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SYNTHESIS OF NOVEL TRIPHENYLENE-TYPE CATIONS CONTAINING BOTH THIOPHENE RINGS AND A TROPYLIUM ION RING. CYCLOHEPTA[*e*]THIENO[2,3-*g*]BENZODITHIOPHENYLIUM ION AND CYCLOHEPTA[*e*]THIENO[3,2-*g*]BENZODITHIOPHENYLIUM ION.

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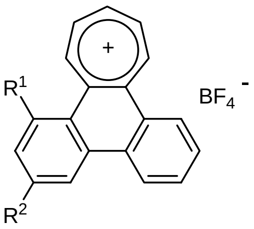
Abstract – An isomeric pair of cyclohepta[*e*]thieno[*g*]benzodithiophenylium ions has been synthesized by an intramolecular Friedel-Crafts type reaction of 2(3)-thienyl-3(2)-cycloheptatrienylthiophenes in a one-pot reaction. These are the isoelectronic cations of triphenylene having both electron-rich and electron-deficient aromatic rings, thiophene and tropylium ion, respectively, in place of phenyl rings.

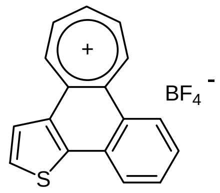
Fused π-conjugated ring systems containing a seven-membered ring such as a tropylium ion, tropone, tropolone, and tropoquinone are of interest from the fundamental viewpoint of their chemical and physical properties, and various kinds of such compounds have been prepared.[1] However, the reported synthetic methods often entailed from tedious multistep procedures at the stage of construction of the unsaturated seven-membered ring. Previously, we reported the one-pot synthesis of cyclohepta[*l*]phenanthrenylium ions (**1** and **2**) by the intramolecular Friedel-Crafts type reaction of 2-tropyliobiphenyls which were prepared in situ from 2-cycloheptatrienylbiphenyls.[2] Our synthetic strategy was to use commercially available 1,3,5-cycloheptatriene as the seven-membered unit and to utilize the electrophilicity of the tropylium ion. Although the intermolecular electrophilic substitution of the tropylium ion with electron-rich aromatic compounds to afford the corresponding cycloheptatrienyl compounds is well known,[3] the intramolecular reaction to afford tropylium ion-fused ring systems is the first case. The successful preparation of cyclohepta[*l*]phenanthrenylium ions opened a route to synthesis of the triphenylene-type compounds including the tropylium ion and electron-rich aromatics. The cyclohepta[*a*]thieno[*c*]naphtharenylium ions (**3** and **4**),[4] cyclohepta[*a*]benzofuro[*c*]naphthalenylium ions

(**5** and **6**),[5] and cyclohepta[*a*]benzothieno[*c*]naphthalenylium ions (**7** and **8**)[5] could be obtained by an application of the above-mentioned tropylium-ion mediated intramolecular cyclization method.



1; $R^1 = H, R^2 = OCH_3$

2; $R^1 = R^2 = OCH_3$



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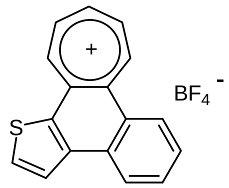

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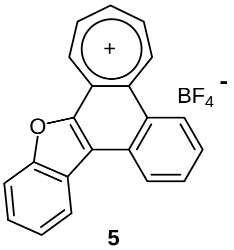

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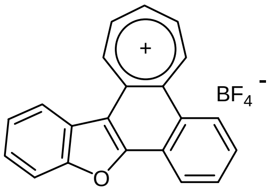

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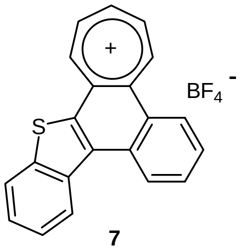

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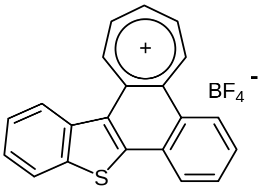

