

Novel aromatics blended with a σ -flavor*

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Abstract: We present the results of our systematic study on the synthesis, structures, and electronic properties of a series of cyclic π -conjugated systems with monocyclic six- to eight-membered rings as well as polycyclic benzenoid aromatics, which are fully surrounded by rigid bicyclic σ -frameworks such as bicyclo[2.2.2]octene (BCO). The study has also been extended to sulfur-containing systems such as thiophene, 1,2- and 1,4-dithiins, and oligothiophene. Such a structural modification using bicyclic frameworks is effective in elevation of the highest occupied molecular orbital (HOMO) levels of neutral π -systems and in remarkable stabilization of the corresponding cationic systems by both σ - π conjugation and kinetic effects. This has led to various new cationic π -conjugated systems such as highly stable radical cations as well as closed-shell mono- and dications, which could have never been attained by any other conventional techniques. The properties of benzene and entirely planar cyclooctatetraene (COT) possessing a marked bond fixation caused by structural modification with a strained bicyclic system (i.e., bicyclo[2.1.1]hexene, BCH) are also described.

Keywords: σ - π conjugation; C–C hyperconjugation; aromaticity; silatropylium ion; cyclooctatetraene; dithiin; oligothiophene.

INTRODUCTION


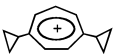
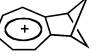
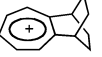
Needless to say, it is the π -conjugated system that plays the most important role in the performance of functional organic molecules. A great number of fundamental as well as applied studies have been conducted to control the properties of π -conjugated molecules [1,2]. So far, the most general and conventional means reported for such control include the manipulation of the size and shape of π -conjugated systems and/or introduction of heteroatom(s) either as a member of the conjugated system or as substituent(s). In contrast, we have attempted to make use of σ -bonds, which are fixed at the conformation nearly parallel to the 2p orbitals of the π -systems, particularly for stabilization of cyclic π -conjugated cationic systems both thermodynamically and kinetically. In general, the energy levels of σ - and π -molecular orbitals are widely separated so that the electronic interaction between them is considered to be quite small. However, when the geometrical fixation of these σ -bonds is rigid and if the maximum number of such σ -bonds are placed, the cumulative effects could be significant. Here we wish to demonstrate how we have utilized this strategy for realization of a wide range of novel cyclic π -conjugated systems [3], particularly those having a positive charge, which could have never been attained by any other known means.

For the geometry of the σ -bonds to be rigidly fixed, incorporation of the π -system with bicyclic frameworks was expected to be highly effective. Then, which size would be the most appropriate for

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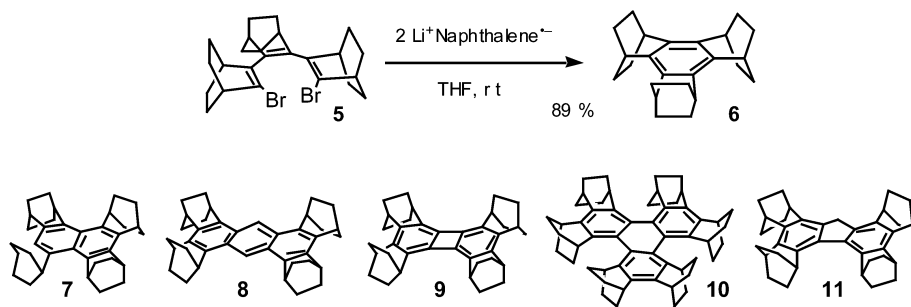
the σ -framework? It was shown that bicyclo[2.2.2]octene (BCO) is the most suitable by the following study. When the stabilization of tropylium ion is taken as an example, the annelation with one BCO group was found to be almost as effective as substitution with two cyclopropyl groups. As shown in Table 1, the pK_{R^+} value, a measure of the thermodynamic stability of carbocations, of BCO-fused tropylium ion **4** is comparable to that of dicyclopropyltropylium ion **2**, whereas that of cation **3** fused with more strained bicyclo[2.1.1]hexene (BCH) is much smaller [4,5]. Based on this result, a series of cyclic π -conjugated systems all surrounded by BCO frameworks have been synthesized and their structure and properties examined in detail.

Table 1 pK_{R^+} values (50 % aq MeCN) of some tropylium ion derivatives.

				
1	2	3	4	
pK_{R^+}	3.88	7.63	5.10	7.80

BENZENOID AROMATIC HYDROCARBONS FUSED WITH BCO UNITS

The tris-BCO derivative of the most fundamental aromatic hydrocarbon, benzene **6**, was cleanly synthesized as a single product by reductive cyclization of the terminal dibromide of BCO trimer **5** (Scheme 1) [6]. By somewhat related methods with the combination of a benzyne fused with two BCO units or with Diels–Alder reaction of BCO-dimer, the polycyclic aromatic hydrocarbons fused with BCO units, naphthalene **7** [7,8], anthracene **8** [8,9], biphenylene **9** [8,10], triphenylene **10** [11], and fluorene **11** [12], were prepared. Reflecting the elevation of highest occupied molecular orbital (HOMO) levels in these compounds, all these hydrocarbons were characterized by well-defined reversible oxidation waves at remarkably low oxidation potentials when examined by cyclic voltammetry (CV) as shown in Table 2. Except in the case of benzene **6**, even the second oxidation peak was clearly observed.



