Cyclic π-Conjugated Systems Annelated with Bicycloalkene Frameworks

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The present article gives an account of the synthesis and chemical properties of the cyclic π-conjugated hydrocarbons annelated with bicyclic σ-frameworks. Particular emphasis is placed on π-systems carrying a positive charge, which is remarkably stabilized by complete annelation with bicyclo[2.2.2]octene. In such systems, not only the kinetic effects but also electronic effects due to σ-π conjugation affect the properties of the π-systems. The thermodynamic properties, redox behavior, and the X-ray crystal structures are discussed.

Introduction

It is the π-electron that plays a dominant role in the chemistry of cyclic π-conjugated systems, whereas the σ-frameworks serve to control the shape of the π-systems. However, the σ-frameworks can also work in a different way. When a C−C σ-bond is located in a position parallel to the p-orbital, the C−C hyperconjugation becomes effective, particularly interacting with the p-orbital that is empty. Such effects have, for example, been demonstrated theoretically for the 2-methyl-2-butyl cation[1] and experimentally for the 1-adamantyl cation.[2]

Thus, it is of particular interest to investigate the properties of the cyclic π-conjugated systems surrounded by rigid σ-frameworks such as bicycloalkenes. In such systems it is not only the inductive effects but the σ-π conjugative effects (i.e., the C−C hyperconjugative effects) that can operate because the bicycloalkenes can provide σ-bonds that are rigidly fixed in a position nearly parallel to the p-orbitals of the π-system.

In this paper, a review has been undertaken with regard to the cyclic π-systems annelated with bicycloalkenes, with particular attention placed on the stabilization of positively charged systems.

Annelation with Bicyclo[2.2.2]octene

Annelation with multiple units of bicycloalkene not only brings about the electronic effects mentioned above, but it can sterically, i.e. kinetically, protect the central π-system. Such units can also exert the so-called "Bredt's-rule protection"[3] against decomposition of the positively charged π-system: Decomposition by deprotonation from the α-position of the substituents is inhibited because such an event would result in the formation of the bridgehead olefin and violation of Bredt's rule.

The question arises as to what would be the most appropriate size of the bicycloalkene to be attached to the π-system? The effect of the annelating bicycloalkene was examined by comparing the thermodynamic stability, expressed by the pK_{R^+} value, and reduction potential of a series of substituted tropylium ions as a representative cationic π-conjugated cyclic system.[4][5] The *tert*-butyl group can be taken as a typical inductively electron-donating group, while the cyclopropyl group is considered as a typical σ-conjugative group. As shown by the pK_{R^+} values given in

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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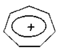
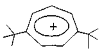
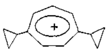
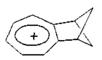
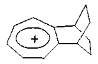
Table 1, the cyclopropyl group can stabilize the tropylium ion much more strongly than the *tert*-butyl group.[4] The bicyclo[2.1.1]hexene (abbreviated as BCH) unit is highly strained with its σ-bonds having considerable p-character. Thus, its annelation was anticipated to be as effective as two cyclopropyl groups in stabilizing the cation. However, the pK_{R^+} value of the BCH-annelated tropylium ion **4** was much lower than that of dicyclopropyltropylium ion **3**: This is ascribed to the internal angle strain of the tropylium ring imposed by the BCH annelation. Instead, annelation with bicyclo[2.2.2]octene (abbreviated as BCO), which is not so strained and can provide σ-bonds that are nearly parallel to the p-orbital of the π-system, was found to stabilize the tropylium ion as effectively as two cyclopropyl groups.[5] From these data, annelation with multiple units of bicyclo[2.2.2]octene (BCO) was expected to be highly effective for stabilization of cyclic π-conjugated systems having a positive charge.

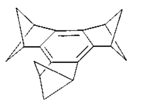
Table 1. Values of pK_{R^+} and reduction potential for the tropylium ions **1**−**5**

Cation	 **1**	 **2**	 **3**	 **4**	 **5**
pK_{R^+}^{a}	3.88	5.42	7.63	5.10	7.80
E_{red}^{b} (V vs Ag / Ag$^+$)	-0.51	-0.72	-0.76	-0.71	-0.765
Ref.	[4]	[4]	[4]	[5]	[5]

^{a}Measured in 50% aq. MeCN. − ^{b}Cathodic peak potential measured in MeCN.

