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The chemistry of cyclic π-systems surrounded by rigid σ-frameworks: Blending a σ-flavor into the aromatics

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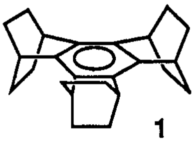
Abstract— Unique new properties are expected for the cyclic π-systems when they are completely surrounded by rigid σ-frameworks. From this viewpoint, a series of π-conjugated cyclic systems composed of five- to eight-membered rings fully annelated with bicyclo[2.2.2]octene units were prepared by reductive cyclization of α,ω-dibromides of bicyclo[2.2.2]-octene-2,3-diyl oligomers (n=3,4,5) as the key step. Not only the steric effects but both the inductive and σ-π conjugative electronic effects of the σ-frameworks were found to greatly stabilize the π-system especially when it bore the positive charge. These hydrocarbons were also characterized by readiness in undergoing reversible one-electron red-ox process. Thus, not only the closed-shell ionic species but also the open-shell states seem to be stabilized by the presence of bicyclic σ-frameworks.

INTRODUCTION

Needless to say, it is the π-electron that plays the dominant role in the chemistry of the aromatic compounds, while the σ-frameworks serve to control the shape of π-electronic systems. Then, what would happen to the properties of the original π-conjugated system when it is completely surrounded by rigid σ-frameworks? Not only the inductive effects but the σ-π conjugative effects would operate especially when the σ-frameworks provide the σ-bonds rigidly fixed at the position nearly parallel to the 2p-orbitals of the π-system. The σ-frameworks would also sterically block the π-system causing kinetic stabilization. A typical example of such structural modification is the annelation with bicyclo[2.2.2]octene (BCO) framework, which is rigid enough and yet free from imposing extra strain to the molecule. Recently we found a convenient method to construct a series of π-conjugated systems ranging from five- to eight-membered rings which are fully annelated with the BCO frameworks, as exemplified by the compounds **1** (ref. 1,2), **2** (ref. 3), **3**$^{2-}$ (ref. 4), and **4** (ref. 5).



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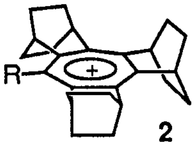

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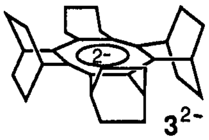
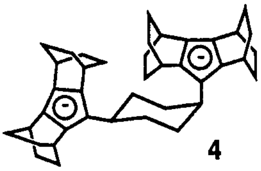


3^{2-}



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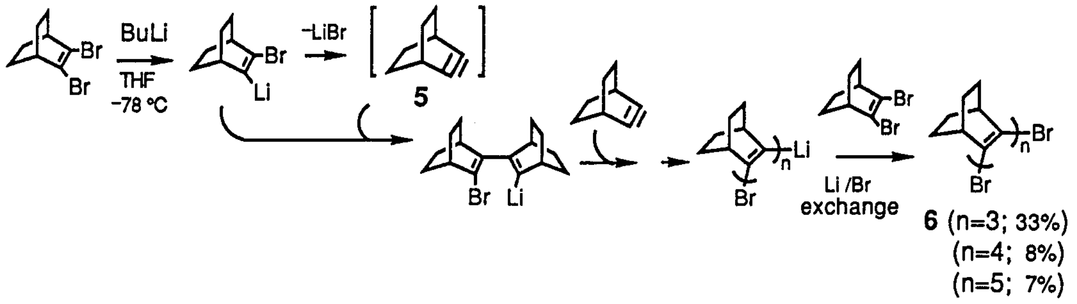
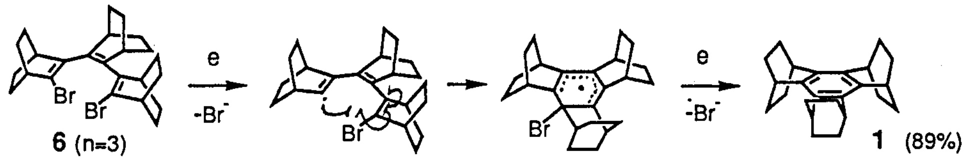
This method utilizes the reductive cyclization of the terminal dibromides of bicyclo[2.2.2]oct-2-ene-2,3-diyl oligomers **6** (n=3,4,5), which were obtained by a rather unexpected reaction involving a highly strained acetylene, bicyclo[2.2.2]octyne (**5**), as a reactive intermediate (ref. 2). The generation of **5** has been proved by a trapping experiment.