Scheme 1

Table 2 Oxidation potential (V vs. Fc/Fc⁺)^a of 6–11.

Compd.	$E_{1/2}$ (1) ^b	E_{pa} (2) ^c	Ref.
6	+1.08	–	[8]
7	+0.33	+1.17	[8]
8	+0.17	+0.86	[8]
9	+0.25	+1.00	[8]
10	+0.44	+1.27	[11]
11	+0.56	+0.88	[12]

^aDetermined by CV in 1,1,2,2-tetrachloroethane containing 0.1 M Bu₄NClO₄; scan rate 20 mV s⁻¹.

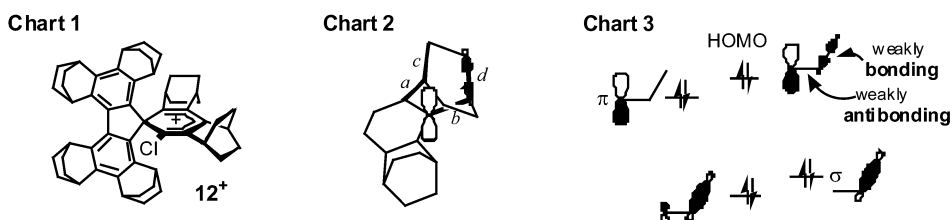
^bReversible wave.

^cIrreversible peak.

The chemical oxidation by the use of SbCl₅ in CH₂Cl₂ afforded the SbCl₆⁻ salts of the radical cation of 7–11, as deeply colored crystals, whose structures were determined by X-ray crystallography in detail except for triphenylene 10^{•+}. The radical cation salt of 10^{•+}SbCl₆⁻ in CH₂Cl₂ solution slowly underwent rearrangement to a stable arenium ion salt with a novel spiro-connected structure 12⁺ (Chart 1), whose structure was also determined by X-ray crystallography [12].

The change in π -bond lengths upon one-electron oxidation of 7–9 is systematically related to the coefficients of the relevant carbons in HOMOs of the neutral molecules. The π -bonds with bonding nature in the HOMO are elongated upon removal of one electron, and those with antibonding nature in HOMO are shortened.

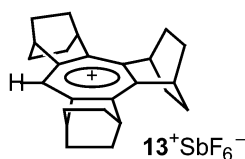
Furthermore, there is a tendency of characteristic changes in the σ -bond lengths of the bicyclic frameworks involved in the σ - π conjugation in radical cations 7^{•+}, 8^{•+}, and 9^{•+} (Chart 2). Although the extents are quite small, the C_{Ar}-C _{α} bonds (*a* and *b*) (antibonding in the HOMO of the neutral molecules; Chart 3) appear to be shortened while all of the C _{α} -C _{β} bonds (*c* and *d*) (bonding in the HOMO) are lengthened, compared to those of the corresponding neutral molecules. These changes in σ -bond lengths can be taken as the experimental evidence for the presence of σ - π conjugation (C–C hyperconjugation) to stabilize these radical cations [8,13].

**Charts 1–3**

All the hydrocarbons, naphthalene 7, anthracene 8, biphenylene 9, and fluorene 11, undergo two-electron oxidation to the corresponding dications by oxidation with excessive amount of SbF₅ or SbCl₅ in CD₂Cl₂ in a vacuum-sealed tube [7,9,10]. The dications were characterized by ¹H and ¹³C NMR. It was found that the ¹H NMR signals for the BCO units' bridgehead protons located in the same plane as the π -systems undergo an upfield shift for 7 (10 π -electron) and 8 (14 π -electron) upon going from the neutral compounds to dications, reflecting the change from aromatic 4n + 2 π -systems to antiaromatic 4n π -systems. Accordingly, the reverse tendency was observed for the 12 π -electron system 9.

Tropylium ion fused with three BCO units

We had long been interested in the problem of ultimate stabilization of an all-hydrocarbon carbocation, and the results shown in Table 1 suggested that we could achieve the formation of a highly stabilized tropylium ion if its π -system is completely surrounded by BCO units. In fact, the cation **13**⁺ prepared from the corresponding cycloheptatriene, which was, in turn, obtained by ring enlargement of symmetrical benzene **6**, was found to have the pK_R^+ value of 13.0, the highest value reported for the all-hydrocarbon carbocation reported at that time [14]. This cation is only half-neutralized in 0.1 N NaOH aqueous solution and can be fully regenerated by acidification. Reflecting such stability, cation **13**⁺ 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) [15].