Benzenes Tris-Annelated with Bicycloalkenes

The benzene derivatives that are fully annelated with bicycloalkenes such as **6**,[6] **7**,[7] **8**,[8] **9**,[9] **10**,[10] and **11**[11] have been synthesized. These benzenes were formally produced by cyclotrimerization of each of the bicycloalkene units. Benzene **7** was assumed to be formed by the direct trimerization of highly strained bicyclo[2.2.1]heptyne.[7] For the formation of benzenes **9** and **10**, the intermediate formation of bicyclo[2.2.2]octyne and its benzo derivative was experimentally confirmed by trapping with diphenylisobenzofuran.[9b,10] The bicyclooctyne, however, does not cyclotrimerize by itself but undergoes stepwise oligomerization as shown in Scheme 1: The alkyne inserts into the C−Li bond of each precursor and the in-situ lithium/bromine exchange furnishes a series of BCO oligomers **12** (n = 2−5).[9b] Benzene **9** was synthesized by the reductive cyclization of the dibromide of BCO trimer (Scheme 2).[9] Recently, a high-yield synthesis of benzene **9** and "mixed" tris-annelated benzenes was reported, and this method utilizes Grignard coupling and electrocyclization.[12]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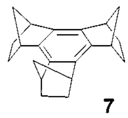
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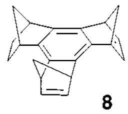
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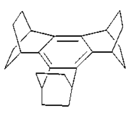
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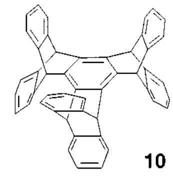
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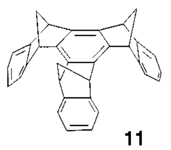
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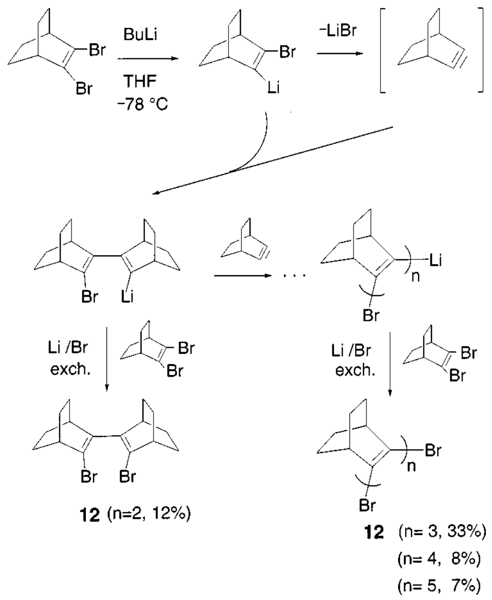
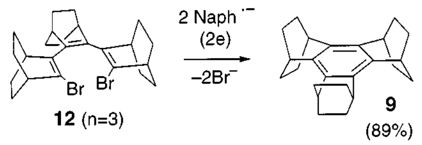


Scheme 1. Oligomerization of the BCO unit



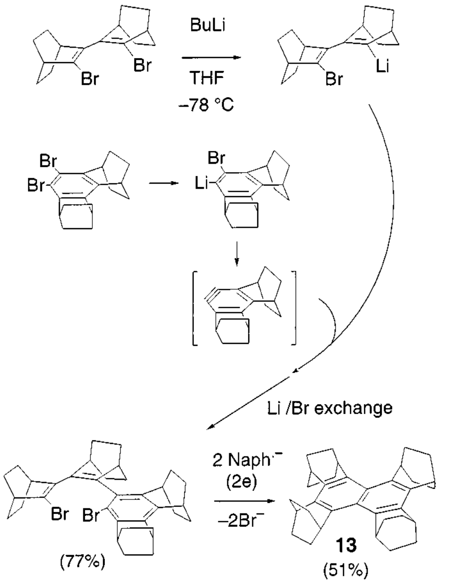
Scheme 2. Cyclization of BCO trimer **12** (n = 3)

Among these benzene derivatives, the X-ray crystal structure has been determined for **6**,[6] **9**,[9a] and **11**.[11] The most characteristic feature is the remarkable bond alternation induced by the molecular strain, particularly for **6**[6] and **11**.[11] Compound **6** is important in that it is the first "bona fide" mononuclear benzenoid hydrocarbon with a cyclohexatriene-like geometry. Its chemical properties, however, have not yet been studied in depth.

