variety of reactions that involve carbocations and radical cations as intermediates. Comparisons can be made with condensed phase and kinetic experiments for distinguishing such phenomena as solvation effects from internal electronic effects and the degree of structural development of activated complexes at the transition state in reactions in which charge is developed. We conclude that the MNDO method can be used to estimate the electronic effects of a wide variety of aromatic systems that are more expensive to deal with by the ab initio model. The MNDO method should be useful in making predictions and quantitative analysis of chemical phenomena as well as of biological processes.

Acknowledgment. We thank the Ohio Supercomputer Center for a grant of time on the CRAY X-MP/28 computer.

Registry No. H, 12408-02-5.

Supplementary Material Available: AMPAC/MOPAC output files for each of the energy-minimized structures (246 pages). Ordering information is given on any current masthead page.

Generation and Oligomerization of Bicyclo[2.2.2]octyne and Properties of Tris(bicyclo[2.2.2]octeno)benzene Obtained from the Linear Trimer

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Received July 3, 1990

Reaction of 2,3-dibromobicyclo[2.2.2]oct-2-ene (**10**) with *n*-butyllithium in THF at −78 °C affords a series of oligomeric dibromides **11** (n = 2–5), which are composed of linearly bonded bicyclo[2.2.2]oct-2-ene units. A trapping experiment indicated that the reaction proceeds via formation of a highly strained acetylene, bicyclo[2.2.2]octyne (**18**), as a reactive intermediate. Upon treatment with sodium naphthalenide, the trimer **11** (n = 3) reductively cyclizes to tris(bicyclo[2.2.2]octeno)benzene (**12**) in high yield. The benzene **12** exhibits a reversible oxidation wave at +1.25 V vs $Ag/AgNO_3$ on cyclic voltammetry and gives a stable cation radical $\mathbf{12}^{\bullet+}$ electrolytically or by oxidation with H_2SO_4 in air. In FSO_3H, **12** is 100% protonated to give the arenium ion **22**. The results of variable-temperature ^{13}C NMR study indicate that the activation energy for the intermolecular proton transfer of **22** is lower than that for the hexamethylbenzenium ion (**23**). The rate of intramolecular hydrogen migration is also much faster in **22**. These results are in agreement with the relative instability of **22** (pK_{AH^+} −10.2) as compared with **23** (pK_{AH^+} −9.01).

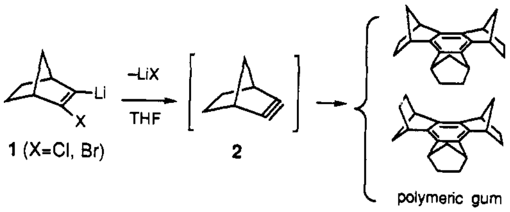
The cyclotrimerization of alkyne is one of the most simple and practical means for the synthesis of benzene derivatives,[1] and a variety of transition-metal catalysts have successfully been employed in this process.[2] Conversely, the formation of benzene derivatives has been taken as evidence for generation of alkynes, especially when the alkyne is structurally too unstable to be isolated;[3] however, the mechanism for such cyclotrimerization has rarely been discussed in detail.

For example, Gassman and Gennick reported generation of bicyclo[2.2.1]heptyne (norbornyne, **2**) and its conversion to the corresponding benzene derivatives **3** and **4** (Scheme I).[4] Although trapping of the alkyne **2** with dienes was not successful,[5] the notable effectiveness of transition-metal catalysts for cyclotrimerization supports the intermediate formation of this most strained bicyclic acetylene.

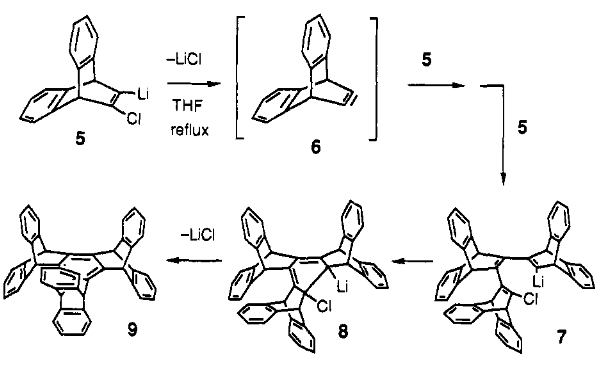
Quite recently, Shahlai and Hart elegantly demonstrated that the bicyclo[2.2.2]octyne derivative **6** generated from the 2-chloro-3-lithiobicycloalkene **5** undergoes stepwise reaction with **5**, which is terminated by electrocyclization followed by LiCl elimination to give the benzene derivative **9** (Scheme II).[6]

In an independent study, we found that lithiation of 2,3-dibromobicyclo[2.2.2]oct-2-ene (**10**) with *n*-BuLi gave both the trimeric dibromide **11** (n = 3) and the benzene derivative **12** in moderate yields (Scheme III).[7] The

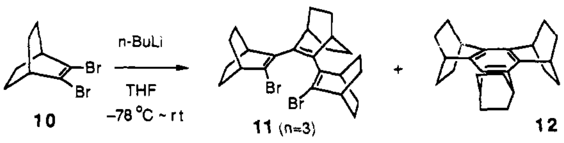
Scheme I



Scheme II



Scheme III



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(1) Heaney, H. In *Comprehensive Organic Chemistry*; Stoddart, J. F., Ed.; Pergamon; Oxford, 1979; Vol. I, p 250.

(2) For example, see: Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1.

(3) Pericàs, M. A.; Riera, A.; Rossell, O.; Serratosa, F.; Seco, M. *J. Chem. Soc., Chem. Commun.* **1988**, 942 and references cited therein.

(4) Gassman, P. G.; Gennick, I. *J. Am. Chem. Soc.* **1980**, *102*, 6864.

(5) See: Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* **1981**, *46*, 4427, footnote 27.

(6) Shahlai, K.; Hart, H. *J. Am. Chem. Soc.* **1988**, *110*, 7136.

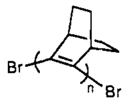
0022-3263/91/1956-0195$02.50/0

benzene **12** was shown to be formed not by direct cyclotrimerization of the acetylenic intermediate but by reductive cyclization of the trimeric dibromide **11** ($n = 3$).[8] In order to elucidate the mechanism of these reactions, it seemed crucial to clarify the intermediacy of bicyclo[2.2.2]octyne as well as to determine the structures of other unidentified products. Here we present the results of such detailed studies together with characteristic properties of the benzene **12**, which reflect the steric and electronic effects of annelation with rigid bicyclo[2.2.2]octene frameworks.

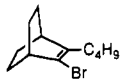
Results and Discussion

Reaction of 2,3-Dibromobicyclo[2.2.2]oct-2-ene (10) with *n*-BuLi. In contrast to the case of the bicyclo[2.2.1]heptyl system where the lithiated species **1** is stable in solution at −78 °C and trapped with chlorotrimethylsilane,[4] reaction of the dibromo olefin **10** with 1 equiv of *n*-BuLi in THF was found to be too fast to be intercepted by chlorotrimethylsilane. When the reaction was carried out and quenched at −78 °C by addition of chlorotrimethylsilane, there were obtained a series of homologous dibromides **11** with **11** ($n = 3$) as a major product, but neither the trimethylsilylated compound nor the benzene **12** was obtained. Only when the reaction was quenched after warming to the room temperature, a small amount (4% yield) of **12** was obtained, suggesting the formation of **12** only at the ambient temperature probably by the action of excessive amount of *n*-BuLi. These reactions were found to proceed regardless of the presence of Ni(II) complexes such as nickelocene and $Ni(PPh_3)_2Cl_2$, which we had erroneously believed to be active as a catalyst.[7]

From the product mixture of the reaction conducted and quenched at −78 °C with methanol, the following compounds were isolated by carefully repeated use of medium-pressure liquid chromatography; monomer (**13**, 3%), dimer (**14**, 1%; **15**, 15%; **16**, 10%), trimer (**11** ($n = 3$), 33%[9]), tetramer (**11** ($n = 4$), 8%), and pentamer (**11** ($n = 5$), 7%). The yields of the dibromides **11** ($n = 3$) and **11** ($n = 4, 5$) were reproducible within ±4% and ±2%, respectively, in different runs, whereas the yields of **13**, **14**, **15**, and **16** varied considerably depending upon slight differences in the amount of *n*-BuLi and the rate of its addition. A dimer **11** ($n = 2$) was formed (12% yield) only when a smaller amount (0.6 equiv) of *n*-BuLi was used.