TRIS(BICYCLO[2.2.2]OCTENO)BENZENE

Upon reduction with two equivalents of sodium naphthalenide, cyclization occurred at the terminal carbons of the dibromides **6** (n=3) to give the benzene derivative **1** in high yield. The reaction presumably proceeds by way of consecutive one-electron transfer and radical cyclization.



The benzene **1** is characterized by its highly symmetrical (D_{3h}) structure as demonstrated by X-ray analysis (Fig. 1; ref. 1), and exhibits a well-defined reversible oxidation peak at $E_{1/2}$ +1.25 V vs Ag/Ag^+ upon cyclic voltammetry (CV), which is quite unusual for polyalkylbenzenes (ref. 1,2). The electrolytically generated cation radical $\mathbf{1}^{+\cdot}$ is persistent under an inert atmosphere and exhibits a thirteen-line ESR signal due to the coupling with twelve anti-protons of the ethano bridges (ref. 2). The same species was also generated by simply dissolving **1** into sulfuric acid under air. This remarkable stability is attributed to both the electronic and steric effects of the rigid σ-frameworks. Particularly effective would be the so-called "Bredt's rule protection" (ref. 6), since the supposedly most labile α-hydrogen of the σ-framework is structurally protected from deprotonation.

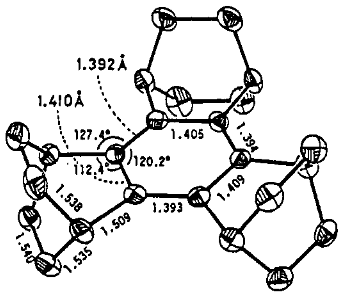


Fig. 1. X-ray crystal structure of **1**.

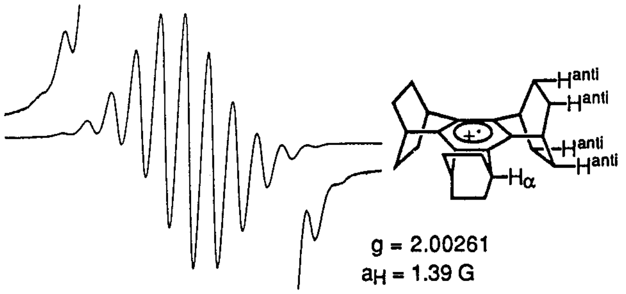
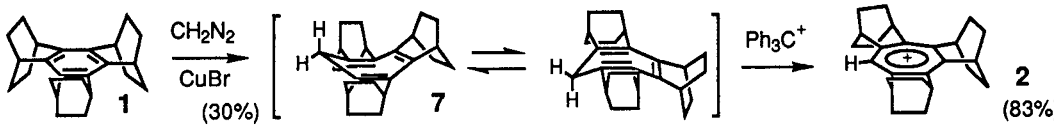


Fig. 2. ESR spectrum of $\mathbf{1}^{+\cdot}$ in acetonitrile.

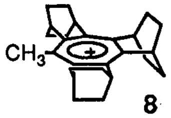
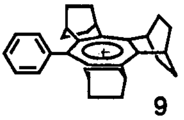
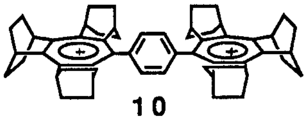
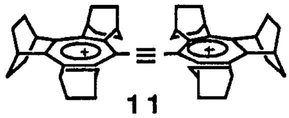
TRIS(BICYCLO[2.2.2]OCTENO)TROPYLIUM ION AND ITS DERIVATIVES

Syntheses

In spite of the severe steric hindrance caused by the surrounding σ-frameworks, the benzene **1** was ring-expanded to the cycloheptatriene **7** by the use of diazomethane in large excess.