On the other hand, benzene **9** was characterized by its reversible one-electron oxidation as observed by cyclic voltammetry; $E_{1/2}$ +1.25 V vs Ag/Ag$^+$. The radical cation produced is stable in solution, exhibiting a 13-line ESR signal due to the coupling with twelve *anti* protons of the ethano bridges.[9b] The formation of the arenium ion and its dynamic behavior were also examined.[9b] The charge-transfer complexation of benzenes **7** and **9** has been studied with various acceptor molecules.[13]

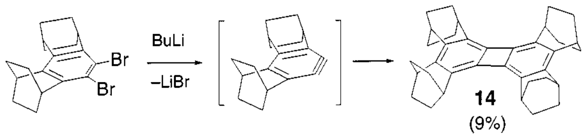
Polycyclic Aromatic Hydrocarbons Annelated with BCO

For the polycyclic aromatic hydrocarbons annelated with BCO units, naphthalene **13**,[14] biphenylene **14**,[15] and anthracene **15**[16] are known. Naphthalene **13** was synthesized using a reaction of the BCO-annelated benzyne with the lithiated BCO dimer as the key step, as shown in Scheme 3.

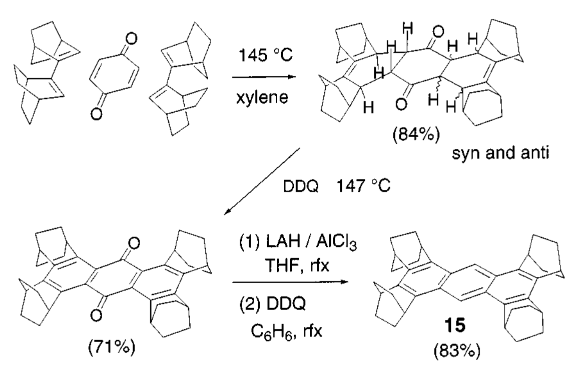


Scheme 3. Synthesis of naphthalene **13**

Biphenylene **14** was formed by dimerization of the BCO-annelated benzyne (Scheme 4). On the other hand, anthracene **15** was synthesized by the Diels−Alder reaction between *para*-benzoquinone and BCO dimer as a key reaction, as shown in Scheme 5. The reactivity of **15** as a diene was found to be enhanced owing to the elevated HOMO level caused by the σ-π conjugation with the bicyclic σ-bonds.[16]



Scheme 4. Synthesis of biphenylene **14**



Scheme 5. Synthesis of anthracene **15**

All these polycyclic hydrocarbons are characterized by two-step one-electron oxidations with remarkably low oxidation potentials, as demonstrated by cyclic voltammetry (Table 2). On chemical oxidation with $SbCl_5$, all these hy-

Table 2. Oxidation potentials [V vs Fc/Fc^+] of naphthalene **13**, biphenylene **14**, and antharacene **15** determined by cyclic voltammetry in 1,1,2,2-tetrachloroethane[a]

Compound	$E_{1/2}$ (1)[b]	E_{pa} (2)[c]	Ref.
13	+0.33	+1.17	[14]
14	+0.22	+0.96	unpublished[d]
15	+0.13	+0.82	unpublished[e]

[a] Supporting electrolyte, Bu_4NClO_4 (0.1 M); scan rate 20 mV s^{-1}. − [b] Half-wave potential; $(E_{pa} + E_{pc})/2$. − [c] Anodic peak potential. − [d] The published data are $E_{1/2}$ = +0.33 V and E_{pa} = +1.03 V in 1,2-dichlorobenzene (ref.[15]). − [e] The published data are $E_{1/2}$ = +0.21 V and E_{pa} = +0.87 V in dichloromethane (ref.[16]).

Table 3. ^{1}H-NMR data for hydrocarbons **13**, **14**, and **15** in $CDCl_3$ and their dications **13**$^{2+}$, **14**$^{2+}$, and **15**$^{2+}$ in CD_2Cl_2

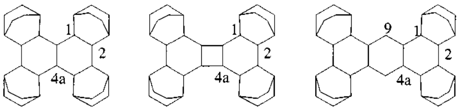
Compd.	δ_{1H} (ppm)			Ref.
	CH	CH	CH_2	
13	—	3.78, 3.46	1.80, 1.40	[14]
13^{2+}	—	2.98, 2.88	2.13, 1.90^a	[14]
14	—	3.00, 2.81	1.73, 1.42	[15]
14^{2+}	—	4.19, 4.13^a	2.35, 1.71^a	–^{a}
15	8.91	4.12, 3.53	1.89, 1.42	[16]
15^{2+}	8.74	3.58, 3.26	2.11, 1.76^a	[16]

^{a} Matsuura, T. Nishinaga, K. Komatsu, unpublished.