11 (n=2–5)



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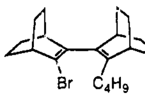
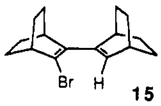


14



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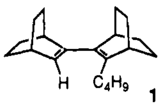

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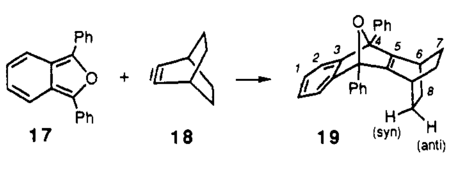
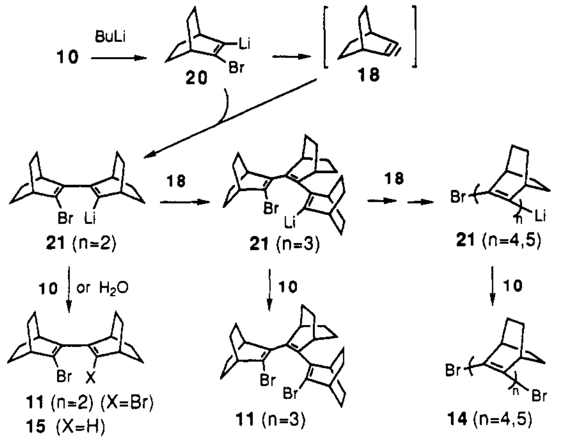
Thus, a series of dibromide **11** ($n = 2$) to **11** ($n = 5$) were all isolated and fully characterized (see the Experimental Section). None of the higher homologues or polymeric material has so far been either observed or isolated.

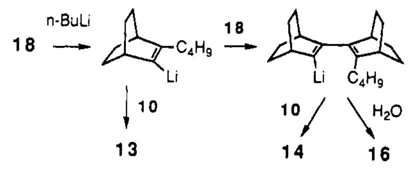
Scheme IV



Scheme V



Scheme VI



From the unusually rapid reaction proceeding at such low temperatures,[10] we suspected the intermediacy of a highly reactive species such as bicyclo[2.2.2]octyne, and then carried out a trapping experiment using 1,3-diphenylisobenzofuran (**17**). In spite of rather low concentration (0.05 M) of **17** due to its low solubility, addition of 1 equiv of *n*-BuLi to **10** (0.05 M) in THF at −78 °C afforded a high yield (86%) of the [4 + 2] adduct (**19**)[11] of the alkyne **18** (Scheme IV). The results of control experiments showing no reactivity of **17** towards the dibromoolefin **10** and lithiated species such as *n*-BuLi confirmed that **19** is actually formed from the highly strained alkyne **18** generated by LiBr elimination after lithiation of **10**.

Thus, the most possible reaction pathway for the formation of a series of dibromides **11** ($n = 2–5$) seems to involve the repeated insertion of the alkyne **18** into the C–Li bond of the lithiated species **20** and **21** as shown in Scheme V. Since our reaction procedure comprises of slow addition of *n*-BuLi to the dibromo olefin **10** whereas lithiation and subsequent reactions appear to be very fast,[10] the lithiated species **21** would undergo Li/Br exchange with the unchanged starting material **10**, furnishing the dibromides **11** as final products. As the reaction proceeds, the proportion of the alkyne **18** which reacts with an ex-

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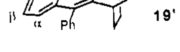
(7) Komatsu, K.; Akamatsu, H.; Jinbu, Y.; Okamoto, K. *J. Am. Chem. Soc.* **1988**, *110*, 633.

(8) Komatsu, K.; Jinbu, Y.; Gillette, G. R.; West, R. *Chem. Lett.* **1988**, 2029.

(9) In our preliminary communication (ref 8) the yield of **11** ($n = 3$) was overestimated since the higher homologues **11** ($n = 4, 5$) were erroneously taken as the trimer **11** ($n = 3$).

(10) Most of the reaction seemed to be completed within 5 min after addition of *n*-BuLi at −78 °C.

(11) The structure of **19** was determined based on 2D (COSY and C/H COSY) NMR spectra using unusual shielding of H-8(syn) (caused by the presence of a facing benzene ring) as a clue. The adduct **19** was found to readily rearrange to the ketone **19′** upon chromatography over silica gel. A similar acid-catalyzed rearrangement has previously been reported (Wittig, G.; Weinlich, J.; Wilson, E. R. *Chem. Ber.* **1965**, *98*, 458).



19′

cessive amount of *n*-BuLi would increase, giving rise to the formation of butylated compounds such as **13**, **14**, and **16** (Scheme VI).

In contrast to our results, in Hart's reaction (Scheme II) the "trimer" **7** bearing Li and Cl at both ends does not further react with the alkyne **6** but undergoes intramolecular cyclization.[6] Probably the two annelated benzene rings in **7** not only sterically hinder the oligomerization but inductively withdraw the negative charge from the lithiated carbon lowering its reactivity. The higher reaction temperature required for elimination of LiCl from **5** also seems to facilitate the thermally allowed disrotatory electrocyclization.

On the other hand, the difference between our results and Gassman's (Scheme I) would be ascribed mainly to the great difference in molecular strain of the bicycloalkyne intermediates. Molecular mechanics calculations using the MM2 program[12] indicated that the difference in strain energy between the bicycloalkyne and its saturated counterpart is 53.7 kcal/mol larger in norbornyne (**2**) than in bicyclooctyne **18**. The more strained **2** is supposed to undergo facile cyclotrimerization or polymerization with itself, while the less strained **18** has relatively longer lifetime[5] to insert into the C–Li bond of **20**. Correspondingly, the s character of the exocyclic C–Li bond extending from the olefinic carbon is estimated to be slightly smaller in **20** (s %, 32.2%) than in **1** (33.1%) from the $J_{\mathrm{C-H}}$ values of bicyclo[2.2.2]oct-2-ene and of norbornene, suggesting the lower stability (i.e., higher reactivity) of **20** than **1**.

Cyclization of the Trimeric Dibromide 11 (*n* = 3). The trimeric dibromide **11** ($n = 3$) was stable in THF under reflux undergoing no electrocyclization. However, when treated with 2 equiv of *n*-BuLi in THF at room temperature, **11** ($n = 3$) smoothly gave the benzene **12** in good yield (80%). The observed formation of octane but not of bromobutane, as well as the necessity of 2 equiv of *n*-BuLi, suggests that this reaction involves a single electron transfer process[13] instead of a metal/halogen exchange. In agreement with this supposition, the use of sodium naphthalenide in place of *n*-BuLi afforded the benzene **12** in better yield (89%) in a cleaner reaction.[14]

Properties of Tris(bicyclo[2.2.2]octeno)benzene (12). The highly symmetrical structure of the benzene **12** is shown by its ^{13}C NMR spectrum exhibiting only three signals at δ 134.2, 28.7, and 26.5 ppm. The X-ray crystallography has shown that **12** has nearly D_{3h} symmetry with a slight bond length alternation: the aromatic bond within the bicyclic system is elongated by 0.015 Å on the average.[8]

In order to characterize the electronic effects of annelation with rigid bicyclic frameworks, an attempt was made to compare the charge-transfer (CT) transition energy of **12** with that of hexamethylbenzene (HMB) using tetracyanoethylene (TCNE) as a common acceptor. However, absolutely no CT absorption was observed for **12** and TCNE at the concentrations 3 times higher than those for HMB (3×10^{-3} M) and TCNE (3×10^{-3} M) which exhibited a strong CT band at $\lambda_{\max}$ 560 nm in CH_2Cl_2 (absorbance 0.70). This is presumably due to the steric effects of the three bicyclic units hindering the close approach of the acceptor molecule.

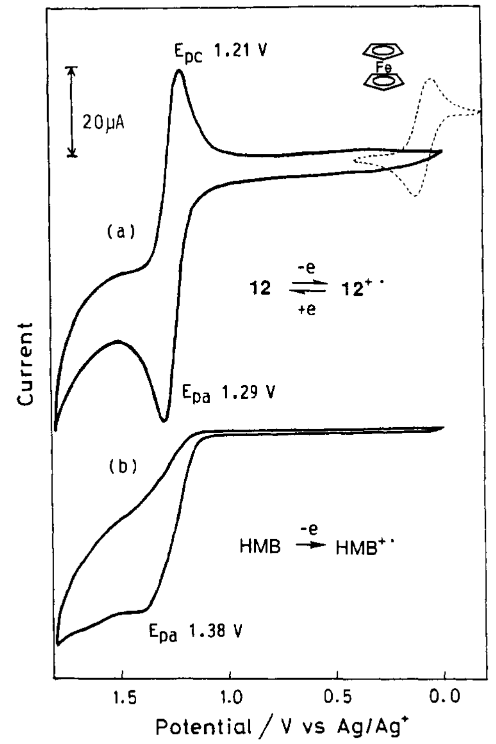


Figure 1. Cyclic voltammograms (a) of **12** and (b) of hexamethylbenzene (HMB) in CH_3CN (1×10^{-3} M): scan rate, 0.1 V s^{-1}; supporting electrolyte, $Bu_4N^+ClO_4^-$ (0.1 M).