Silatropylium ion fused with three BCO units

The remarkable thermodynamic stability of tropylium ion **13**⁺ suggested that it might be possible to prepare its silicon analog, i.e., the silatropylium ion fused with three BCO units. Previously, Olah and coworkers have shown that it is impossible to generate the silatropylium ion fused with two benzene rings [16]. However, theoretical calculations indicate that about half of the positive charge on silicon atom can be delocalized into the rest of the π -system in silatropylium ion and the system is aromatic to certain extent as estimated from calculated values of NICS (nucleus independent chemical shift) and MSE (magnetic susceptibility exaltation) (Fig. 1). We thought that the π -conjugated plane rigidly held by three BCO frameworks would be suitable to incorporate the positively charged silicon atom.

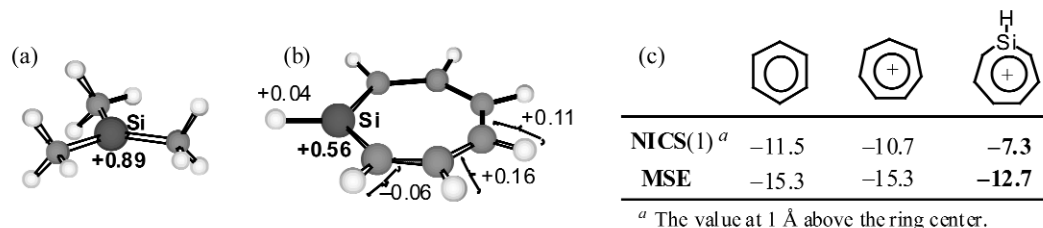


Fig. 1 (a) Mulliken charge for trimethylsilyl cation and (b) for silatropylium ion based on B3LYP/6-31G* calculations, and (c) NICS and MSE values calculated based on CSGT/B3LYP/6-311+G* and GIAO/HF/6-31+G*, respectively.

When the hydride abstraction was conducted by addition of one equivalent of triphenylmethyl tetrakis(pentafluorophenyl)borate ($Ph_3C^+TPFPB^-$) to a solution of silepin **14** in CD_2Cl_2 at $-60^\circ C$, the quantitative formation of tris-BCO-annulated silatropylium ion **15**⁺ was confirmed by the 1H NMR spectrum shown in Fig. 2 [17]. The ^{29}Si NMR signal was observed at δ 142.9 ppm, which is 192.2 ppm down-field-shifted compared with the precursor silepin **14** (δ -49.3 ppm). The ^{13}C NMR signals for the seven-membered ring carbons (δ 175.9, 153.2, 149.7 ppm) also exhibited down-field shifts compared with **14** (δ 152.0, 145.5, 141.8 ppm), indicating considerable positive-charge delocalization in the seven-membered ring. In particular, the 0.6–0.9 ppm down-field shift observed for the BCOs bridge-

head protons of **15**⁺ as compared with those of **14** (δ 2.78 (4H), 2.59 (2H)) is taken as the experimental proof for the presence of aromatic ring current in this silatropylium ion.

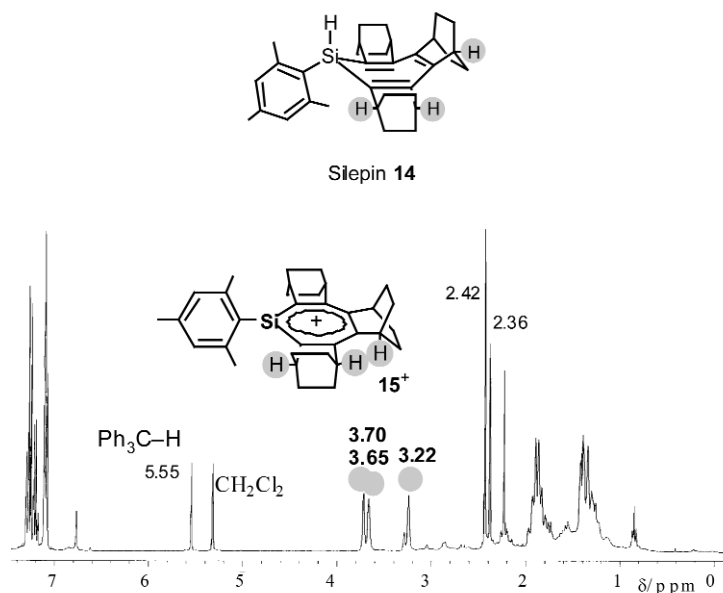


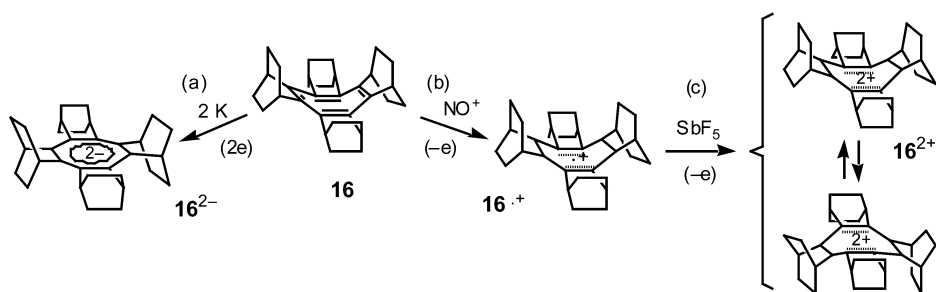
Fig. 2 ¹H NMR (300 MHz) of silatropylium ion **15**⁺ in CD₂Cl₂ observed at -50 °C.