Table 4. ^{13}C-NMR data for hydrocarbons **13**, **14**, and **15** in $CDCl_3$ and their dications **13**$^{2+}$, **14**$^{2+}$, and **15**$^{2+}$ in CD_2Cl_2^{a}

Compd	δ_{13C} (ppm)					Ref.
	C-1 C-2	C-4a	C-9	CH	CH_2	
13	135.32 135.29	125.1	—	32.7 28.8	26.6 26.4	[14]
13^{2+}	210.8 160.7	154.0	—	41.9^b 30.6^b	25.9^b 22.9^b	[14]
14	136.6 131.0	140.4	—	31.3 28.7	26.4 26.0	[15]
14^{2+}	159.9^b 147.9^b	183.8^b	—	38.1 35.8^b	26.8 24.8^b	–^{b}
15	135.5 125.4	115.5	136.1	29.3 28.8	27.0 26.2	[16]
15^{2+}	160.9 159.9	131.0	181.9	32.9 29.9	24.1 22.8	[16]

^{a} Numbering system:

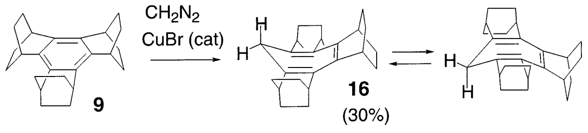


^{b} A. Matsuura, K. Komatsu, unpublished.

drocarbons give isolable salts of the stable radical cations. When treated with SbF_5, which has a stronger oxidizing power, these hydrocarbons are transformed into the corresponding dications, which can be characterized by ^1H (Table 3) and ^{13}C NMR (Table 4). The dications of **13** and **15** exhibit the presence of a paramagnetic ring current because of the peripheral 8 and 12 π-electronic system, whereas the dication of **14** exhibits the presence of a diamagnetic ring current typical for a peripheral 10 π-system.

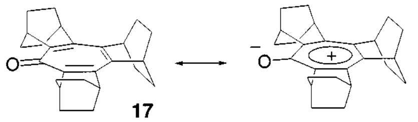
Cycloheptatriene, Tropone, and Heptafulvene Annelated with BCO

The BCO-annelated benzene **9** can be ring-expanded to cycloheptatriene **16**, which undergoes rapid ring inversion (Scheme 6).[17] The energy barrier for ring inversion was determined as 8.5 kcal mol^{-1}, which is only 2.5 kcal mol^{-1} larger than that for the parent compound (6 kcal mol^{-1}).[18] This result suggests that the presence of the BCO groups does not substantially destabilize the planar transition-state structure by steric strain.



Scheme 6. Ring enlargement of benzene **9**

The cycloheptatriene **16** was oxidized by SeO_2 to the corresponding tropone **17**.[19] The basicity of tropone **17** was found to be nearly 2 p*K* units higher than that of the parent compound,[20] indicating the effects of the BCO annelation to enhance the polarity of the molecule by stabilizing the positively polarized seven-membered ring. The heptafulvene derivative **18**[19] was also found to be more polarized as compared with the parent compound,[21] as shown by ^{13}C-NMR and IR spectra.



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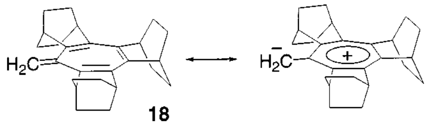

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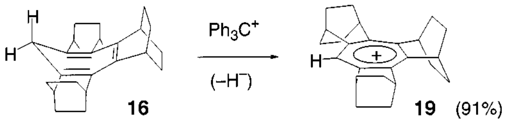
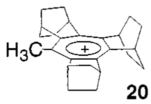
The low-temperature ^{13}C-NMR spectrum indicated that the π-system of tropone **17** is planar, whereas that of heptafulvene **18** is in the boat conformation; the energy barrier for the ring inversion is 8.5 kcal mol^{-1}.[19]

Tropylium Ions Annelated with BCO

Cycloheptatriene **16** can be readily converted into tropylium ion **19**, which exhibits an extraordinarily high thermodynamic stability (Scheme 7).[22] The stabilization effect of each BCO unit is almost additive, and the $pK_R{}^+$ value of the tropylium ion **19** having three BCO groups is 13.0 in 50% acetonitrile. This is the highest $pK_R{}^+$ value ever reported for substituted tropylium ions. Reflecting such stability, cation **19** does not react with typical nucleophiles such as $N_3{}^-$ (pK_a of the conjugate acid, 4.59), $CH_3CO_2{}^-$ (4.76), $CrO_4{}^{2-}$ (6.50), $C_6H_5S^-$ (6.50), $SO_3{}^{2-}$ (7.21), $C_6H_5O^-$ (9.99), and $CO_3{}^{2-}$ (10.33).[23] However, **19** does react with organolithium reagents at the 7-position and affords the tropylium ion derivatives **20**,[22] **21**,[24] **22**,[24] **23**,[24] and **24**[25] after the appropriate ionization method. The $pK_R{}^+$ and reduction potential data of these mono- and dications are given in Table 5.