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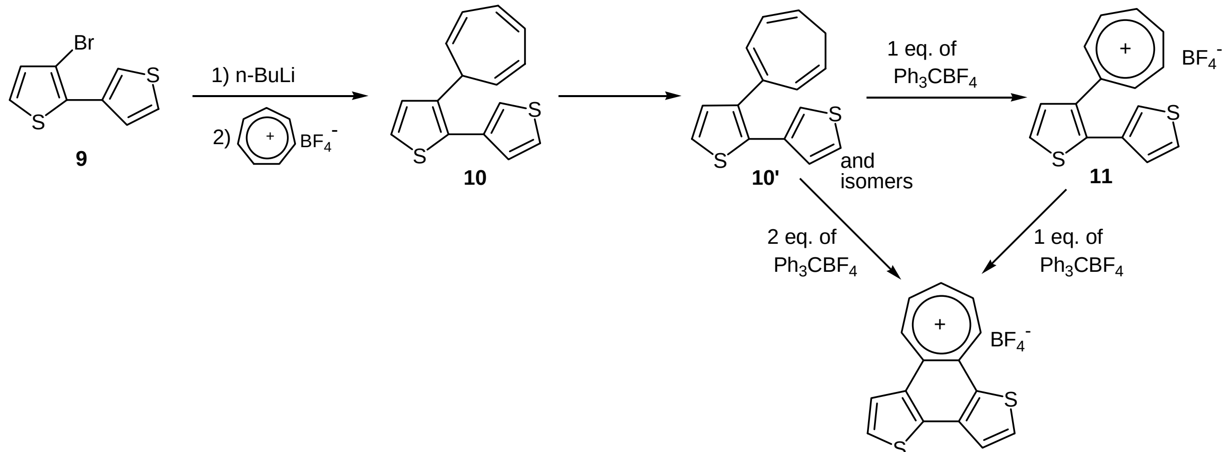
Hence, we report a facile one-pot synthesis of the cyclohepta[*e*]thieno[*g*]benzodithiophenylium ions, which contain both an electron-deficient tropylium moiety and two electron-rich thiophene rings, by such type of reaction. Molecules with highly polarized π-electron systems are of great interest for their potential applications in nonlinear optical devices and, moreover, polynuclear aromatic compounds incorporating thiophene ring have attracted much attention as advanced materials[6] and as pharmacodynamic and therapeutical agents.[7]

Synthesis of cyclohepta[e]thieno[2,3-g]benzodithiophenylium ion (12).

The synthetic sequence leading to **12** from 3-bromo-2,3'-bithiophene (**9**)[8] is depicted in Scheme 1.