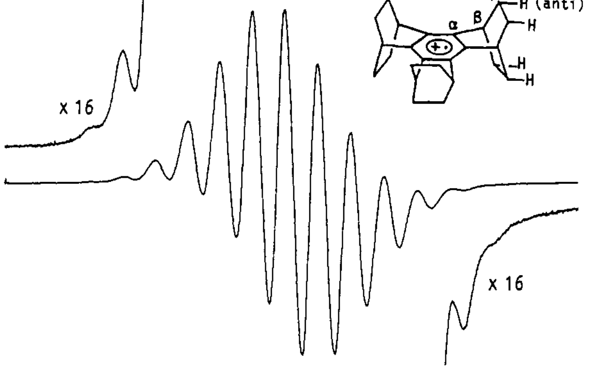


Figure 2. An ESR spectrum of **12**$^{\cdot+}$ electrolytically generated in CH_3CN (a_H = 1.39 G, g = 2.00261).

Then, cyclic voltammetry was conducted for **12** and HMB in CH_3CN to give voltammograms shown in Figure 1. In contrast with HMB which exhibited an irreversible oxidation peak at the peak potential (E_{pa}) 1.38 V vs Ag/Ag$^+$, the benzene **12** showed a well-defined reversible oxidation peak at $E_{1/2}$ 1.25 V (E_{pa} 1.29 V) under the same conditions. Clearly, **12** is more readily oxidized than HMB, and the excellent reversibility reflects the stability of the generated cation radical **12**$^{\cdot+}$.

In good agreement with this, the electrolytic oxidation of **12** in an ESR cell at the potential of +1.50 V in CH_3CN gave an ESR spectrum assignable to **12**$^{\cdot+}$, which was composed of 13 lines in the relative intensities proportional to the coefficients in the binomial expansion as is shown in Figure 2: the g value was 2.00261. This splitting with the coupling constant of 1.39 G is apparently due to coupling with 12 magnetically equivalent protons. These are supposedly anti-γ-protons of the ethano bridges since the C–H(anti) bond and the 2p orbital of the π-system are fixed at a W-like arrangement.[15]

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(12) Allinger, N. L., QCPE program MM2, 1982.

(13) When the reaction was quenched with methanol after much shorter reaction period (<5 min), only **12** and unchanged **11** ($n = 3$) were present, but no formation of monoprotonated monobromotrimer was observed. This result denies the occurrence of Br/Li exchange under the present reaction conditions. As to the single electron transfer reaction caused by alkyllithiums, see: Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag; Berlin, 1987; p 132.

(14) For examples of reductive cyclization of α,ω-dihaloalkanes by the action of sodium naphthalenide, see: Garst, J. F.; Barbas, J. T. *J. Am. Chem. Soc.* **1974**, *96*, 3239.

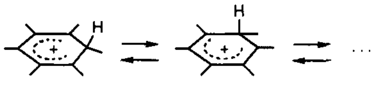
The stability of **12**$^{\bullet+}$ was demonstrated by the fact that the ESR signal can persist for 5–10 min at room temperature under argon even after cutting off the anodic current. The same spectrum was also obtained by simply dissolving the benzene **12** in concentrated H_2SO_4 under air. The produced cation radical is remarkably stable in a capillary tube at room temperature, persisting for several weeks. It has been well known that condensed aromatic hydrocarbons give rise to stable cation radicals in H_2SO_4. However, to the best of our knowledge **12** is the first example of a polyalkylbenzene which behaves in the same manner.[16]

This unusual stability of **12**$^{\bullet+}$ is ascribed to several factors. First, the supposedly most labile C–H bond at the benzylic carbon is fixed in the plane of the π-system and is therefore "Bredt's rule protected" as in the case of adamantylideneadamantane cation radical.[15] Second, the positively charged π-system is stabilized both by the inductive electron donation from the three annelated bicyclooctene units and by the possible σ-π conjugation between the 2p orbitals of the π-system and the σ-bonds rigidly held at the arrangement nearly parallel to the 2p orbitals. Third, the steric hindrance by the methylene protons of the σ-frameworks against the attack by nucleophilic species may be kinetically protecting the π-system in the central ring in **12**$^{\bullet+}$.

Formation of Arenium Ion from the Benzene 12 and Its Dynamics. Formation of arenium ions from various benzene derivatives and their dynamic behaviors in highly acidic media have been extensively studied.[17] It has been established that the arenium ion can undergo either *inter*molecular proton exchange with the conjugate base of the solvent (eq 1) or with the unprotonated aromatics (eq 2), or *intra*molecular hydrogen migration (eq 3), depending on the nature of the acid and the structure of the arenium ion.[17] For these apparently degenerate

$$\mathrm{AH^+ + S^- \rightleftarrows A + HS}\ (\mathrm{A} = \text{aromatics},\ \mathrm{HS} = \text{acid}) \tag{1}$$

$$\mathrm{AH^+ + A \rightleftarrows A + AH^+} \tag{2}$$



(3)

transformations, it is sometimes difficult to clearly differentiate between the inter- and intramolecular processes.[18] Regarding this point, the benzene **12** is expected to be advantageous in that these processes can be readily differentiated by distinguishing the ethano bridges of the two different sides of the central benzene ring.

Although **12** gave the cation radical when dissolved in H_2SO_4 under air, the electronic spectrum of **12** dissolved in FSO_3H under vacuum exhibited the absorptions at λ_{max} 286 (log ε 3.87) and 393 nm (3.97), which are typical for alkyl-substituted cyclohexadienyl cations.[19] Thus, **12** was shown to give an ordinary σ-complex type cation **22** rather than the π-complex type cation **22′** in FSO_3H.

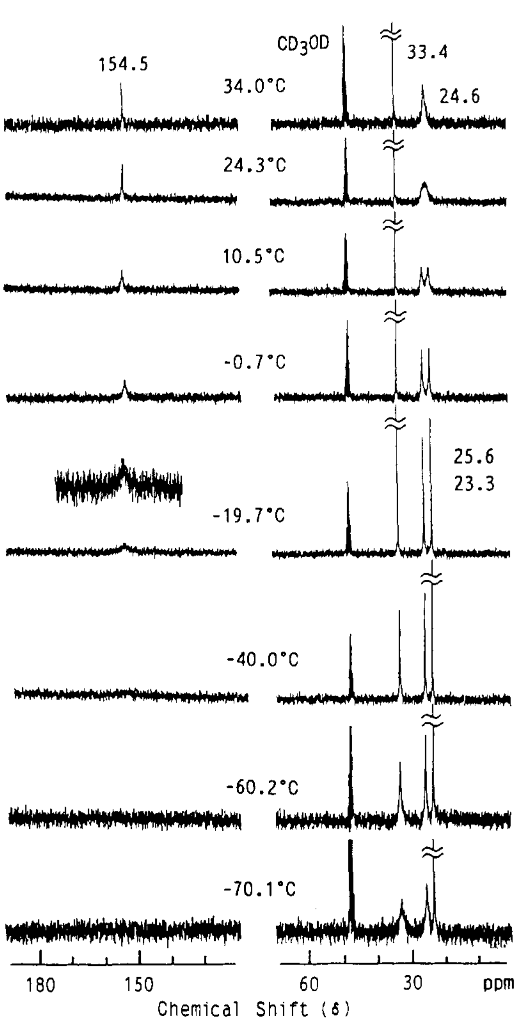
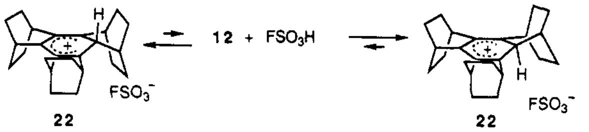
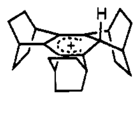
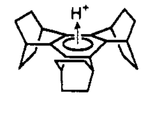


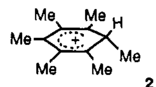
Figure 3. Temperature-dependent ^{13}C NMR (67.8 MHz) spectra of **22** in FSO_3H with CD_3OD in a capillary tube used as an NMR lock.