The energy barrier for ring inversion of **7** was unexpectedly low (8.5 kcal/mol; ref. 7) and almost comparable to the value for unsubstituted cycloheptatriene (about 6 kcal/mol; ref. 8), whereas the values for hexamethyl- and tribenzo-derivatives are much larger than 20 kcal/mol (ref. 7, 9). This suggests that the steric repulsion between the bridgehead hydrogens is not too severe in the nearly planar transition-state structure for the ring inversion. In accordance with this prediction, the supposedly planar tropylium ion **2** was readily obtained from **7**, and was found to exhibit remarkably high thermodynamic stability. From its $pK_{R}+$ value (13.0 in 50% aq. acetonitrile; ref. 3), **2** is regarded as the most stable tropylium ion ever synthesized. The tropylium ion **2** (λ_{max} (CH_3CN) 256 nm (log ε 4.71) 308 (4.01)) reacted with alkyl-, alkynyl, and aryl-lithium reagents at the 7-position, and was transformed into the corresponding 7-substituted derivatives **8** - **11** in good yields (ref. 3b, 10). The $pK_{R}+$ value (50% aq. acetonitrile) and the red-ox behavior of these stable cations (CV in acetonitrile) are shown below together with the data of electronic absorptions .

	 **8**	 **9**	 **10**	 **11**
$pK_{R}+$	12.4 ±0.5	12.0 ±0.1	11.5 ±0.2	7.0 ±0.1, 11.5 ±0.1
E_{pc} /V vs Ag/Ag⁺	-1.09 (irrev.)	-1.13 (rev.)	-1.01 (quasi rev.)	-0.52 (rev.), -0.70 (rev.) (in CH_2Cl_2)
λ_{max} /nm (log ε) (CH_3CN)	262 (4.73) 317 (3.93)	260 (4.67) 314 (3.92)	261 (4.98) 314 (4.23)	282 (4.83) 386 (4.39)

Thermodynamic stability

In spite of its electron donating ability, the methyl substituent in **8** was shown to rather destabilize the original cation **2** by about 0.6 $pK_{R}+$ unit (ref. 3). This is supposedly resulting from the distortion from coplanarity either of the exocyclic bonds or of the tropylium ring itself due to the severe steric congestion around the seven-membered ring. The similar destabilization has previously been observed for the heptamethyltropylium ion (ref. 11). Similarly, the 7-phenyl derivative **9** is destabilized by 1.0 $pK_{R}+$ unit. Due to the steric requirements, the phenyl ring can only take the conformation nearly orthogonal to the tropylium ring, and therefore would merely act as an inductively electron-withdrawing group. In this way, the *p*-phenylene unit in the dication **10** is expected to act as an insulator of π-conjugation between the two cationic units. In fact, both of the two tropylium units are simultaneously neutralized at pH 11.5.

In sharp contrast, the triple bond in the dication **11** with no such steric requirements can act as a conjugative connector of the two tropylium ring if the two rings assume the coplanar conformation across the triple bond. As another possibility, the two cationic units may take the conformation orthogonal to each other, utilizing the conjugation with the p-orbitals different from each other. The X-ray crystallography on **11**·$2SbF_6^-$ has not yet been conducted, but theoretical calculations (MINDO/3) for the model dication (the parent ditropylioacetylene dication) indicate that the two tropylium units are nearly orthogonal with the dihedral angle of 88° in the optimized structure. In any case, the electronic interaction between two positively charged moieties across the triple bond results in considerable destabilization of the dicationic system as a whole. Thus the first neutralization of the dication **11** occurs at the pH value as low as 7.0 (=$pK_{R+}{}^1$), while the second neutralization of the monocation occurs at pH 11.5 (=$pK_{R+}{}^2$).