Scheme 1

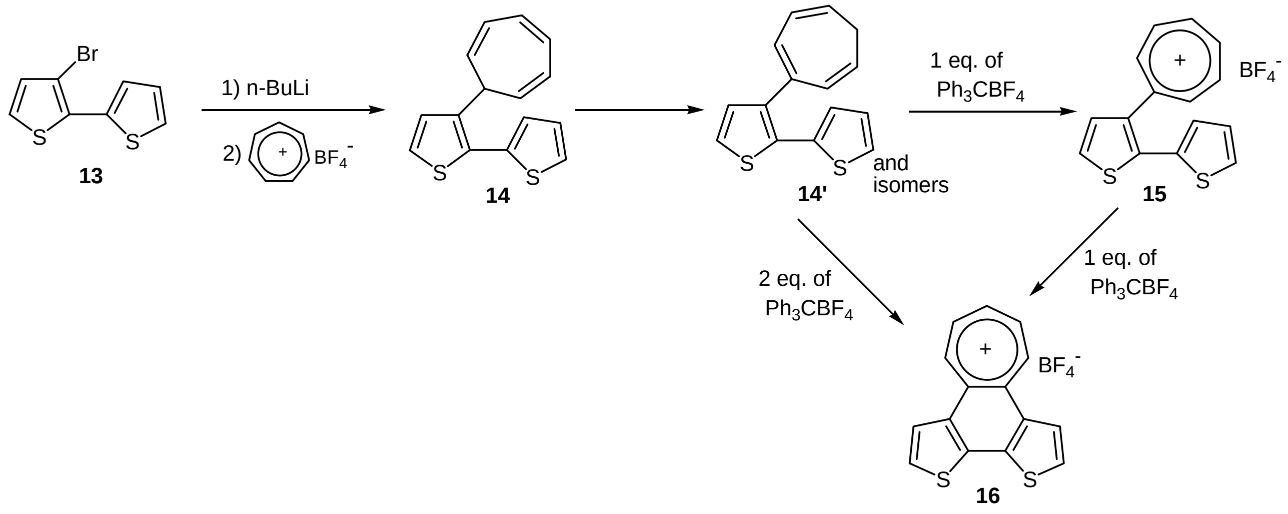


3-Bromo-2,3’-bithiophene (**9**) was treated with n-BuLi in dry ether at –78 ˚C, followed by addition of powdered tropylium tetrafluoroborate to give 3-cycloheptatrienyl-2,3’-bithiophene (**10**) as a pale yellow oil. In order to diminish the steric hindrance in the subsequent hydride-abstraction process, **10** was thermally isomerized by 1,5-sigmatropic shift to the isomeric mixture (**10’**). When **10’** was treated with an equimolar amount of triphenylmethyl tetrafluoroborate in acetonitrile at ambient temperature for 10 min followed by addition of dry ether, 3-tropylio-2,3’-bithiophene tetrafluoroborate (**11**) was obtained as a bright orange powder in 86.0 % yield. On treatment of the cation (**11**) with an equimolar amount of triphenylmethyl tetrafluoroborate at ambient temperature for 30 h, the desired tetracyclic cation, cyclohepta[*e*]thieno[2,3-*g*]benzodithiophenylium ion (**12**), was obtained as a brown powder in 62.0 % yield. When **10’** was treated with 2.0 equivalents of triphenylmethyl tetrafluoroborate in dry acetonitrile at ambient temperature for 30 h followed by addition of dry ether, **12** was obtained in 68.5 % yield. Thus, **12** was obtained from **10’** in one pot.

Synthesis of cyclohepta[e]thieno[3,2-g]benzodithiophenylium ion (16).

In a similar manner as described above, the other isomer, cyclohepta[*e*]thieno[3,2-*g*]-benzodithiophenylium ion (**16**), could be successfully obtained from 3-bromo-2,2’-bithiophene (**13**)[9] (Scheme 2).