Scheme VII




22


22′



23

Subsequently, the NMR spectra were examined for the solution of **12** in FSO_3H sealed under vacuum. The ^1H NMR (90 MHz) spectrum exhibited broadened methine and methylene signals at room temperature. At lower temperatures the broadening became more pronounced for *syn*-methylene signals but no well-resolved spectrum was obtained even at −80 °C. In contrast, temperature de-

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[15] For the cation radical of adamantylideneadamantane, it has been proven that, between anti- and syn-γ-protons, the anti protons have much larger coupling constant (3.27 G) than the syn protons (0.47 G) because of a similar W-like arrangement (Gerson, F.; Lopez, J.; Akaba, R.; Nelsen, S. F. *J. Am. Chem. Soc.* **1981**, *103*, 6716).

[16] It has been reported that hexamethylbenzene can be oxidized to the cation radical in concentrated H_2SO_4 by photochemical ionization (Hulme, R.; Symons, M. C. R. *Proc. Chem. Soc.* **1963**, 241; *J. Chem. Soc.* **1965**, 1120) or by the action of SO_2 (Carter, M. K.; Vincow, G. *J. Chem. Phys.* **1967**, *47*, 302).

[17] For reviews, see: Brouwer, D. M.; Mackor, E. L.; MacLean, C. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley; New York, 1970; Vol. 2, p 837. Ahlberg, P.; Jonsall, G.; Engdahl, C. *Adv. Phys. Org. Chem.* **1983**, *19*, 223. Koptyug, V. A. In *Contemporary Problems in Carbonium Ion Chemistry (Topics in Current Chemistry, Vol. 122)*; Rees, Ch., Ed.; Springer-Verlag: Heidelberg, 1984; Part III.

[18] (a) MacLean, C.; Mackor, E. L. *Disc. Faraday Soc.* **1962**, *34*, 165. (b) Birchall, T.; Gillespie, R. J. *Can. J. Chem.* **1964**, *42*, 502. (c) Brouwer, D. M.; MacLean, C.; Mackor, E. L. *Disc. Faraday Soc.* **1965**, *39*, 121. (d) Olah, G. A. *J. Am. Chem. Soc.* **1965**, *87*, 1103.

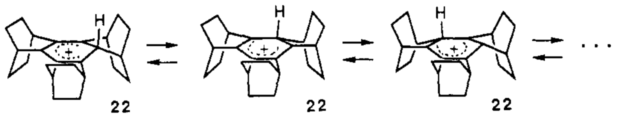
[19] For example, heptamethylbenzenium ion exhibits UV (concentrated HCl) λ_{max} 287 (log ε 3.83) and 397 nm (3.93) (Doering, W. v. E.; Saunders, M.; Boyton, H. G.; Earhart, H. W.; Wadley, E. F.; Edwards, W. R.; Laber, G. *Tetrahedron* **1958**, *Tetrahedron* **1958**, *4*, 178).

Table I. Activation Energies and Rates for Intermolecular Proton Exchange of Arenium Ions (AH^+) in FSO_3H

AH^+	$[AH^+]$, M	$[SbF_5]$, M	E_a, kcal mol^{-1}	k_1 (25 °C), s^{-1}
22	0.21	0	12.0	404
	0.21	0.28	11 ± 1	210 ± 15
	0.21	0.95	–[a]	20
23[b]	0.48	0	13.7	805
	1.54	0	15.5	17300
$Me_3C_6H_4^+$ [b,c]	0.34	0	13.6	5610
	1.13	0	13.8	18300
	1.05	0.78	14.1	3570

[a] Not determined owing to the slow exchange rate. [b] Data taken from ref 18b. The values of $[AH^+]$ and $[SbF_5]$ in M were converted from the values in mol %, while the values of k_1 were calculated from the data at lower temperatures. [c] 1,3,5-Trimethylbenzenium ion.

Scheme VIII



pendency of the ^{13}C NMR (67.8 MHz) spectrum was much more straightforward as shown in Figure 3. At the temperature near 40 °C, there were observed only three signals at δ 154.5, 33.4, and 24.6 ppm. By comparison with the ^{13}C NMR data reported by Olah for hexamethylbenzenium ion (**23**)[20] (the weighted average for chemical shifts of ring carbons, 152.7 ppm), the signal at δ 154.5 ppm is assigned to the time-averaged signal for the central ring carbons undergoing fast degenerate rearrangement. The signals at δ 33.4 and 24.6 ppm were shown to be a doublet and a triplet in an off-resonance spectrum and are assigned to the time-averaged signals of bridgehead and methylene carbons, respectively.

Upon lowering the temperature, the signals for methylene carbons broadened and split into the doublet at about 10 °C while the other two signals still remained as singlets. This temperature-dependent change of the methylene-carbon signal must have resulted from rapid proton transfer between two sides of the central benzene ring (Scheme VII), which is a typical intermolecular process. This corresponds to the process shown by eq 1, as is evidenced by the fact that the addition of SbF_5 to lower the concentration of FSO_3^- suppresses the rate of proton transfer (see Table I). In order to compare with the activation parameters obtained by Birchall and Gillespie[18b] for the similar exchange process for **23** in FSO_3H, a complete line shape analysis was made for this temperature-dependent change of the methylene signal (Figure 4). From the Arrhenius plot (correlation coefficient, 0.9993) of the rate data obtained at the temperatures ranging from −19.7 to 44.5 °C, the value of E_a was determined as 12.0 kcal/mol (Table I), which is lower than the value determined for **23** (13.7–15.5 kcal/mol depending upon the hydrocarbon concentration).[18b] This lowering of E_a may have resulted from destabilization of the protonated species **22** as compared with **23** because of the strain generated in the bicyclooctane framework (vide infra).

On the other hand, the appearance of the signals at δ 154.5 and 33.4 ppm as singlets at the temperature near 10 °C suggests that a hydrogen is rapidly migrating only at one side of the central ring (Scheme VIII), which is a typical intramolecular process (eq 3). Upon further lowering the temperature, gradual broadening was observed for all the signals except the one resonating at the highest field, implying that the intramolecular hydrogen migration is being slowed down (the signal at the highest field presumably corresponds to the methylene carbons at the other side of the site of protonation). However, even at −81 °C, these signals were still broadened (the lowest field signal was broadened into the baseline) and no sign of "freezing out" of the protonated species was observed. Addition of SbF_5 did not affect the temperature dependency of this process, supporting that this represents a purely intramolecular transformation. This is in sharp contrast to the hexamethyl derivative **23**, which exhibited a frozen out spectrum in FSO_3H at −78 °C.[20,21] This unusually fast intramolecular hydrogen migration in **22** would be ascribed to destabilization of the protonated species as compared with **23** because of the molecular strain imposed by a deformed bicyclo[2.2.2]octyl unit upon the cyclohexadienyl π-system. Such strain should be released in the transition state, thus, leading to appreciable lowering of the activation energy.

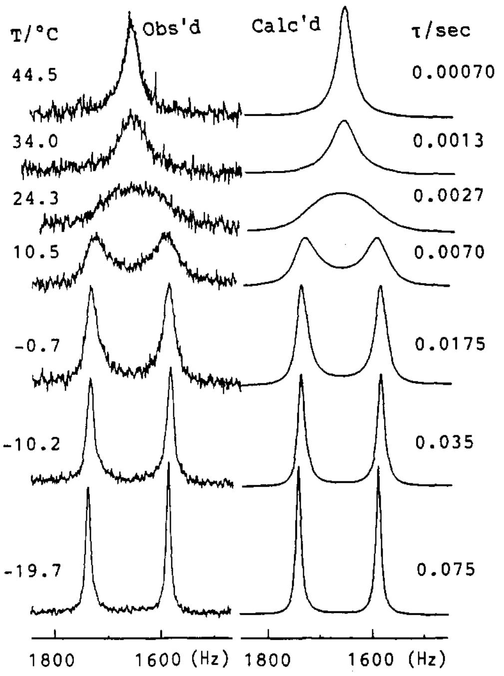


Figure 4. Experimental and simulated spectra for the ^{13}C NMR signals of methylene carbons of **22** in FSO_3H.

Determination of Basicity of the Benzene 12. In order to estimate the degree of such destabilization caused by protonation, an attempt was made to quantitatively compare the basicity of the benzene **12** with that of HMB.