In accordance with above discussions, the electronic spectrum exhibits considerable bathochromic shift only for the alkynyl conjugated dication **11** among the cations **2**, **8**, **9**, **10**, and **11**.

Red-ox behavior

Reflecting the high thermodynamic stability, the cations **2**, **8**, **9**, and **10** are quite reluctant to the one-electron reduction. The reduction requires the potential 0.5 - 0.6 V more negative than the parent tropylium ion (E_{pc} -0.52 V vs Ag/Ag$^+$). As shown in Fig. 3, the cations **9**, **10**, and **11** exhibit the reversible red-ox waves, whereas the reduction is irreversible for cations **2** and **8**.

From the phenyl-substituted cation **9**, a stable cycloheptatrienyl radical is generated as was demonstrated by a persisting ESR signal of a broad single line (peak-to-peak width 2.98 G, g=2.00233) upon electrolytic reduction at -1.5 V vs Ag/Ag$^+$ in acetonitrile. This is one of quite few examples of the stable tropyl radical that does not undergo dimerization (ref. 12).

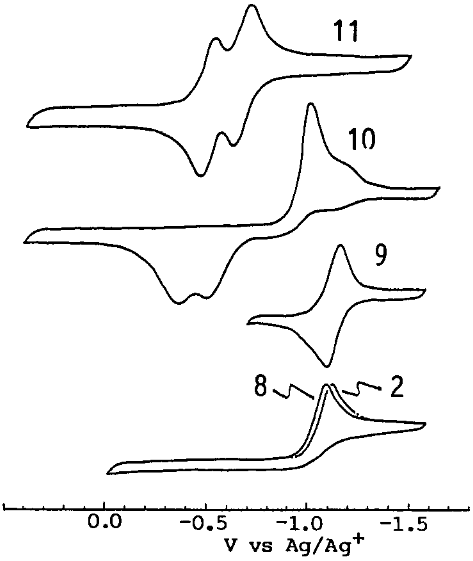


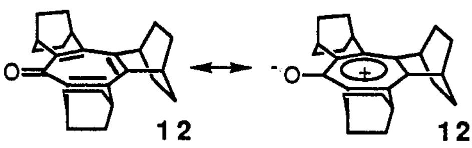
Fig. 3. The cyclic voltammograms for the cations **2**, **8**, **9**, and **10** in acetonitrile and **11** in dichloromethane; scan rate, 0.1 V·s^{-1}.

In the case of the dication **10**, the reduction appears to occur via a nearly one-step two-electron transfer, which is accompanied by considerable structural change corresponding to the shift of anodic peak by about 0.5 V (ca. 12 kcal/mol). Furthermore, no ESR signal was observed upon electrolytic reduction, suggesting that the product of two-electron reduction of **10** may possibly be the closed shell cross-conjugated compound rather than the diradical.

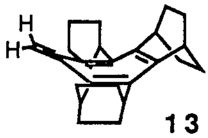
On the other hand, the dication **11** was shown to be more readily reduced than the rest of cations, by way of reversible and consecutive one-electron transfer processes. In this case, the complete electrolytic reduction afforded a species that exhibited a strong single-line ESR signal which persisted in dichloromethane at room temperature under argon (peak-to-peak width, 3.0 G, g=2.00257). However, it is not yet clear if this species is a triplet diradical or not.

TRIS(BICYCLO[2.2.2]OCTENO)-TROPONE AND -HEPTAFULVENE

The tropone and heptafulvene derivatives **12** and **13** were synthesized by oxidation of **7** with selenium dioxide and deprotonation of **8**, respectively (ref. 13). From lower wavenumber shifts of the IR stretching frequency (by ca. 40 and 10 cm^{-1}, respectively) of the exocyclic double bond (**12**, 1558 cm^{-1}; **13**, 1574 cm^{-1}), the compounds **12** and **13** are apparently more polarized than the parent compounds. Compared with parent tropone the basicity of **12** is nearly 2 pK units enhanced by contribution of the polarized structure **12'**, and its seven-membered ring is supposed to be essentially planar with no detectable energy barrier for ring inversion.