Scheme 7. Formation of tropylium ion **19**



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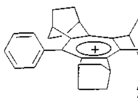

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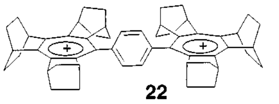

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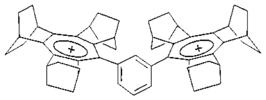

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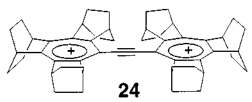

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Table 5. Values of $pK_R{}^+$ and reduction potential for the tropylium ions **19–24**

Cation	**19**	**20**	**21**	**22**	**23**	**24**
pK_{R+} [a]	13.0	12.4	12.0	11.5	10.4 [b] 12.2	7.0 [b] 11.5
E_{red} [c] (V vs Ag / Ag^+)	-1.12 [d]	-1.09 [d]	-1.12 [e]	-1.01 [d]	-1.14 [e,f] -1.24	-0.49 [e,f] -0.66
Ref.	[22]	[22]	[24]	[24]	[24]	[25]

[a] Measured in 50% aq. MeCN. – [b] Two-step neutralization. – [c] Measured in MeCN. – [d] Cathodic peak potential. – [e] Half-wave potential. – [f] Two-step reduction.

In spite of the presence of the electron-donating methyl substituent, cation **20** is less stable than **19**, probably due to the presence of too much steric congestion to maintain the planarity of the central tropylium ring. The benzene ring in cations **21**, **22**, and **23** is almost perpendicular to the plane of the tropylium ring, and contributes to destabilizing the cation due to the electron-withdrawing inductive effect.[24]

For the dication **24**, the X-ray crystallography study indicated that mean planes of the two tropylium rings are neither coplanar nor perpendicular, but are twisted with respect to each other with a dihedral angle of 44° (Figure 1).[25] The repulsive interaction between the two tropylium rings in **24** results in considerable destabilization, as shown by the $pK_R{}^+$ data.

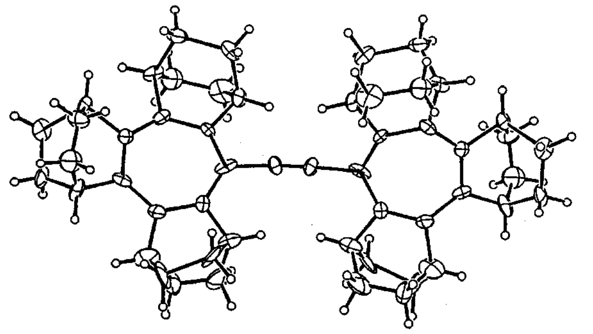
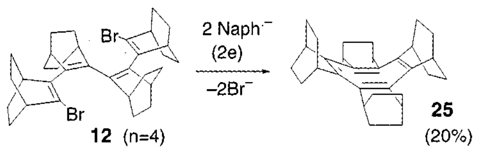


Figure 1. ORTEP drawing of dication salt **24** $(SbF_6)_2$ ($SbF_6{}^-$ is omitted for clarity)

Upon cyclic voltammetry, each of the two tropylium rings of dication **22** behaves independently and undergo a one-electron reduction simultaneously. In contrast, each tropylium ring in **23** and **24** recognizes the other in the redox events and accepts two electrons in a stepwise manner.[24][25] Exhaustive electrolytic reduction of **23** produces a triplet diradical, as observed by ESR at −120°C.[24]

Cyclooctatetraene Annelated with BCO

The dibromide of the BCO tetramer (**12**, $n = 4$) can be reductively cyclized to give cyclooctatetraene (COT) **25** (Scheme 8). As shown by the X-ray crystal structure (Figure 2), **25** has a tub-shaped π-system typical for the COT ring.[26] Because of the steric constraint caused by the BCO annelation, a planar structure has a considerable angular strain and the ring inversion of the neutral COT **25** is inhibited, the energy barrier for ring inversion being estimated to be larger than 50 kcal mol^{-1} by either molecular orbital (PM3) or molecular mechanics calculations. Nevertheless, COT **25** [^{13}C NMR ([D_8]THF): $\delta = 140.0$, 33.4, 26.6, 25.8] can be reduced by potassium metal to give



Scheme 8. Cyclization of BCO tetramer **12** (n = 4)

planar dianion $\mathbf{25}^{2-}$, which exhibits only three ^{13}C-NMR signals at $\delta = 97.8$, 35.8, and 30.6.[26] Apparently, the gain in the Hückel aromaticity (10 π-electron system) overcomes the angular strain in the planar system.

