, vinyl-H), 5.07 (2 H, AB, $J = 12$ Hz), 3.5–1.8 (8 H, m, −CH$_2$); ^{13}C NMR δ 190.9 and 188.8 (−HC=O); UV λ_{max} 360 nm (sh, ϵ 615); mass spectrum *m/e* 290, 289, 261, 260; molecular weight calcd for $C_{20}H_{18}O_2$ 290.131, found (high-resolution mass spectrum) 290.130. Anal. ($C_{20}H_{17}NO$) C, H, N.

The **minor product 7** was recrystallized from dichloromethane to give orange prisms: mp 235–237°C; IR ν_{max} 1691 cm^{-1} (−HC=O); ^{1}H NMR δ 9.35 (1 H, s, −CHO), 7.4–7.0 (4 H, m, ArH), 6.68 (1 H, d, vinyl-H), 5.69 (1 H, d, vinyl-H), 5.04 (2 H, s, vinyl-H), 3.6–1.8 (8 H, m, −CH$_2$); UV λ_{max} 368 nm (sh, ϵ 576); mass spectrum *m/e* 287, 258; molecular weight calcd for $C_{20}H_{17}NO$ 287.131, found (high-resolution mass spectrum) 287.131. Anal. ($C_{20}H_{17}NO$) C, H, N.

15-Cyano[2$_2$](1,6)cyclooctatetraenyl(1,4)cyclophane (9). To a solution of 49 mg (0.171 mmol) of **7** in 15 mL of toluene there was added 158 mg (0.17 mmol) of chlorotris(triphenylphosphine)rhodium(I) and the mixture was boiled under reflux for 22 h. It was then cooled, diluted with hexane, and filtered. After concentration of the filtrate, the residue was chromatographed over silica gel by using chloroform for elution to give yellow crystals containing some triphenylphosphine. This was chromatographed a second time over silica gel by using a 4:1 mixture of chloroform–hexane for elution to give 33.7 mg (76%) of yellow crystals: mp >180 °C dec; ^{1}H NMR δ 7.4–6.7 (4 H, m, ArH), 5.7–4.7 (5 H, m, vinyl-H), 3.5–1.6 (8 H, m, −CH$_2$); mass spectrum *m/e* 259, 244; molecular weight calcd for $C_{19}H_{17}N$ 259.136, found (high-resolution mass spectrum) 259.135. Anal. ($C_{19}H_{17}N$) C, H, N.

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(27) Lyttle, M. H.; Streitwieser, A., Jr.; Kluttz, R. Q. *J. Am. Chem. Soc.* **1981**, *103*, 3232–3233.

$[2_2]$(1,6)Cyclooctatetraenyl(1,4)cyclophane (8). To a solution of 186 mg (0.641 mmol) of **6** in 70 mL of toluene there was added 1.32 g (1.43 mmol) of chlorotris(triphenylphosphine)rhodium(I) and the mixture was boiled under reflux for 18 h. The mixture was then cooled to room temperature, diluted with pentane, and filtered. Concentration of the filtrate followed by chromatography over silica gel using a 4:1 mixture of chloroform and hexane for elution to give yellow crystals contaminated with triphenylphosphine. Repetition of the chromatography then gave a pure sample that, after recrystallization from a mixture of ether and methanol, afforded 97.5 mg (65%) of lemon yellow needles: mp 93–95 °C; ^{1}H NMR δ 7.14 (2 H, s, ArH), 7.05 (2 H, s, ArH), 5.44 (2H, m, vinyl-H), 5.19 (2 H, m, vinyl-H), 4.82 (2 H, s, vinyl-H), 3.15–1.50 (8 H, m, $-CH_2-$); ^{13}C NMR δ 140.8, 138.3, 133.9, 131.8, 130.5, 129.0, 127.9, 37.8, 33.2; UV λ_{max} 280 nm (sh, ϵ 507), 290 (sh, ϵ 405), 325 (sh, ϵ 156); mass spectrum m/e 234, 219, 205; molecular weight calcd for $C_{18}H_{18}$ 234.141, found (high-resolution mass spectrum) 234.141. Anal. ($C_{18}H_{18}$) C, H.