Cyclooctatetraene fused with four BCO units

While the facile reduction of tub-shaped cyclooctatetraene (COT) to a planar radical anion or to a 10 π aromatic dianion is commonly known, its reversal (i.e., the oxidation to a radical cation or to a 6 π aromatic dication) has received only sporadic attention [18]. Although there have been some studies on indirect observation of the COT radical cation [19], there is no example for direct observation or isolation of the radical cation salt. It was expected that the COT totally enclosed with four BCO units would be a good model for this oxidation. Thus, the tetrakis-BCO COT **16** was synthesized by reductive cyclization of Br-(BCO)₄-Br, and its tub-shape structure was confirmed by X-ray crystallography [20].

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 **16** is inhibited, its energy barrier being estimated to be larger than 50 kcal mol⁻¹ by theoretical calculations. Nevertheless, COT **16** (¹³C NMR (THF-*d*₆) δ 140.0, 33.4, 26.6, and 25.8 ppm) can be reduced by potassium metal to give planar dianion **16**²⁻, which exhibits only three ¹³C NMR signals at δ 97.8, 35.8, and 30.6 ppm indicative of the planar COT ring (Scheme 2a) [20]. Apparently, the gain in stabilization owing to the 10 π -aromaticity overcomes the angular strain in the planar system.

Owing to the electronic effects of the BCO units, the levels of the HOMO of COT **16** (−4.87 eV; B3LYP/6-31G**//B3LYP/6-31G*) are raised as compared with that of unsubstituted COT (−5.54 eV). This is reflected in the CV, which exhibited two consecutive reversible oxidation waves at such low potentials as +0.39 V and +1.14 V vs. Ag/Ag⁺ in CH₂Cl₂-CF₃CO₂H-(CF₃CO)₂O (20:1:1) [21]. In comparison, the parent COT only exhibits an irreversible oxidation peak at +1.20 V in acetonitrile. Accordingly, the one-electron oxidation of **16** with NO⁺SbCl₆⁻ afforded the first isolable salt of the stable COT radical cation **16**^{•+} as deep green crystals (Scheme 2b) [22]. X-ray crystallography demonstrated that this radical cation has a tub-shaped eight-membered ring (Fig. 3), as has been predicted theoretically [18a].



Scheme 2

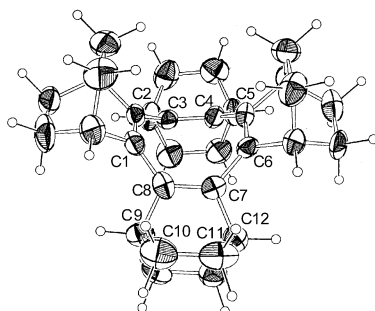


Fig. 3 The X-ray structure of radical cation salt $16^{\cdot+}\text{SbCl}_6^-$ (SbCl_6^- is omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$) are: C1-C2, 1.389(10); C2-C3, 1.440(10); C3-C4, 1.356(10); C4-C5, 1.444(11); C8-C9, 1.529(10); C9-C10, 1.540(10); C10-C11, 1.537(13); C6-C7-C8, 126.1(7); C7-C8-C1, 127.9(7); C7-C8-C9, 114.1(6); C8-C7-C12, 113.8(8).

When the radical cation of the BCO-annulated COT $16^{\cdot+}$ was further oxidized with SbF_5 (Scheme 2c), a stable dication was produced that exhibited only three ^{13}C NMR signals at δ 177.9, 41.0, and 23.9 ppm at room temperature. While the reported COT dications having 1,4-dimethyl, 1,3,5,7-tetramethyl, or 1,3,5,7-tetraphenyl substituents are stable only at low temperature [18b,c], the COT dication 16^{2+} is stable in CH_2Cl_2 at room temperature. However, the signal for the methylene carbon atoms of the ethano bridge was split into two signals at a low temperature (-80°C), indicating that the ground-state structure of this dication is in a tub form, which is undergoing rapid ring inversion with an energy barrier of $10.8\text{ kcal mol}^{-1}$ [21].

Sulfur-containing cyclic π -conjugated systems fused with BCO units

Thiophene and dithiins

Among sulfur-containing aromatic π -conjugated systems, the most fundamental compound with 6 π -electrons, thiophene, fused with two BCO units **17** was also synthesized [23] together with the 8 π -electron systems having two sulfur atoms, 1,2- and 1,4-dithiins **18** and **19** [24,25]. The HOMOs of all these compounds are considerably raised as demonstrated by reversible oxidation waves at remarkably low potentials in their cyclic voltammograms (Table 3).