Owing to the electronic effects of the BCO units, the levels of occupied molecular orbitals of COT **25** are raised while those of unoccupied molecular orbitals are not affected. This is reflected in the cyclic voltammogram, which exhibited two consecutive reversible oxidation waves at such low potentials as +0.39 V and +1.14 V vs Ag/Ag^+ in $CH_2Cl_2/CF_3CO_2H/(CF_3CO)_2O$ (20:1:1).[27] In comparison, the parent COT only exhibits an irreversible oxidation peak at +1.20 V in acetonitrile. These results imply that the cationic species can be readily generated from COT **25**.

Compared with the anionic COT, the cationic species of COT has received only sporadic attention. The radical cation of the parent COT was predicted to be tub-shaped rather than planar by MNDO calculations.[28] However, the radical cation was so unstable that it could only be observed by flow ESR as a short-lived species.[29] The same species was also observed by electronic spectroscopy only at low temperature (−196°C) in a Freon matrix.[30]

In sharp contrast, the COT **25** completely surrounded by BCO units afforded the first isolable salt of the stable radical cation $\mathbf{25}^{\cdot+}$ by one-electron oxidation of **25** with $NO^+SbCl_6{}^-$ (Scheme 9).[31] X-ray crystallography data demonstrated that this radical cation has a tub-shaped eight-membered ring (Figure 3), as has been predicted theoretically.

The COT dication is a member of the Hückel aromatic system with six π-electrons. There have been reported tetra- and di-substituted COT dications $\mathbf{26}^{2+}$ and $\mathbf{27}^{2+}$, which are stable only at low temperature (−78°C) in SO_2ClF solution.[32] At temperatures above −20°C, the dication rearranges into the bicyclic structure $\mathbf{28}^{2+}$.[32] On the other hand, when the radical cation of the BCO-annelated COT

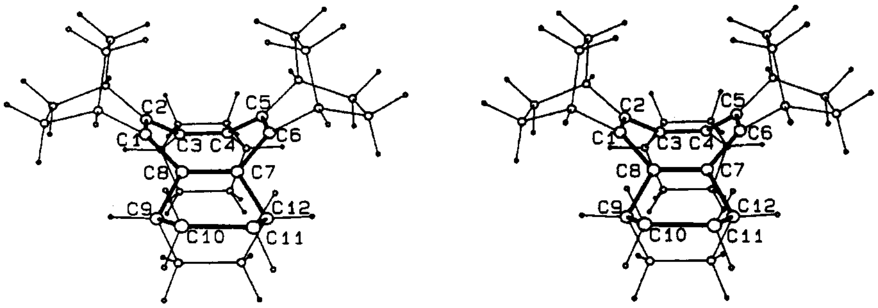
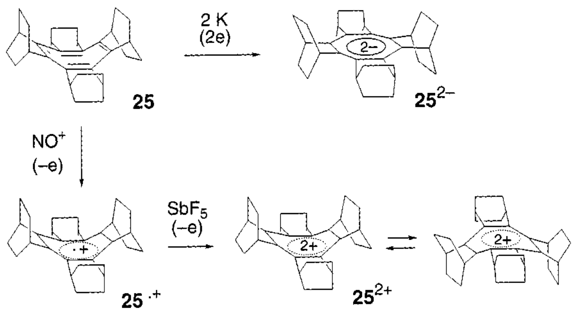


Figure 2. Molecular structure of COT **25** (stereoview); selected bond lengths [Å] and angles [°]: C1−C2 1.339(3), C2−C3 1.465(2), C3−C4 1.342(2), C4−C5 1.469(2), C5−C6 1.331(3), C6−C7 1.464(2), C7−C8 1.336(2), C8−C1 1.475(2), C8−C9 1.515(2), C9−C10 1.544(4), C10−C11 1.531(3); C6−C7−C8 126.5(1), C7−C8−C1 127.0(1), C7−C8−C9 113.8(1), C8−C7−C12 113.7(1)