13,16-Dicyano$[2_4]$(1,2,5,6)cyclooctatetraenyl(1,2,4,5)cyclophane (12). The addition of dicyanoacetylene to $[2_4]$(1,2,4,5)cyclophane (**10**) was carried out as described previously[11] and gave **11** in 93% yield. A solution of 64.5 mg (0.192 mmol) of **11** in 60 mL of tetrahydrofuran was degassed by three freeze–pump–thaw cycles and then was irradiated in a quartz tube with a 450-W medium-pressure Hanovia lamp at room temperature for 40 min. The resulting solution was concentrated and the residue chromatographed over silica gel by using chloroform as the eluant to give 45.5 mg (71%) of yellow crystals: mp >180°C dec. When first prepared, the spectral properties of **12** showed ^{1}H NMR δ 6.72 (2 H, s, ArH), 6.12 (2 H, s, vinyl-H), and 1.93–3.4 (16 H, m $-CH_2-$) and UV λ_{max} 260 nm (ϵ 4160) and 318 (ϵ 1035), as described previously.[11]

Thermal Isomerization of 12 to 13 and Its Kinetic Analysis. Attempted recrystallization of **12** from chloroform, or simply heating a solution of **12** in chloroform, led in quantitative yield to its conversion to **13**. Recrystallization of **13** from a mixture of chloroform and hexane gave thermally stable, yellow flakes: mp 226–228 °C; ^{1}H NMR δ 6.8 (2 H, s, ArH), 3.5–2.2 (18 H, m, $-CH_2-$); IR ν_{max} 2200 cm^{-1} ($-C{\equiv}N$); UV λ_{max} 342 nm (ϵ 5670), 354 (ϵ 5460); mass spectrum *m/e* 336. Anal. ($C_{24}H_{20}N$) C, H, N. The structure assigned to **13** was confirmed by X-ray analysis.[12]

For the **kinetic analysis**, a solution of **12** in deuteriochloroform was monitored by measuring the change in the ratio of the integrated areas of the aromatic protons to the integrated area of the vinyl protons with time at a particular temperature. From this the values of the rate constants and the half-lives for the thermal isomerization can be calculated, and these data are presented in Table I. From a plot of ln k vs. T^{-1} the slope of the line gives E_A/R and the energy of activation was found to be 26.0 kcal/mol.

13,16-Diformyl$[2_4]$(1,2,5,6)cyclooctatetraenyl(1,2,4,5)cyclophane (14). To a solution of 137 mg of freshly prepared **12** in 120 mL of dichloromethane held at −78 °C there was added 1.3 mL of a 1 M DIBAL solution in hexane. After the solution had been stirred for 3 h, it was allowed to warm to −40 °C over 3 h and then was quickly brought to 0 °C. A saturated aqueous solution of ammonium chloride was added and the resulting mixture was extracted with chloroform. Concentration of the chloroform extract followed by chromatography of the residue over silica gel using chloroform for elution gave, on concentration of the main eluate fraction, 66.3 mg (47%) of pale yellow crystals: mp >200 °C dec; ^{1}H NMR δ 9.20 (2 H, s, -CHO), 6.67 (2 H, s, ArH), 6.18 (2 H, s, vinyl-H), 3.4–1.8 (16 H, m, $-CH_2$); mass spectrum *m/e* 342, 313; molecular weight calcd for $C_{24}H_{22}O_2$ 342.162, found (high-resolution mass spectrum) 342.161. Anal. ($C_{24}H_{22}O_2$) C, H.

$[2_4]$(1,2,5,6)Cyclooctatetraenyl(1,2,4,5)cyclophane (15). To a solution of 86.3 mg (0.252 mmol) of **14** in 60 mL of toluene there was added 500 mg (0.54 mmol) of chlorotris(triphenylphosphine)rhodium(I), and the mixture was boiled under reflux for 13 h. The mixture was cooled, diluted with pentane, and filtered. Concentration of the filtrate followed by chromatography of the residue over silica gel using chloroform for elution gave a white solid contaminated with triphenylphosphine. This impure product was dissolved in chloroform, and ether was added to effect precipitation of the triphenylphosphine. After filtration, the filtrate was concentrated and the residue was recrystallized from chloroform to give 47 mg (60%) of white crystals: mp 206–208 °C; ^{1}H NMR δ 6.7 (2 H, s, ArH), 5.22 (4 H, s, vinyl-H), 3.3–1.7 (16 H, m, $-CH_2$); UV λ_{max} 282 nm (ϵ 714), 291 (ϵ 741); mass spectrum *m/e* 286, 260; molecular weight calcd for $C_{22}H_{22}$ 286.172, found (high-resolution mass spectrum) 286.172. Anal. ($C_{22}H_{22}$) C, H.