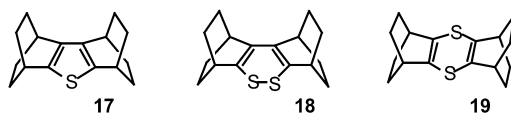


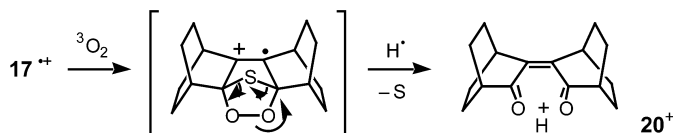
Table 3 Oxidation potential (V vs. Fc/Fc⁺)^a of **17**, **18**, and **19** in CH₂Cl₂.

Compd.	$E_{1/2}$ (1)	$E_{1/2}$ (2)	Ref.
17	+0.79	–	[23]
18	+0.18	+0.72	[24]
19	+0.00	+0.82	[25]

^aDetermined by CV in dichloromethane containing 0.1 M Bu₄NClO₄; scan rate 100 mVs⁻¹.

Chemical one-electron oxidation of thiophene **17** with 1.5 equiv of either SbCl₅ or SbF₅ in CH₂Cl₂ gave a yellow solution, which exhibited a five-line electron spin resonance (ESR) signal ($a_{\text{H}} = 0.346$ mT, $g = 2.00215$) at room temperature [23]. The results of theoretical calculations (B3LYP/6-31G(d)) on **17**^{•+} indicated that the spin is mostly localized on the 2,5-positions, and this spin is conveyed to the corresponding four equivalent *anti*-protons of the ethano bridge with a_{H} value of 0.323 mT in good agreement with the observed value.

Reflecting the high spin density on 2,5-positions, radical cation **17**^{•+} reacted with triplet oxygen smoothly in CH₂Cl₂ to give SbCl₆⁻ or SbF₆⁻ salt of stable carbocation **20**⁺ in 54 or 55 % yield, respectively (Scheme 3). The structure of the salt **20**⁺SbF₆⁻ isolated as pale yellow crystals was determined by X-ray crystallography to have an unusual proton-chelating 2-butene-1,4-dione system as shown in Fig. 4 [23]. Among the NMR data of the cation **20**⁺, it is noteworthy that the ¹H NMR signal of the chelated proton was observed at such a low field as 21.15 ppm. This indicates that the proton not only carries an almost full positive charge, but is subjected to the strong deshielding effect of the two carbonyl groups.



Scheme 3

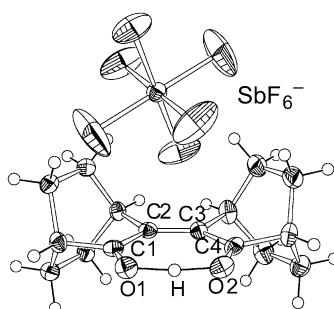


Fig. 4 The X-ray structure of carbocation salt **20**⁺SbF₆⁻.

Upon one-electron oxidation of 1,2-dithiin **18** with 1.5 equiv of SbCl_5 under vacuum in CH_2Cl_2 , a bright yellow solution was formed, which exhibited a nine-line ESR signal, which was in agreement with the result of theoretical calculations (UB3LYP/6-31G*). Whereas the CH_2Cl_2 solution of $\mathbf{18}^{+\bullet}$ in a low concentration (4×10^{-4} M) was quite stable, the radical cation was found to undergo an unexpected disproportionation when kept in a higher concentration (0.06 M). Thus, after about 5 min at room temperature, there were obtained thiophene **17** (29 %), the 2-butene-1,4-dione derivative formed by deprotonation of cation $\mathbf{20}^+$ (23 %), and orange-colored crystals identified as a SbCl_6^- salt of a radical cation having a novel 2,3,5,6-tetrathiabicyclo[2.2.2]oct-7-ene structure $\mathbf{21}^{+\bullet}$ by X-ray crystallography (Fig. 5) in 32 % yield [24]. This salt was remarkably stable and showed no decomposition upon standing under air for at least one week.

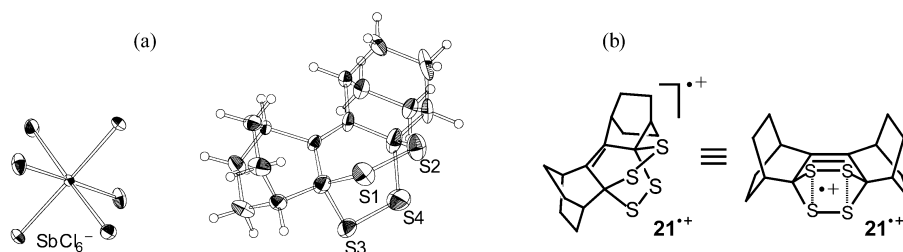


Fig. 5 (a) The X-ray structure of radical cation salt $\mathbf{21}^{+\bullet}\text{SbCl}_6^-$ and (b) 4c-7e structure of $\mathbf{21}^{+\bullet}$.