As long as the same acid system is used in slightly different concentrations, the basicity of the aromatics should be directly compared using the acidity function H_0 of the solvent in which half-protonation is attained: from eq 5, where C_A and C_{AH^+} represent the concentration of A (arene) and AH^+ (arenium ion) respectively, H_0 is equal to the acidity of the protonated species AH^+ at the half-protonation point.

$$A + H^+ \rightleftarrows AH^+ \tag{4}$$

$$H_0 = pK_{AH^+} + \log (C_A/C_{AH^+}) \tag{5}$$

The pK_{AH^+} value of HMB is shown to be −9.01 from the degree of protonation of HMB in varying concentration of H_2SO_4[22] and the correlation between H_0 and H_2SO_4

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[20] Olah, G. A.; Liang, G.; Jindal, S. P. *J. Org. Chem.* **1975**, *40*, 3259.

[21] For reports on static spectra of benzenium ions at low temperatures, see ref 17.

Table II. Degrees of Protonation of 12 in H_2SO_4 under Vacuum

H_2SO_4, %	H_0	protonation, %
99.2	−10.80	70
98.9	−10.70	63
98.7	−10.58	61
97.0	−10.22	47
96.4	−10.10	54
96.2	−10.07	44
95.9	−10.02	46
95.7	−9.98	42
94.7	−9.80	30
84.2	−8.00	0

concentration.[23] On the other hand, it was shown by UV spectroscopy under vacuum that the benzene 12 is 100% protonated in mixtures of FSO_3H–H_2SO_4 ranging from 100:0 (v/v) (H_0 −15.07)[24] to 10:90 (v/v) (H_0 −12.4)[25] and partially protonated in H_2SO_4 of the concentration ranging from 94 to 99%. The exact H_0 value for each of the H_2SO_4 solution used for protonation of 12 was calibrated from the degree of protonation of HMB using eq 5 to give the results shown in Table II. The degree of protonation of 12 was plotted against H_0 of the solvent, and the H_0 value for the half-protonation point was determined to be −10.2. This value is 1.2 unit more negative than H_0 of HMB, indicating that 12 is less basic than HMB. In other words, the protonated form 22 is thermodynamically less stable, with respect to the neutral form, than 23 by 1.6 kcal/mol at 25 °C. This is in good agreement with the results of temperature-dependent NMR studies described above. Thus, annelation of the benzene ring with three rigid bicyclo[2.2.2]octene frameworks is shown to impose considerable molecular strain upon transformation to the arenium ion. This destabilization seems to surpass the electronic stabilization gained by annealation with bicyclo[2.2.2]octene units.

Conclusions

We have shown that lithiation of 2,3-dibromobicyclo[2.2.2]oct-2-ene (10) in THF readily affords a series of oligomeric dibromides 11 (n = 2–5) by way of intermediate formation of bicyclooctyne 18. Electron transfer to the dibromide 11 (n = 3) was found to cause cyclization to give the benzene 12 quite efficiently. This provides a new synthetic method applicable for construction of various new π-conjugated carbocycles, and an attempt to prepare a totally new cyclooctatetraene derivative from 11 (n = 4) is now under investigation. Annelation with the bicyclo[2.2.2]oct-2-ene framework was shown to stabilize, both sterically and electronically, the positively charged π-system in the cation radical $12^{\bullet+}$ but rather destabilizes the corresponding arenium ion 22 because of the distortion generated in the bicyclic σ-framework. However, the arenium ion 22 was found to be a system quite unique in that the *inter*- and *intra*molecular hydrogen-transfer processes are clearly differentiated in temperature-dependent ^{13}C NMR spectroscopy.

Experimental Section

Melting points were determined on a Yamato MP-21 apparatus and are uncorrected. Elemental analyses were performed by Microanalytical Center, Kyoto University, Kyoto. NMR spectra were recorded on JEOL GSX270 (270 MHz for ^1H and 67.8 MHz for ^{13}C NMR) or on JEOL FX90 (90 MHz for ^1H and 22.5 MHz for ^{13}C NMR) spectrometers using Me_4Si as an internal standard unless otherwise noted. IR and UV–vis spectra were taken on Hitachi 215 and 200-10 spectrometers, respectively. ESR spectra were recorded on a JEOL PE-2X spectrometer. Mass spectra were taken on a JEOL JMS-01SG spectrometer. Cyclic voltammograms were obtained by the use of a Hokuto-Denko HA104 potentiostat, a HB107A function generator, a Hitachi 057 X-Y recorder, and a three-electrode cell composed of platinum wire working and counter electrodes and a Ag/0.01 M $AgNO_3$ (CH_3CN) reference electrode. The observed potential was corrected with reference to ferrocene ($E_{1/2}$ +0.089 V) added as an internal standard after each measurement. A Sartorius 4503MP6 microbalance was employed for weighing samples of less than 2 mg.

THF was freshly distilled from sodium benzophenone ketyl before use. Pyridine was distilled from KOH. $CHCl_3$ and CH_2Cl_2 were distilled from P_2O_5. FSO_3H was distilled under argon; bp 161–165 °C. FSO_3H–SbF_5 (1:1) was purchased from Aldrich Chemical Co. and used after appropriate dilution with FSO_3H. Bicyclo[2.2.2]oct-2-ene was purchased from Aldrich Chemical Co. and potassium *tert*-butoxide from E. Merck Co. All reactions where anhydrous conditions were required were conducted under an atmosphere of argon or nitrogen. Medium-pressure liquid chromatography (MPLC) was carried out using silica gel 60 (E. Merck, particle size 0.040–0.063 mm, 230–400 mesh ASTM) unless otherwise noted.

2,3-Dibromobicyclo[2.2.2]oct-2-ene (10). Into a stirred solution of bicyclo[2.2.2]oct-2-ene (4.93 g, 45.6 mmol) in pyridine (8 mL) and $CHCl_3$ (12 mL) cooled at −40 °C was added a solution of bromine (6.89 g, 43.0 mmol) in $CHCl_3$ (10 mL) dropwise over 2.5 h at −40 °C. After washing the reaction mixture with 10% HCl and with 10% $NaHCO_3$, the $CHCl_3$ layer was separated, washed with 10% NaCl, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by MPLC eluted with hexane to give *trans*-2,3-dibromobicyclo[2.2.2]octane[26] (8.33 g, 72.3%) as white crystals: mp 51–53 °C (lit.[26] mp 55–55.5 °C); ^1H NMR ($CDCl_3$) δ 4.42 (br s, 2 H, CHBr), 1.95–1.45 (br m, 10 H, CH_2 + CH); ^{13}C NMR ($CDCl_3$) δ 61.3 (d), 34.9 (d), 25.5 (t), 19.2 (t); IR (KBr) 2940, 2860, 1442, 1270, 1228, 1202, 1163, 950, 748 cm^{-1}.

A solution of *t*-BuOK (4.57 g, 40.7 mmol) in THF (40 mL) was slowly added to a stirred solution of *trans*-2,3-dibromobicyclo[2.2.2]octane (9.98 g, 37.2 mmol) in THF (10 mL). After being stirred for 2 h at 45–50 °C the mixture was treated with water and extracted with ether to give crude 2-bromobicyclo[2.2.2]oct-2-ene (7.00 g, 100%) as a colorless oil, which was used for the next reaction without further purification: ^1H NMR ($CDCl_3$) δ 6.33 (dd, J = 7.6, 2.2 Hz, 1 H, =CH), 2.70 (s, 1 H, CH), 2.55 (s, 1 H, CH), 1.46 (br s, 8 H, CH_2); ^{13}C NMR δ 133.7 (d), 122.9 (s), 40.9 (d), 33.2 (d), 26.1 (t), 25.7 (t); IR (CCl_4) 2950, 2870, 1615, 1472, 1452, 1338, 1253, 1010, 870, 677 cm^{-1}.

Bromine (9.18 g, 57.4 mmol) was slowly added over the course of 4 h to a stirred solution of 2-bromobicyclo[2.2.2]oct-2-ene (10.22 g, 54.6 mmol) in CCl_4 (54 mL) at 75 °C. The mixture was washed with 10% $Na_2S_2O_3$ and 10% NaCl, dried ($MgSO_4$), and evaporated to give 2,2,3-tribromobicyclo[2.2.2]octane (18.2 g, 96.2%) as white crystals: mp 160–161.5 °C (recrystallized from ethanol); ^1H NMR ($CDCl_3$) δ 4.92 (br s, 1 H, CHBr), 2.57 (br s, 1 H, CH), 2.40–1.40 (m, 9 H, CH_2 + CH); ^{13}C NMR ($CDCl_3$) δ 76.8 (s), 66.9 (d), 46.0 (d), 38.0 (d), 25.3 (t), 24.9 (t), 23.6 (t), 17.5 (t); IR (KBr) 2950, 2870, 1473, 1455, 1340, 1220, 960, 898, 860, 783 cm^{-1}. Anal. Calcd for $C_8H_{11}Br_3$: C, 27.70; H, 3.20. Found: C, 27.49; H, 3.20.