Scheme 9. Redox reactions of COT **25**

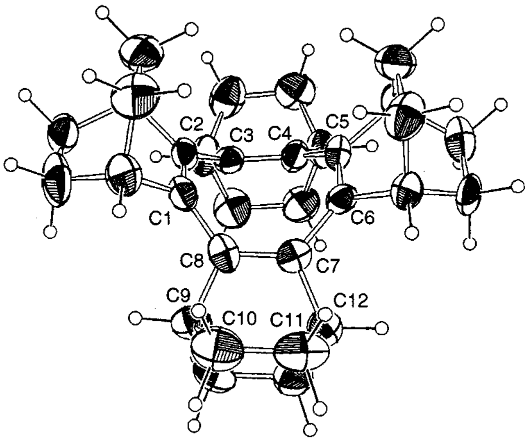
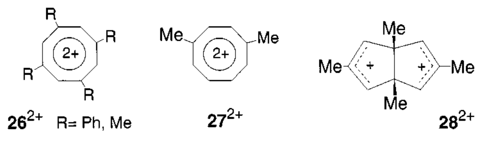


Figure 3. ORTEP drawing of radical cation salt $25^{\cdot+}SbCl_6^-$ ($SbCl_6^-$ is omitted for clarity); selected bond lengths [Å] and angles [°]: C1−C2 1.389(10), C2−C3 1.440(10), C3−C4 1.356(10), C4−C5 1.444(11), C5−C6 1.377(10), C6−C7 1.445(11), C7−C8 1.338(11), C8−C1 1.464(10), C8−C9 1.529(10), C9−C10 1.540(10), C10−C11 1.537(13); C6−C7−C8 126.1(7), C7−C8−C1 127.9(7), C7−C8−C9 114.1(6), C8−C7−C12 113.8(8)

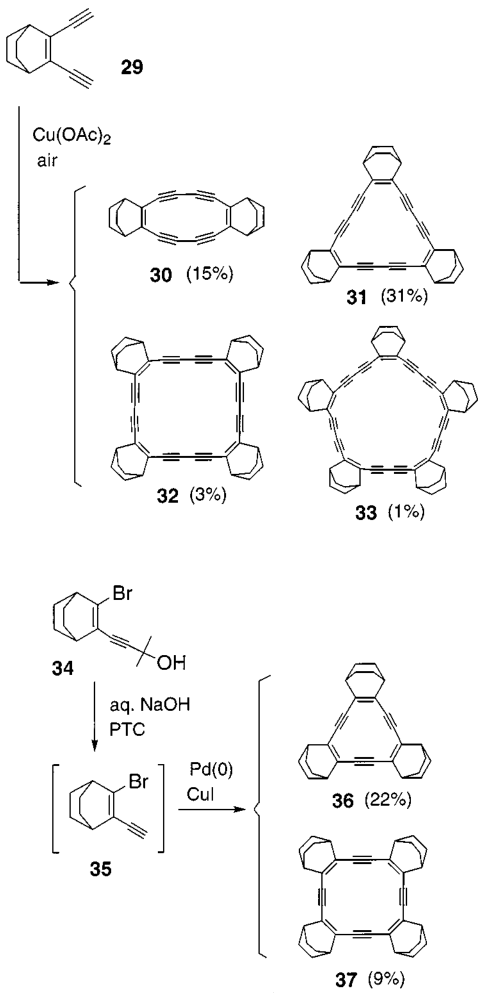
25 was further oxidized with SbF_5 (Scheme 9), a stable dication was produced that exhibited only three ^{13}C-NMR signals at $\delta = 177.9$, 41.0, and 23.9 at room temperature. However, the signal for the methylene carbon atoms of the ethano bridge were split to give two signals at low temperature (−80°C), indicating that the ground-state structure of this dication is in the tub structure, which is undergoing rapid ring inversion with an energy barrier of 10.8 kcal mol^{-1}.[27]



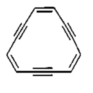
Dehydroannulenes Annelated with BCO

A wide variety of dehydroannulenes has been synthesized and studied owing to the interest in their electronic structures[33] as well as in their supramolecular structures.[34] Dehydroannulenes fused with detachable cyclic units have been utilized as possible precursors of a new family of carbon allotropes, the cyclo[*n*]carbons.[35] In contrast to these studies, annelation with BCO groups was expected to rigidly hold the π-system and to raise the HOMO level.