In radical cation $\mathbf{21}^{+\bullet}$, the two disulfide linkages are fixed in close proximity. The averaged distance of $\text{S1}\cdots\text{S3}$ and $\text{S2}\cdots\text{S4}$ is 2.794(3) Å. This is longer than the typical S–S bond length (2.0 Å) in alkyl disulfide, but much shorter than the sum of van der Waals radii of a sulfur atom (3.70 Å), suggesting the presence of a strong transannular interaction between these disulfide linkages. The optimized structure of $\mathbf{21}^{+\bullet}$ calculated at the UB3LYP/6-31G* level reproduced the observed structure fairly well, with the calculated distance of $\text{S1}\cdots\text{S3}$ and $\text{S2}\cdots\text{S4}$ being 2.923 Å. The calculation also indicated that spin and charge are almost exclusively delocalized on four sulfur atoms. The formation of a two-center three-electron (2c-3e) S–S bond is well known. In the case of $\mathbf{21}^{+\bullet}$, the stabilized four-sulfur system can be described as a 4c-7e system [24]. This novel radical cation $\mathbf{21}^{+\bullet}$ is supposed to be formed by the reaction of radical cation $\mathbf{18}^{+\bullet}$ with disulfur liberated by ring contraction of $\mathbf{18}^{+\bullet}$ to thiophene radical cation $\mathbf{17}^{+\bullet}$. The reaction of $\mathbf{18}^{+\bullet}$ with elemental sulfur indeed resulted in the formation of $\mathbf{21}^{+\bullet}$.

In the same way, chemical oxidation of 1,4-dithiin **19** with SbF_5 in CH_2Cl_2 gave radical cation salt $\mathbf{19}^{+\bullet}\text{SbF}_6^-$ in 67 % yield as a brown-colored single crystal, which was quite stable under air. The X-ray crystallography on this salt indicated that the dithiin ring is totally planar with marked shortening of the C–S bond as compared with that of neutral **19** as shown in square brackets in Fig. 6 [26].

The ESR spectrum of $\mathbf{19}^{+\bullet}$ taken at a rather high concentration ($\sim 10^{-3}$ M) exhibited a signal splitting caused by $M_S = \pm 3/2$ of ^{33}S (natural isotopic abundance, 0.75 %). The obtained value of a_S was 0.86 mT [26], which was smaller than that (0.92 mT) for thianthrene radical cation ($\mathbf{22}^{+\bullet}$) [27]. Thus, the spin density on the sulfur atom of $\mathbf{19}^{+\bullet}$ should be lower than that of $\mathbf{22}^{+\bullet}$, and this indicates that the BCO units are even more effective in delocalizing both the positive charge and spin density than the fused benzene rings.

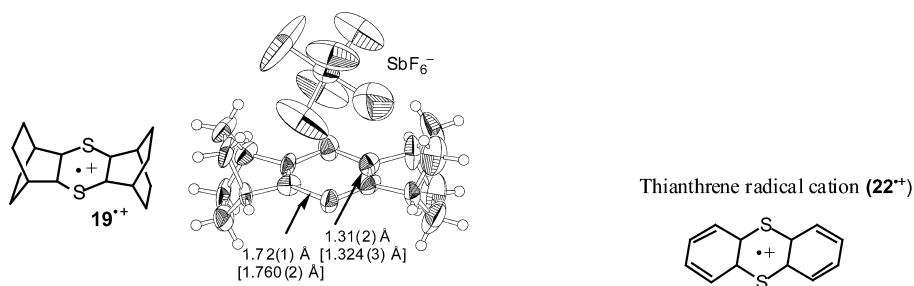


Fig. 6 The X-ray structure of radical cation salt 19^+SbF_6^- with π -bond lengths.

Oligothiophenes

The radical cation and dication of oligothiophenes are considered as important models of partial structure(s) of p-doped state of polythiophenes, i.e., polaron or bipolaron [28], which play important roles in the field of applied chemistry as components of organic electronic devices. Based on the aforementioned results, the oligothiophenes entirely surrounded by BCO frameworks would give positively charged species with high stability. Furthermore, the problem of π -dimer formation observed in most of oligothiophene radical cations was expected to be prevented by the steric effect of the σ -frameworks. Thus, a series of oligothiophenes **23** ($n = 2, 3, 4, 6$) were synthesized, utilizing the Stille cross-coupling and oxidative coupling at the 2-position of the thiophene derivatives [29].

As shown in Table 4, the CV of a series of **23** exhibited well-defined reversible oxidation waves at the potentials generally 0.1–0.2 V lower than those of the corresponding oligothiophenes end-capped with cyclohexane rings [30]. Accordingly, the one-electron oxidation of **23** ($n = 2, 3$) with one equivalent of $\text{NO}^+\text{SbF}_6^-$ in CH_2Cl_2 took place smoothly to give the corresponding radical cation salts 23^+SbF_6^- as air-stable, deeply colored crystals (dark green for $n = 2$ and dark purple for $n = 3$) in 60–70 % yield.

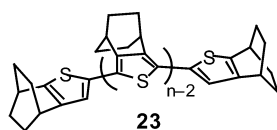


Table 4 Oxidation potential (V vs. Fc/Fc^+)^a of **23**.

n	$E_{1/2}$ (1)	$E_{1/2}$ (2)
2	+0.47	+1.07
3	+0.27	+0.70
4	+0.19	+0.46
6	+0.19	+0.28

^aDetermined by CV in dichloromethane containing 0.1 M Bu_4NClO_4 ; scan rate 100 mVs^{-1} .