12 **12'**



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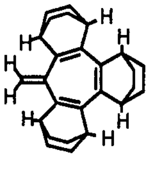
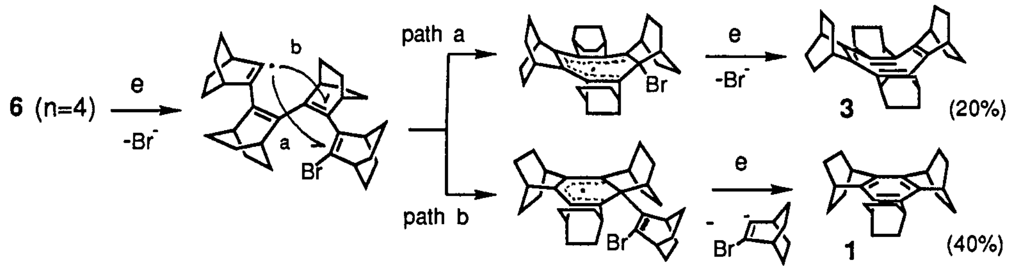


13'

In the case of the heptafulvene **13**, however, the planar structure **13'** is sterically unfavored due to the repulsion between the bridgehead and exomethylene hydrogens, and is 8.5 kcal/mol less stable than the boat form as estimated from the results of the dynamic NMR study. Nonetheless, the heptafulvene **13** is far more stabilized than the parent compound, which is a labile polyolefinic hydrocabon stable only in solution (ref. 14), by virtue of both the electronic effects and steric protection by the surrounding rigid σ-frameworks.

TETRAKIS(BICYCLO[2.2.2]OCTENO)CYCLOOCTATETRAENE

Reduction of the terminal dibromide of the "BCO" tetramer **6** (n=4) with two equivalents of sodium naphthalenide resulted in expected cyclization at terminal carbons to give the cyclooctatetraene (COT) derivative **3**. However, the major product was unexpectedly the benzene **1** with loss of one BCO unit. The whole reaction may have proceeded as shown below. The formation of a less strained six-membered ring seems to be more favored than the cyclization between the remote terminal carbons which should require the whole molecule to take a preorganized structure close to a tub-form of COT (ref. 4).



The X-ray crystal structure of the COT **3** is shown in Fig. 4 (ref. 4). Values of the external dihedral angle (θ) of the COT ring range from 41.3 to 44.9°. The structure was satisfactorily reproduced by MMP2 calculations except the θ value calculated somewhat larger (46.35°), and no extra strain was shown to be accumulated by cyclization of four BCO units. In spite of the severe congestion supposedly generated in the planar structure, the COT **3** was smoothly reduced to the orange-colored dianion $\mathbf{3}^{2-}$ upon treatment with potassium mirror in THF-d_8 under vacuum.

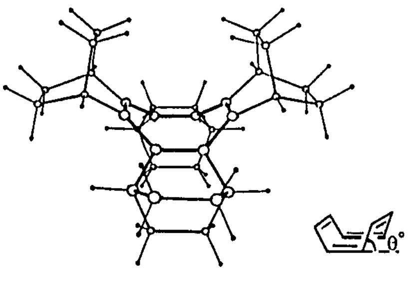
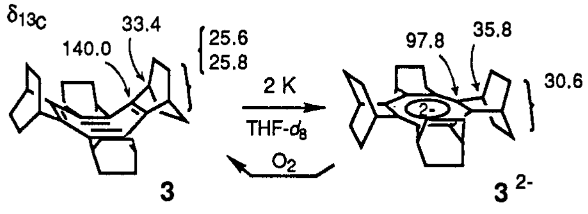
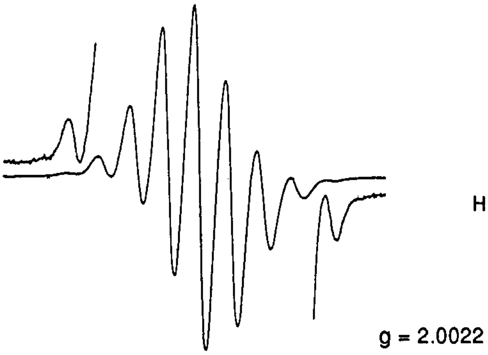