Oxidative coupling under Eglinton conditions transformed the enediyne **29** into a series of dehydroannulenes annelated with BCO, **30**−**33**.[36] On the other hand, the bromo(ethynyl) olefin **35** which was generated from **34** was coupled with itself by the use of CuI and Pd^0 catalysts to give dehydroannulenes **36** and **37**.[36] From the molecular modeling and X-ray crystallography of some of the compounds, the cyclic π-systems in **30**, **31**, and **36** are considered to be essentially planar while those in **32**, **33**, and **37** have folded structures. The redox potentials of these and one parent dehydroannulene (**38**) are shown in Table 6. Upon comparison of the antiaromatic planar dehydroannulenes having 12 π-electrons, the one having three BCO units (compound **36**) apparently has the lowest oxidation potential, i.e. the highest tendency to be oxidized. This can be taken as the characteristic of the BCO annelation effect.



PTC= Phase transfer catalyst



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The raising of the HOMO level, particularly in annulene **37**, was also demonstrated by complexation of a silver ion (AgOTf or $AgSbF_6$) in its cavity as shown in Figure

Table 6. Redox potentials [V vs Ag/Ag$^+$] of dehydroannulenes determined by cyclic voltammetry in benzonitrile[a]

Compound	E_{red}	E_{ox}
38	−1.58	+1.17[b]
30	−1.67	+0.93[b]
31	−1.96	+1.21[b]
32[c]	−1.53	
33	−1.90[b]	+1.07[b]
36	−1.93	+0.54
37	−1.96	+0.62[d]

[a] Supporting electrolyte, Bu_4NClO_4 (0.1 m); scan rate 0.1 V s^{-1}. – [b] Peak potential of the irreversible peak. – [c] Because of the low solubility, the measurement was performed in benzonitrile/dichloromethane (4:3). The observable range in this solvent was from +1.0 V to −2.0 V. – [d] The second irreversible peak was observed at +0.88 V.

4.[37] The complexation with $AgSbF_6$ was found to be stronger, the Ag−C(alkyne) distances being shorter, particularly for one set of the opposing acetylene linkages.

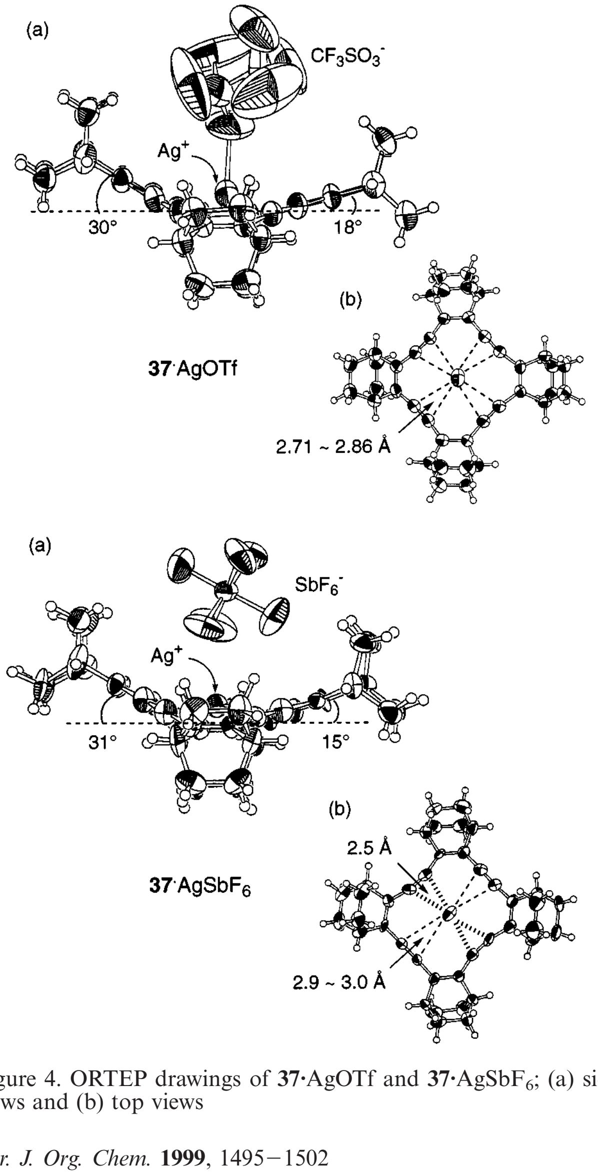

Figure 4. ORTEP drawings of **37**·AgOTf and **37**·AgSbF$_6$; (a) side views and (b) top views

Concluding Remarks

This short survey has demonstrated that the structural modification of the surroundings of the cyclic π-system can greatly affect the properties of the π-system itself. In particular, the annelation with bicyclo[2.2.2]octene units is shown to be effective in raising the HOMO and in stabilizing the cationic π-systems both kinetically and thermodynamically. Further studies on this structural modification will bring about the realization of hitherto unknown cationic species of theoretical interest.

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