The X-ray crystallography of the salt 23^+SbF_6^- ($n = 2$) was conducted for the first time for the radical cation salt of bithiophene, and indicated that the π system is completely planarized as shown in Fig. 7. This planarization is accompanied by considerable shortening of the inter-ring bond (1.398(8) Å) as compared with that in neutral **23** ($n = 2$) (1.455(3) Å), demonstrating a great contribution of the quinoidal structure [31]. Similarly, the molecular structure was determined for 23^+SbF_6^- ($n = 3$), which has the inter-ring bonds a little more twisted (Fig. 8) [31].

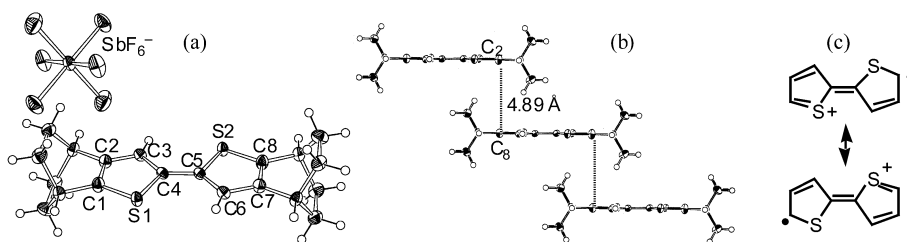


Fig. 7 (a) X-ray structure of radical cation salt $23^{+}SbF_6^{-}$ ($n = 2$). Selected bond lengths (Å) and angles ($^{\circ}$) are: S1-C1, 1.696(5); C1-C2, 1.408(6); C2-C3, 1.371(6); C3-C4, 1.403(6); C4-S1, 1.752(4); C4-C5, 1.398(8); C3-C4-C5-C6, 180.0. (b) Crystal packing drawing; the SbF_6^{-} ions are omitted for clarity. (c) The quinoid resonance structure.

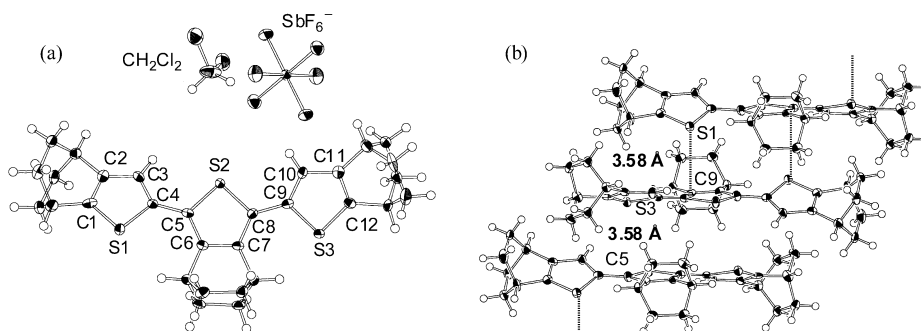


Fig. 8 (a) The X-ray structure of radical cation salt $23^{+}SbF_6^{-}$ ($n = 3$). Selected bond lengths (Å) and angles ($^{\circ}$) are: S1-C1, 1.697(6); C1-C2, 1.394(9); C2-C3, 1.389(11); C3-C4, 1.390(11); C4-S1, 1.761(6); C4-C5, 1.421(9); C5-C6, 1.424(9); C6-C7, 1.389(9); S2-C5, 1.751(6); C3-C4-C5-C6, $-155.5(8)$; C7-C8-C9-C10, $-149.4(8)$. (b) Crystal packing drawing; the SbF_6^{-} ions and CH_2Cl_2 are omitted for clarity.

In contrast to these two cases, the similar treatment of oligothiophene tetramer and hexamer **23** ($n = 4, 6$) with one equivalent of $NO^{+}SbF_6^{-}$ afforded not the radical cation, but the dication salts $23^{2+}2SbF_6^{-}$ ($n = 4, 6$) as dark green crystals with gold luster. The X-ray crystallography was conducted on these two salts for the first time for the dications of oligothiophenes [31]. Again, the π -system of the terthiophene dication $23^{2+}2SbF_6^{-}$ ($n = 4$) was found to be completely planar with all the thiophene rings in *anti* conformation (Fig. 9a), but the planarity slightly decreased in the sexithiophene dication $23^{2+}2SbF_6^{-}$ ($n = 6$) (Fig. 9b). The comparison of the C–C bond length in the π -conjugated system indicates that the electronic structure of the terminal rings is closer to that of neutral thiophene, while the quinoidal character becomes greater in the rings closer to the central position in the case of hexamer dication $23^{2+}2SbF_6^{-}$ ($n = 6$) [31].