A solution of *t*-BuOK (3.64 g, 31.0 mmol) in THF (32 mL) was added to a stirred solution of 2,2,3-tribromobicyclo[2.2.2]octane (10.2 g, 29.5 mmol) in THF (8 mL). After being stirred at 45 °C for 1.5 h, the mixture was treated with water and extracted with ether to give crude 10, which was purified by MPLC. Elution with hexane afforded 10 (7.34 g, 93.6%) as white crystals: mp 51.5–53 °C (recrystallized from ethanol); ^1H NMR ($CDCl_3$) δ 2.95 (br s, 2 H, CH), 1.55 (br s, 8 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 122.5 (s), 43.8 (d), 26.2 (t); IR (KBr) 2950, 2860, 1605, 1450, 1322, 1128, 1045, 1025, 999, 850, 670 cm^{-1}; UV (CH_3CN) λ_{max} 206 nm (log ϵ

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Table III. Spectral and Analytical Data of 11 (n = 2, 3, 4, 5)

compd (mp, °C)	^{1}H NMR ($CDCl_3$) δ		^{13}C NMR ($CDCl_3$) δ			IR (KBr) ν, cm^{-1}			UV (c-C_6H_{12}) λ_{max}, nm (log ε)
	CH_2	CH	CH_2	CH	=CH				
11 (n = 2)[a]	1.53	2.76	26.3	38.1	119.4	2940	2860	1605	236 (3.79)
	(16 H)	(4 H)	26.4	42.2	143.9	1450	1328	1120	
(118–125)						1040	998	870	
						810	750	675	
11 (n = 3)[b]	1.50	2.60	26.4	34.8	118.9	2945	2860	1635	221 (3.91)
	(24 H)	(4 H)	26.7	39.3	139.7	1585	1468	1450	268 (3.89)
(172.5–174)		2.79	26.8	42.4	143.9	1330	1120	1030	333 (2.74)
		(2 H)				998	870	840	
						815	720	670	
11 (n = 4)[c]	1.49	2.58	26.5	35.6	118.0	2940	2860	1670	238 (4.18)
	(32 H)	(4 H)	26.6	35.8	139.6	1615	1467	1447	274 (3.99)
(204–206)		2.72	26.8	41.2	142.1	1325	1150	1040	
		(4 H)	26.9	42.8	144.4	1020	993	870	
						840	815	670	
11 (n = 5)[d]	1.38	2.35	26.4	34.7	118.2	2940	2855	1608	225 (4.16)
	1.40	(2 H)	26.5	36.1	137.9	1468	1448	1323	235sh (4.11)
(227.5–229)	1.46	2.56	26.81	37.9	141.1	1150	1025	995	280 (3.94)
	1.53	(2 H)	26.84	39.3	143.9	875	840	813	329 (4.01)
	1.56	2.77	27.5	42.9	144.2	670			
	(40 H)	(4 H)							
		2.90							
		(2 H)							

[a] MS m/z (relative intensity) 374 (50), 372 (100), 370 (50). [b] Anal. Calcd for $C_{24}H_{30}Br_2$: C, 60.27; H, 6.32; Br, 33.41. Found: C, 60.55; H, 6.36; Br, 33.61. [c] Anal. Calcd for $C_{32}H_{40}Br_2$: C, 65.76; H, 6.90; Br, 27.34. Found: C, 66.04; H, 6.93; Br, 27.35. [d] Anal. Calcd for $C_{40}H_{50}Br_2$: C, 69.56; H, 7.30; Br, 23.14. Found: C, 69.53; H, 7.36; Br, 22.93.

3.81), 251 (2.54). Anal. Calcd for $C_8H_{10}Br_2$: C, 36.12; H, 3.79. Found: C, 35.82; H, 3.76.

Reaction of 10 with n-Butyllithium. (a) General Procedure. To a stirred solution of **10** (2.81 g, 10.5 mmol) in THF (48 mL) cooled at −78 °C was slowly added over 5 min a solution of 1.9 M n-BuLi in hexane (5.0 mL, 9.5 mmol). The solution, which turned to light orange, was stirred at −78 °C for 0.5 h and then quenched with methanol (2 mL). The mixture was then treated with water (25 mL) and extracted with ether (35 mL × 4) and with CH_2Cl_2 (50 mL × 3). Drying ($MgSO_4$) and evaporation of the solvents gave a crude mixture (1.61 g) composed of a white powder and a yellowish viscous oil. To this mixture was added CH_2Cl_2 (14 mL), and insoluble materials were separated by filtration. The filtrate was evaporated, and the residue was washed with CH_2Cl_2 (20 mL) and then with hexane (10 mL). All the insoluble materials were combined and dried in vacuo to give 0.163 g of a white powder. This powder was dissolved in hexane (65 mL), applying ultrasound irradiation, and each 20-mL portion was subjected to MPLC over silica gel using a high absorbent/sample ratio (550 g/50 mg of sample) and hexane as an eluent. From the earlier fractions was isolated **11** (n = 4) (0.0744 g) as a white powder. An additional 0.0424 g was obtained from the last fractions of another MPLC described below (total yield, 7.6%). For the analytical and spectral data of **11** (n = 2–5) (recrystallized from hexane), see Table III. From the following fractions was isolated **11** (n = 5) (0.0880 g) as a white powder. An additional 0.0191 g was similarly obtained (total yield, 7.4%). The rest of the mixture (1.45 g) was subjected to MPLC over silica gel eluted with hexane using the adsorbent/sample ratio of 250 g/1 g of sample. From the first fractions was obtained a mixtue (0.154 g) of minor products (more than four components) whose structures were not determined. The second fractions gave **13** (0.0628 g, 2.5%) as an unstable pale yellow oil, for which elemental analysis could not be conducted: ^{1}H NMR ($CDCL_3$) δ 2.72 (br s, 1 H, CH), 2.59 (br s, 1 H, CH), 2.20 (t, 2 H, CH_2), 1.80–1.20 (br m, 12 H, CH_2), 0.92 (t, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 143.4 (s), 117.3 (s), 41.9 (d), 36.9 (d), 33.3 (t), 29.7 (t), 26.7 (t), 26.2 (t), 22.4 (t), 14.1 (q). From the third fractions was obtained **14** (0.0183 g, 1.0%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.80 (br s, 1 H, CH), 2.60 (br s, 1 H, CH), 2.44 (br s, 2 H, CH × 2), 2.07 (t, 2 H, CH_2), 1.56–1.26 (m, 20 H, CH_2), 0.89 (t, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 143.5 (s), 140.4 (s), 135.9 (s), 117.2 (s), 42.0 (d), 38.4 (d), 34.3 (d), 33.5 (d), 32.4 (t), 30.4 (t), 26.9 (t), 26.6 (t), 26.3 (t), 26.2 (t), 22.9 (t), 14.1 (q). Anal. Calcd for $C_{20}H_{29}Br$: C, 68.76; H, 8.37; Br, 22.87. Found: C, 68.79; H, 8.62; Br, 23.08. The fourth fractions contained a mixture of dimeric compounds **15** and **16**. Fair separation of these two components was attained by repeated MPLC. **15**: pale yellow oil (0.239 g, 15.4%); ^{1}H NMR ($CDCl_3$) δ 6.27 (dd, J = 7.0, 1.8 Hz, 1 H, =CH), 2.94 (br s, 1 H, CH), 2.79 (br s, 1 H, CH), 2.56 (br s, 2 H, CH × 2), 1.49 (br s, 16 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 143.8 (s), 142.0 (s), 130.9 (d), 116.0 (s), 43.3 (d), 38.1 (d), 32.0 (d), 30.0 (d), 26.4 (t), 26.1 (t) 26.0 (t), 25.8 (t). **16**: colorless oil (0.141 g, 9.9%); ^{1}H NMR ($CDCl_3$) δ 6.08 (dd, J = 6.8, 1.8 Hz, 1 H, =CH), 2.79 (br s, 2 H, CH × 2), 2.52 (br s, 2 H, CH × 2), 1.65–1.26 (m, 22 H, CH_2), 0.88 (t, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 144.9 (s), 144.5 (s), 140.7 (s), 128.9 (d), 42.1 (d), 39.5 (d), 35.7 (d), 33.7 (d), 33.0 (t), 31.6 (t), 26.8 (t), 26.5 (t), 26.4 (t), 26.1 (t), 22.7 (t), 14.3 (q). Elemental analysis was not conducted because of incomplete separation. The fifth fractions mainly contained **11** (n = 3) contaminated with **11** (n = 4) and **11** (n = 5). By repeated MPLC **11** (n = 3) (0.550 g, 32.8%) was isolated as white powder, as well as **11** (n = 4) (0.0424 g) and **11** (n = 5) (0.0191 g).