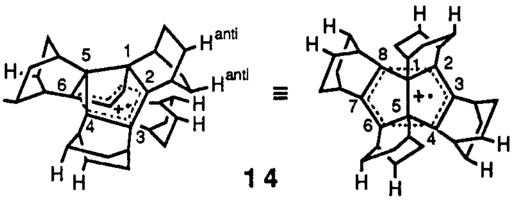
Fig. 4. X-ray crystal structure of **3**.



In contrast to the reduction of COT compounds, which has been extensively studied, the oxidation has been studied only little (ref. 15) due to instability of the unsaturated eight-membered ring toward oxidative conditions. The COT **3** seemed to be a good candidate for such study from the viewpoint of its structural rigidity. When examined by CV in dichloromethane, the COT **3** exhibited a well-defined reversible oxidation wave at $E_{1/2}$ +0.49 V vs Ag/Ag^+, and a green-colored solution of the cation radical was formed upon electrolytic oxidation, which showed an ESR signal persisting even at room temperature (Fig. 5). The same species was also obtained by chemical oxidation using antimony pentachloride (or nitrosonium hexachloroantimonate), and was isolated as a stable dark green crystals of $SbCl_6^-$ salt, which can be stored at 0°C for over a month without decomposition. This green salt can be reduced back to **3** by tetraethylammonium iodide, and its solution in acetonitrile exhibited two absorptions in a visible range: λ_{max} 408 nm (ε 1500) and 745 (1800).

The ESR signal of this species consists of a rather broad nine-line spectrum showing the coupling with equivalent (or nearly equivalent) eight protons, which is apparently not compatible with a simple planar COT structure as in the case of $\mathbf{3}^{2-}$. This appearance of the ESR signal together with the resemblance of the electronic spectrum to that of the semibullvalene cation radical recorded in Freon matrix at -196°C (ref. 16) suggests that the observed cation radical no longer retains the simple COT structure but has a structure such as **14** with the original eight-membered ring connected at C-1 and C-5 by a weak σ-bond. In this structure, extensive homoconjugation is expected over C-2,3,4,6,7,8 with high spin density at the carbons C-2, C-4, C-6, and C-8 in accord with coupling with eight anti-protons.





14

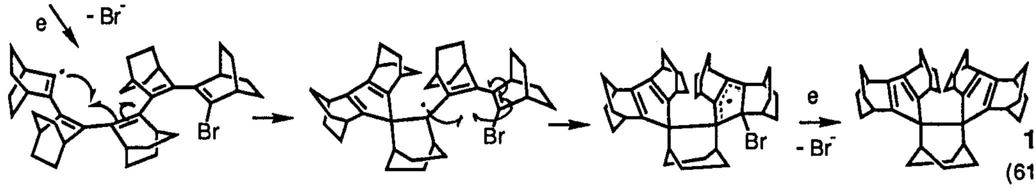
Fig. 5. ESR spectrum of $\mathbf{3}^{+\cdot}$ in dichloromethane.

This is the first example in which the cation radical from a COT derivative is isolated as a stable salt, and this extraordinary stability can be, again, attributed to the electronic and steric protection of the positively-charged π-system with the rigid σ-frameworks.