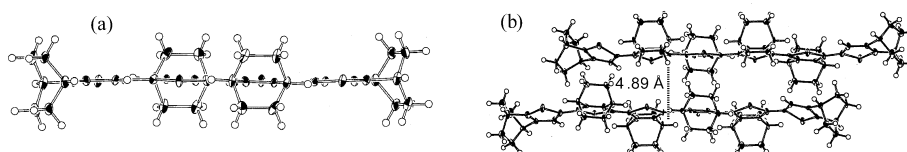
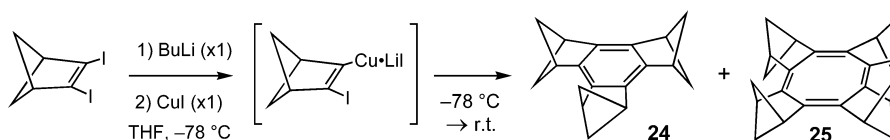


Fig. 9 Side views of the X-ray structures of (a) $23^{2+}2SbF_6^{-}$ ($n = 4$) and (b) $23^{2+}2SbF_6^{-}$ ($n = 6$). The SbF_6^{-} ions and CH_2Cl_2 are omitted for clarity.

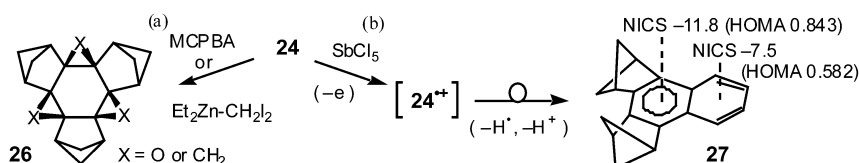
Benzene and cyclooctatetraene fused with bicyclo[2.1.1]hexene units

As described in introduction, the cyclic π -conjugated systems fused with BCH should be affected by an angle strain and by Millis–Nixon effects as well as σ – π conjugative effects more greatly than the structural modification with BCO units. Benzene fused with three BCH units **24** was first prepared by Siegel and was shown to have a novel cyclohexatriene-like structure with strong double-bond fixation [32]. However, its chemistry has not been fully scrutinized due to the low yield (<1 %) of its synthesis. Searching for the more efficient route, we conducted the cross-coupling cyclization as shown in Scheme 4, and obtained the cyclotrimer, that is benzene **24**, in 43 % together with the cyclotetramer, COT **25**, in 21 % [33].



Scheme 4

As expected from its olefinic structure, benzene **24** was found to undergo ready oxidation and Simmons–Smith-type reaction to give tris-epoxide and tris-cyclopropanated compounds **26** ($X = O, CH_2$) as shown in Scheme 5a [33].



Scheme 5

Benzene **24** also underwent one-electron oxidation, but the radical cation was not stable and immediately rearranged into naphthalene derivative **27** by aromatization of one of the BCH units (Scheme 5b). Naphthalene **27** is unique in that one of the six-membered rings is much more aromatic than the other one as shown by X-ray crystallography (bond length comparison), the NICS calculations, and NMR data [34].

On the other hand, the X-ray crystallography on COT **25** demonstrated that the COT ring becomes the first example of a totally planar conjugated system with 8 π -electrons (Fig. 10), as theoretically predicted [35]. Bond alternation is quite large so that the 8 π -antiaromaticity is decreased. The strong interaction of the π -system with the σ -bonds in the highly strained BCH units also prevents the antiaromatic destabilization of this unique COT. Its chemistry, including ready formation of a planar radical cation [36], is being studied in detail.

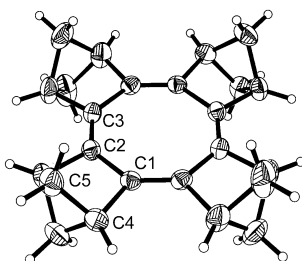


Fig. 10 The X-ray structure of COT **25**. The selected bond lengths (Å) and angles (°) are: C1-C2, 1.500(2); C2-C3, 1.330(2); C1-C4, 1.518(2); C4-C5, 1.549(2); C1-C2-C3, 134.8(1) C2-C1-C4, 100.3(1).

CONCLUSION

Our study initiated from curiosity concerning how much we can stabilize carbocations possessing no electronic perturbation by heteroatom(s) has led to a discovery that placement of BCO units to entirely surround π -conjugated systems can be a highly effective means of stabilizing various organic cations. This is ascribed to the electronic interaction between the σ - and π -systems and to steric protection. Thus, “the blending of a σ flavor into π -systems” can be a unique technique for realization of otherwise hard-to-synthesize novel cationic π -systems. This is so effective that salts of various radical cations generated from π -conjugated molecules such as condensed benzenoid aromatics, COT, thiophene, dithiins, and oligothiophenes have been isolated and their structures determined by X-ray crystallography (except thiophene) for the first time. This method also allowed generation of the first silatropylium ion. In contrast, the use of more strained BCH systems has been shown to result in strong bond fixation, which can be utilized for realization of the first planar COT without any benzoannulation. This concept of the manipulation of σ -bond arrangement for creation of π -conjugated systems having novel electronic structure could be developed further. One possible application would be the examination of various radical cations as a model of polarons for the p-doped state of conductive π -conjugated polymers.

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