When the reaction was carried out for 1 h at −78 °C and quenched after the temperature was raised to room temperature, a similar procedure as above afforded **13** (2.0%), **14** (7.4%), **15** (7.3%), **16** (1.0%), **11** (n = 3) (35.0%), **12** (4.4%), **11** (n = 4) (10.2%), and **11** (n = 5) (8.6%).

(b) Reaction Using a Smaller Equivalent of n-Butyllithium. A solution of 1.6 M n-BuLi in hexane (0.375 mL, 0.60 mmol) was added dropwise to a stirred solution of **10** (0.266 g, 1.00 mmol) in THF (5 mL) over 5 min at −78 °C. After stirring for 0.7 h at −78 °C, the solution was slowly warmed to room temperature over the course of 2 h and worked up in the same way as described above. From the crude product (0.148 g) were separated by means of MPLC eluted with hexane the components with R_f 0.57–0.64 (hexane/silica gel), which were then completely separated by the use of gel permeation chromatography (column, Shodex GPC HF-2002 with 20-mm diameter;[27] eluent, THF). From the first fraction was obtained **11** (n = 3) (0.0295 g, 18.4%). The second fraction afforded **11** (n = 2) (0.0226 g, 12.1%). From the third fraction was recovered **10** (0.0141 g, 5.3%).

(c) Effects of Added Chlorotrimethylsilane. A solution of 1.6 M n-BuLi in hexane (0.15 mL, 0.23 mmol) was added dropwise over 1 min to a stirred solution of **10** (0.0608 g, 0.229 mmol) in THF (1.1 mL) at −78 °C. After stirring for 3 min chlorotrimethylsilane (0.25 g, 2.3 mmol) was added, and the mixture was stirred for 15 min at −78 °C. The mixture was slowly warmed

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[27] We thank Professor Toshimitsu Suzuki and Professor Yoshihisa Watanabe of Kyoto University for the use of this column.

to room temperature and then evaporated under reduced pressure. The residue was extracted with ether to give a crude product (0.0411 g), whose ^{1}H and ^{13}C NMR spectra showed the presence of **11** ($n = 3$) as a main component and only a negligibly small signal of the trimethylsilyl group.

(d) Effects of Added Metallic Catalysts. The reaction was carried out in the same way as described in section a in the presence of 5 mol % of either nickelocene, $NiBr_2(PPh_3)_2$, or $Pd(PPh_3)_4$. In each reaction the product was shown to be mainly **11** ($n = 3$) with no appreciable increase in the yield of **12**.

(e) Trapping of Bicyclo[2.2.2]octyne (18) with Diphenylisobenzofuran (17). Into a stirred solution of **10** (0.299 g, 1.12 mmol) and **17** (0.302 g, 1.12 mmol) in THF (22 mL) cooled at −78 °C was slowly added a solution of 1.9 M *n*-BuLi in hexane (0.60 mL, 1.14 mmol) over the course of 3 min. After stirring at −78 °C for 0.5 h, the solution was quenched with methanol, treated with water, and worked up. To the crude product was added hexane (2 mL), and unchanged **17** (0.0798 g, 26.3%) was isolated as an insoluble yellow powder. The hexane-soluble materials were separated by MPLC over activated alumina (Nakalai, 300 mesh). From the fraction eluted with hexane was recovered unchanged **10** (0.0587 g, 19.7%), while the following fractions eluted with hexane–ether (40:1) afforded **19** (0.268 g, 63.6%; 86.3% based on consumed **10**) as white crystals: mp 98–101 °C (recrystallized from pentane); ^{1}H NMR ($CDCl_3$) δ 7.75 (dm, 4 H, H-ortho), 7.49 (t, 2 H, H-para), 7.43 (dm, 4 H, H-meta), 7.09 (dd, $J = 5.2, 3.1$ Hz, 2 H, H-2), 6.92 (dd, $J = 5.2, 3.1$ Hz, 2 H, H-1), 3.10 (br s, 2 H, H-6), 1.56 (br d, 4 H, H-7), 1.40 (d, $J = 7.9$ Hz, 2 H, H-8(anti)), 0.34 (d, $J = 7.9$ Hz, 2 H, H-8(syn)); ^{13}C NMR ($CDCl_3$) δ 157.4 (s, C-5), 152.1 (s, C-3), 135.1 (s, C-ipso), 128.6 (d, C-ortho), 128.5 (d, C-meta), 128.4 (d, C-para), 124.5 (d, C-1), 120.1 (d, C-2), 93.7 (s, C-4), 31.8 (d, C-6), 26.8 (t, C-8), 25.4 (t, C-7); IR (KBr) 3050, 2940, 2860, 1600, 1500, 1447, 1335, 1305, 995, 980, 750, 700, 670 cm^{-1}. Anal. Calcd for $C_{28}H_{24}O$: C, 89.33; H, 6.42. Found: C, 88.60; H, 6.27.

When subjected to MPLC over silica gel eluted with hexane–ether (10:1), the adduct **19** quantitatively isomerized to the ketone **19′**: yellow crystals; mp 218–220 °C (recrystallized from hexane); ^{1}H NMR ($CDCl_3$) δ 7.65–7.03 (m, 13 H, aromatic H), 6.68 (dd, $J = 7.1, 1.3$ Hz, 1 H, H-α), 3.13 (br s, 1 H, CH), 2.57 (br s, 1 H, CH), 1.58 (br d, 4 H, CH_2), 1.35 (br s, 4 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 146.5 (s), 139.9 (s), 138.7 (s), 138.6 (s), 133.3 (d), 132.8 (s), 130.6 (d), 129.8 (s), 129.2 (d), 128.7 (d), 128.6 (d), 128.4 (d), 127.3 (d × 2), 126.8 (d), 126.5 (d), 126.2 (d), 61.2 (s), 32.4 (d), 31.8 (d), 27.6 (t), 24.6 (t), 22.1 (t), 21.3 (t); IR (KBr) 3080, 2940, 2860, 1680, 1593, 1445, 1280, 1250, 778, 763, 748, 710, 700 cm^{-1}. Anal. Calcd for $C_{28}H_{24}O$: C, 89.33; H, 6.42. Found: C, 89.34; H, 6.47.

Synthesis of Tris(bicyclo[2.2.2]octeno)benzene (12) by Reductive Cyclization of 11 (*n* = 3). (a) By the Use of *n*-Butyllithium. A solution of 1.6 M *n*-BuLi in hexane (0.20 mL, 0.32 mmol) was added to a stirred solution of **11** ($n = 3$) (0.0709 g, 0.148 mmol) in THF (1.5 mL) at room temperature. After stirring for 0.5 h, the resulting pale orange solution was treated with water, extracted with ether, and dried over $MgSO_4$. GLC (column, silicone gum SE30) and ^{13}C NMR analyses on the ethereal solution which was carefully concentrated to ca. 0.5 mL indicated the formation of **12** and octane (^{13}C NMR δ 32.5 (t), 29.9 (t), 23.1 (t), 14.2 (q)) as main products. By complete evaporation and purification on a short silica gel column eluted with hexane, there was obtained **12** (0.0378 g, 80.4%) as white crystals (colorless needles from ligroin): mp 277–279 °C (sealed tube); ^{1}H NMR ($CDCl_3$) δ 3.29 (s, 6 H, CH), 1.75 (d, $J = 7.0$ Hz, 12 H, CH_2(anti)), 1.35 (d, $J = 7.0$ Hz, 12 H, CH_2(syn)); ^{13}C NMR ($CDCl_3$) δ 134.2 (s), 28.7 (d), 26.5 (t); IR (KBr) 2945, 2855, 1465, 1450, 1328, 1230, 1183, 1145, 1030, 860, 810 cm^{-1}; UV (CH_3CN) λ_{max} 222 sh nm (log ϵ 3.62), 260 (2.47). Anal. Calcd for $C_{24}H_{30}$: C, 90.51; H, 9.49. Found: C, 90.34; H, 9.55.