Photolysis of 5 To Give 24. A solution of 86.8 mg (0.306 mmol) of 15,16-dicyano$[2_2]$(1,6)cyclooctatetraenyl(1,4)cyclophane (**5**) in acetone was degassed by three freeze–pump–thaw cycles and then was irradiated with a 450-W medium-pressure Hanovia lamp by using a Pyrex filter for 5.5 h. After removal of solvent, chromatography of the residue over silica gel using chloroform for elution gave a white solid. Recrystallization of this from a mixture of hexane and chloroform gave 29.9 mg (34%) of large white plates: mp 252–254 °C; IR ν_{max} 2310, 2250, 2220 cm^{-1} ($-C{\equiv}N$, $-C{\equiv}C-$); ^{1}H NMR δ 7.35 (4 H, AB, J = 8 Hz, ArH), 7.08 (4 H, s, ArH), 3.0–2.5 (8 H, m, $-CH_2-$); ^{13}C NMR (proton coupled) δ 147.1 (s), 139.4 (s), 136.5 (s), 132.1 (d), 129.3 (d), 128.7 (d), 128.3 (d), 119.0 (s), 109.9 (s), 105.1 (s), 86.2 (s), 56.1 (s), 37.8 (t), 36.8 (t), 32.7 (t), 25.0 (t); UV λ_{max} 258 nm (sh, ϵ 1057), 266 (sh, ϵ 1042), 272 (sh, ϵ 846), 278 (sh, ϵ 453); mass spectrum *m/e* 284, 220, 203, 166; molecular weight calcd for $C_{20}H_{16}N_2$ 284.131, found (high-resolution mass spectrum) 284.131. Anal. ($C_{20}H_{16}N_2$) C, H, N.

Formation of the Dianion 25 and Its Reaction with Uranium Tetrachloride. To a solution of 17 mg (0.073 mmol) of **8** in 10 mL of tetrahydrofuran there was added several small chips of lithium metal with stirring. The solution turned an immediate deep red and it was then stirred overnight. The unreacted lithium was removed by decantation and to the resulting solution was added a solution of 13 mg of uranium tetrachloride in 5 mL of tetrahydrofuran. The solution became an immediate deep green. After the solution had been stirred at room temperature for 6 h, it was concentrated under reduced pressure to give a deep green solid. The ^{1}H NMR spectrum (360 MHz) of a solution of this solid in tetrahydrofuran-d_8 showed broad resonance signals at δ −19.0, −33.5, and −39.5, as might be expected for the uranocene structure **26**.[24] The deep green solid was extremely labile and, when air was admitted to a flask containing a small particle, it ignited spontaneously. A mass spectrum taken with the green solid did not show a signal for the parent molecular ion but did have a strong signal at *m/e* 472, corresponding to a fragmentation species of $C_{18}H_{18}U^+$ in which one of the cyclophane moieties had been lost. Because of the sensitivity of the green solid, further attempts at characterization were unsuccessful. However, although the data are incomplete, the properties observed for the green solid are in accord with the assigned uranocene structure **26**.

(η^6-Hexamethylbenzene)(η^6-$[2_2]$(1,6)cyclooctatetraenyl(1,4)-cyclophane)ruthenium(II) Bis(tetrafluoroborate) (27). A solution of 34 mg (0.10 mmol) of bis(η^6-hexamethylbenzene)dichlorobis(μ-chloro)ruthenium(II)[26] and 40 mg (0.20 mmol) of silver tetrafluoroborate in 2 mL of acetone was stirred at room temperature for 20 min. The precipitate of silver chloride was removed before adding 24 mg (0.10 mmol) of **8** and 2 mL of trifluoroacetic acid. The mixture was boiled under reflux for 0.5 h, cooled, and diluted with 30 mL of ether. The resulting yellow precipitate was collected by filtration and washed with ether. It was then taken up in 3 mL of nitromethane and again precipitated by addition of excess ether. This gave 35.3 mg (51%) of a yellow solid: mp >200 °C dec; ^{1}H NMR (CD_3NO_2) δ 6.63 (2 H, s, ArH), 6.46 (2 H, s, ArH), 5.82 (2 H, br. s, vinyl-H), 5.74 (2 H, br s, vinyl-H), 5.41 (2 H, s, vinyl-H), 3.3–2.0 (8 H, m, $-CH_2-$), 2.65 (18 H, s, $-CH_3$). Anal. ($C_{30}H_{36}RuB_2F_8$).

The cyclic voltammogram of **27** was measured at a 100 mV/s scan rate in acetonitrile containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate in a three-electrode cell, as described previously.[22] The value of $E_{1/2}$ vs. SCE observed was −0.89 V with i_a/i_c = 0.25.

Acknowledgment. We thank the National Science Foundation for their support of this investigation under Grant CHE-8210282.

Registry No. 3, 1633-22-3; **5**, 78509-42-9; **6**, 87640-01-5; 7, 87640-02-6; **8**, 84954-88-1; **9**, 87640-03-7; **10**, 54100-59-3; **11**, 70565-97-8; **12**, 70566-11-9; **13**, 77273-55-3; **14**, 87640-04-8; **15**, 84954-89-2; **24**, 87655-17-2; **26**, 87640-05-9; **27**, 87640-07-1; dicyanoacetylene, 1071-98-3; bis(η^6-hexamethylbenzene)dichlorobis(μ-chloro)ruthenium(II), 67421-02-7; uranium tetrachloride, 10026-10-5.