THE SPIRO-CONNECTED BICYCLO[2.2.2]OCTENE PENTAMER

In contrast to the reaction of lower homologs, the reduction of the pentameric dibromide **6** (n=5) did not yield either the monocyclized or ring-contracted product, but afforded at -78°C a bicyclo[2.2.2]octane having two spiro-connected cyclopentadiene rings, **15** ($C_{40}H_{50}$) (ref. 17). The reaction has most probably proceeded by way of the "tandem-" or "domino-" double cyclization shown below.

6 (n=5)



15
(61%)

As shown by the X-ray structure (Fig. 6), the hydrocarbon **15** is characterized by a highly congested structure with the two cyclopentadiene rings fixed at an arrangement facing but splayed out with each other by an angle of ca. 89° (ref. 18).

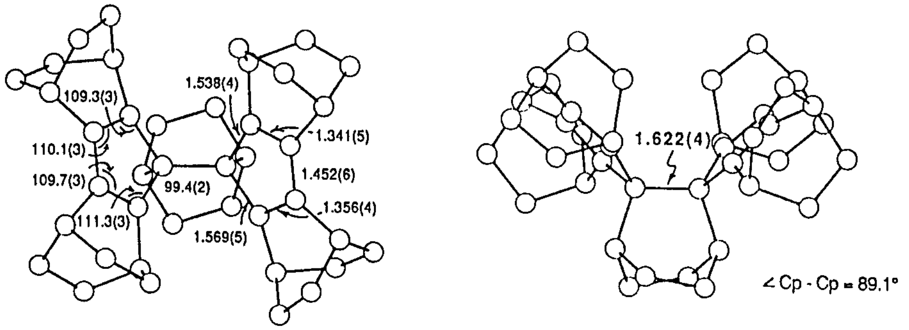
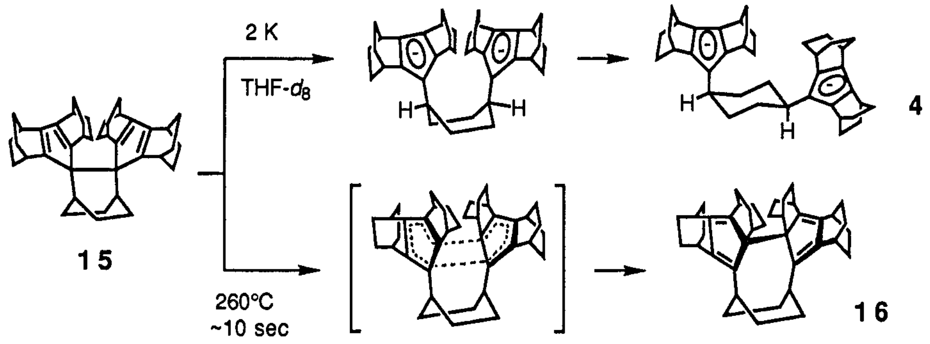


Fig. 6. X-ray crystal structure of **15** (left, top view; right, side view).

The most remarkable feature of this molecule is the elongation of the central single bond (1.622 Å) as compared with the normal value of 1.54 Å. Comparison of the results of two different types of calculations, molecular mechanics (MM2) and semi-empirical molecular orbital calculations (MNDO), suggests that this elongation has originated not only from the steric congestion but mainly from the through-bond interaction between the 2p orbitals of the two cyclopentadiene rings fixed at such close proximity.

Reflecting such weakening, this central bond of the compound **15** was readily cleaved by potassium metal to give a new cyclohexane having two BCO-annelated cyclopentadienide ion **4** (ref. 5). The bond cleavage also takes place thermally to give the isomeric hydrocarbon, which is tentatively assigned as **16** formed by the symmetry-allowed [5,5]sigmatropic reaction.



CONCLUDING REMARKS

Results of the present study have demonstrated that not only the elaboration on the π-system itself but also the structural modification of its surroundings with σ-frameworks can become an effective means for endowment of novel properties to various aromatic hydrocarbons the chemistry of which has been known for decades. The full exploitation of such methodology may be useful for creation of yet unknown hydrocarbon molecules with unique properties.

Acknowledgements

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