(b) By the Use of Sodium Naphthalenide as a Reductant. To a stirred solution of **11** ($n = 3$) (0.659 g, 1.38 mmol) in THF (20 mL) was slowly added over the course of 5 min a solution of 0.74 M sodium naphthalenide in THF (4.6 mL, 3.4 mmol). Addition of each drop of the naphthalenide solution caused rapid coloration to deep red-purple, which slowly changed to brown. After stirring for 0.5 h the reaction mixture was quenched with water and extracted with ether to give 0.969 g of the crude product, whose ^{1}H NMR spectrum indicated the presence of only **12** and naphthalene. The mixture was evacuated at 10^{-3}–10^{-4} mmHg at room temperature for 5 h to remove naphthalene, which was collected in a liquid nitrogen trap (0.424 g, 98.8%). The residual yellowish white powder was recrystallized from ligroin (21 mL) to give **12** (0.160 g) as colorless needles. The additional amounts (0.130 g + 0.090 g, total yield 88.5%) were obtained as the second and third crops from the filtrate.

ESR Measurements of $12^{\bullet+}$. (a) Electrolytic Oxidation. An originally made electrolytic cell was used. The cell consisted of a 5-mm o.d. Pyrex glass tube (length, 65 mm) which was connected to a 3-mm o.d. tube (length, 40 mm) at the bottom and a 20-mm o.d. tube (length, 40 mm) at the top. A platinum wire (diameter, 0.5 mm) reaching the bottom, which was shielded with a polyethylene tube except at the bottom part, served as a working electrode, while a coiled gold wire (diameter, 0.5 mm) placed in an upper part served as a counter electrode. A reference electrode ($Ag/AgNO_3$) was also inserted into an upper part together with a capillary polyethylene tube for the purpose of introducing an argon gas.

A solution of **12** (0.0057 g, 0.018 mmol) in 5 mL of a 0.1 M solution of $Bu_4N^+ClO_4^-$ in CH_3CN was placed in this cell. After bubbling with argon for a few minutes, the solution was electrolyzed at +1.5 V vs $Ag/AgNO_3$. The ESR signal shown in Figure 2 appeared 1–2 min after initiation of electrolysis and lasted for 5–10 min after cutting off the anodic current. The same result was also obtained using CH_3NO_2 as a solvent.

(b) Oxidation in Sulfuric Acid under Air. To **12** (0.0028 g) placed in a test tube was added concentrated H_2SO_4 (0.1 mL). Only a part of the hydrocarbon dissolved. The pale-yellow supernatent solution was taken in capillary glass tubes and subjected to the ESR measurement. The essentially same spectrum as shown in Figure 2 with g value of 2.00265 was obtained.

Formation of the Arenium Ion 22. (a) UV–Vis Measurements. A vacuum-line quartz cell[28] (cell path, 10 mm) was used, which was connected to a Pyrex glass tube having side arms. In one of the side arms was placed **12** (0.785 mg, 2.47 × 10^{-3} mmol) weighed in a small glass container by the use of a microbalance. In another side arm was placed FSO_3H (3.00 mL) by the use of a pipette under an argon atmosphere. The cell tube was evacuated to 10^{-4}–10^{-3} mmHg while the solvent was cooled by liquid nitrogen. After three freeze–pump–thaw cycles, the tube was sealed under vacuum. The spectrum was recorded right after dissolving **12** in FSO_3H by mixing at room temperature.

(b) ^{13}C NMR Measurements. In a 5-mm o.d. NMR tube was placed **12** (0.0330 g, 0.104 mmol) together with a capillary tube containing methanol-d_4 as a lock solvent. Into this tube was added FSO_3H (0.50 mL) or FSO_3H–SbF_5 under an argon atmosphere, and the tube was immediately evacuated with cooling at −78 °C and sealed under vacuum or under an argon atmosphere. The ^{13}C NMR spectra were taken at various temperatures, and the chemical shifts were recorded with reference to the signal of methanol-d_4 taken as δ 47.87 ppm.

(c) Acidity Measurements of Arenium Ions 22 and 23. The pK_{AH^+} value of hexamethylbenzene (HMB) was taken as −9.01 from the literature data.[22,23] A series of aqueous H_2SO_4 ranging from 94% to 99% were prepared, and the precise H_0 value of each aqueous H_2SO_4 was determined from eq 5 using HMB as an indicator. Degrees of protonation of **12** and HMB in each H_2SO_4 were determined as described below for the case of **12** as an example. Each 50 μL of a stock solution of **12** in acetic acid (2.76 × 10^{-3} M) was dissolved in 5.00 mL of the appropriate H_2SO_4 solution in a vacuum quartz cell described above and sealed under vacuum. In solutions with relatively low acidity, the ion **22** was found to be rather unstable and gradually decreasing in its absorption. Therefore readings were made during the first 5–10 min and the data extrapolated to time zero to obtain an estimate of the absorption for the time of mixing. The results are shown in Table II.

Acknowledgment. We are grateful to Professor Harold Hart of Michigan State University for his interest and helpful discussions and to Professor Takashi Kawamura

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of Gifu University for providing the facilities for ESR measurements and for his kind advice on a electrochemical ESR cell. We also thank Mr. Hidekazu Akamatsu for preliminary experimental work. This work was partially supported by a Grant-in-Aid from Ministry of Education, Science and Culture of Japan.

Supplementary Material Available: Figure 5 plotting the percent protonation of **12** against H_0 of the solvent (1 page). Ordering information is given on any current masthead page.

12-Crown-4 Ethers: Solid-State Stereochemical Features of Dibenzo-12-crown-4, Derived Dicyclohexano-12-crown-4 Isomers, and a Lithium Thiocyanate Complex As Determined via ^{13}C CPMAS Nuclear Magnetic Resonance and X-ray Crystallographic Methods

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Received June 28, 1990

Solid-phase ^{13}C NMR spectra are presented for the title systems. For dibenzo-12-crown-4, *cis-anti-cis*-dicyclohexano-12-crown-4, and the LiNCS complex of the cis-syn-cis isomer, asymmetric units derived from the NMR data are consistent with single-crystal X-ray data. In the uncomplexed cis-syn-cis isomer, intermolecular crystal packing effects are shown to render intramolecularly equivalent carbons nonequivalent. Some factors contributing to the ^{13}C steric shifts in these molecules are discussed.

Introduction

The stereochemical features of solid 12-crown-4 ether itself have been well documented, its crystallographic conformation having been elucidated by X-ray methods at a temperature of −150 °C.[1] Upon complexation with a variety of metal ions, three different ring conformations also have been determined by X-ray crystallography.[2-6] In contrast, the related dibenzo-12-crown-4 ether (**1**) has been reported to be incapable of acting as a host molecule for complexation.[7] The crystal structure of **1** has been reported,[8,9] and the results indicate a large deviation from planarity for the four oxygen atoms, which may account in part for the material's inability to form isolable complexes with metal ions.

To date, no reports of the solid-state properties of the related dicyclohexano-12-crown-4 ether systems have appeared. These molecules are expected to exhibit more stereochemical flexibility than their dibenzo precursor and hence may be capable of forming isolable complexes. Herein we present the details of the X-ray crystallographic results for the cis-anti-cis (**2**) and cis-syn-cis (**3**) isomers of dicyclohexano-12-crown-4, as well as the LiNCS complex of **3**.

In addition, we have recorded the ^{13}C CPMAS NMR spectra of **1**, **2**, **3**, and **3**·LiNCS, which further illustrate the utility of this technique[10-13] for the determination of the asymmetric units in the crystal. Some remarkably large steric ^{13}C shifts have been observed in these solids and with the X-ray data in hand, a detailed discussion of geometrical influences on carbon chemical shifts is presented.

Chart I. Comparison of Torsion Angles for C7 and C8 of 2 (H's Not Included)

C_7		C_8	
network	θ, deg	network	θ, deg
O2–*C7*–C8–O1	78.2	O_2–C7–*C9*–O1′	78.2
C7–O2–C2–C1	149.4	*C8*–O1′–C1′–C2′	99.1
C7–O2–C2–C3	90.7	*C8*–O1′–C1′–C6′	136.4
C7–C8–O1′–C1′	165.4	*C8*–C7–O2–C2	106.1
C8–*C7*–O2–C2	106.1	*C7*–C8–O1′–C1′	165.4

Results and Discussion

The structural formulae and numbering schemes for the molecules studied herein are depicted in Figure 1. The numbering schemes employed are chosen to be consistent with X-ray data output rather than with IUPAC convention. Bond lengths and angles for **2**, its configurational isomer **3**, and **3**·LiNCS are listed in Table I. Torsion angles involving ring skeletal atoms for **2**, **3**, and **3**·LiNCS are provided in Table II and Chart I along with data for 12-crown-4 itself. Figure 2 shows stereoviews of the derived crystal structures while the ^{13}C CPMAS NMR spectra are presented in Figures 3–5. In Table III are listed the solid-phase ^{13}C NMR chemical shifts for **1**, **2**, **3**, and **3**·

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