Scheme 2

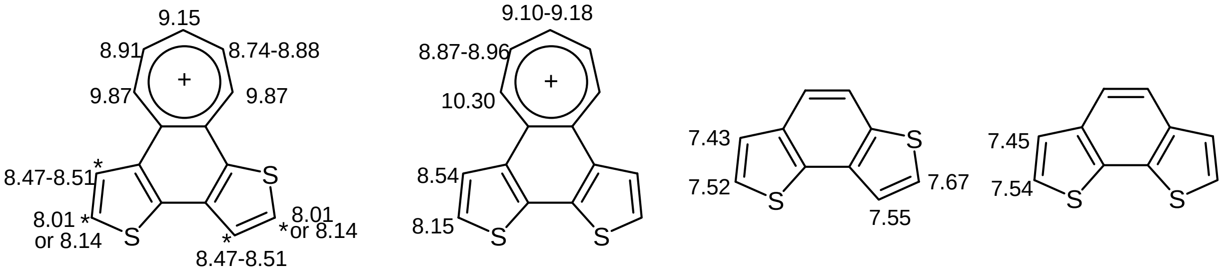


Thus, compound (**13**) was treated with n-BuLi in dry ether at –78 ˚C, followed by addition of powdered tropylium teterafluoroborate to give 3-cycloheptatrienyl-2,2’-bithiophene (**14**) in 70.0 % yield. Refluxing the xylene solution of **14** gave the isomeric mixture (**14’**) in almost quantitative yield. When **14’** was treated with an equimolar amount of triphenylmethyl tetrafluoroborate in acetonitrile at ambient temperature for 10 min followed by addition of dry ether, 3-tropylio-2,2’-bithiophene tetrafluoroborate (**15**) was obtained as a reddish-brown powder in 78.2 % yield. Unlike **10’**, on treatment with two equimolar amounts of triphenylmethyl tetrafluoroborate at ambient temperature for 50 h, **14’** was converted into the uncyclized tropylium ion derivative (**15**), but not the desired tetracyclic cation, cyclohepta[*e*]thieno[3,2-*g*]benzodithiophenylium ion (**16**). However, when the reaction was carried out in refluxing temperature of 1,2-dichloroethane, the desired tetracyclic cation (**16**) was obtained in 68.9 % yield. Moreover, when **15** was treated with an equimolar amount of triphenylmethyl tetrafluoroborate in refluxing temperature of 1,2-dichloroethane for 30 h, **16** was also obtained in 75.2 % yield.[10] The difference of the reactivity between **11** and **15** can be understood in view of the higher nucleophilicity of the 2-position than that of the 3-position in the thiophene ring.

The structures of the obtained tetraacyclic cations, **12** and **16,** were supported by their elemental analyses and their ^{1}H-NMR, IR, and electronic spectra data.

The electronic spectra of these cations exhibit broad, long wave-length absorption at the visible region (**12**: 517 nm, **16**: 520 nm in MeCN), indicating the charge delocalization to some extent in these molecules.

The ^{1}H-NMR spectra of these cations and the related compounds are illustrated in Figure 1. All of the thiophene-ring protons in these cations are at considerably lower field than those of thiophene itself (δ: 7.26 ppm, H2; δ: 7.14 ppm, H3)[11] and benzodithiophenes.[12]



12 **16**

*These assighments are tentative due to the severe peak overlapping.

Figure 1. ^{1}H-NMR spectral data of **12**, **16** and benzo[*b,b'*]dithiophene (δ values; in CD_3CN (**12**, **16**), in CD_3Cl (benzo[*b,b'*]dithiophenes,[12] 250 MHz))

On the contrary, the chemical shifts of seven-membered ring protons (except the protons in Bay region) in **12** and **16** are slightly upper field than those of the tropylium ion itself (δ = 9.20). These facts also indicate the charge delocalization in the peripheral manner.

In summary, a new versatile and high-yielding reaction sequence for the synthesis of two isomeric pairs of cyclohepta[*e*]thieno[*g*]benzodithiophenylium tetrafluoroborate, which are novel, full-conjugated systems having both electron-rich and electron-deficient aromatic rings, the thiophene rings and tropylium ion ring, respectively, from the corresponding cycloheptatrienyl derivatives.

EXPERIMENTAL

All melting points were uncorrected. ^{1}H NMR spectra were obtained on a Hitachi R-24A spectrometer (60 MHz) and/or Bruker AC250 spectrometer (250 MHz). UV-VIS spectra were taken on a Shimadzu UV-2200A spectrophotometer. MS spectra were recorded on a Shimadzu GCMS QP2000A instrument.

Preparation of 3-cycloheptatrienyl-2,3'-thiophene (10)

To a solution of 3-bromo-2,3'-thiophene (**9**) (5.3 g, 22 mmol) in 60 mL of dry ether, 24 mmol of n-BuLi (15 mL of 1.6 M hexane solution) was added slowly at –78˚C under a nitrogen atmosphere. The reaction mixture was stirred at –78˚C for 2 h. Then powdered tropylium ion (3.9 g, 22 mmol) was added in limited amounts. The reaction mixture was stirred for 5 h, allowed to warm to rt, and stirred overnight. After addition of 100 mL of ether, the solution was then neutralized with 5 % aqueous ammonium chloride solution. The ether layer was separated, dried over anhydrous sodium sulfate, and the solvent was evaporated. The residue was purified by column chromatography (silica gel, hexane) to give **10** as a pale yellow oil in 48.8 % yield (2.8 g). δ_H (250 MHz, $CDCl_3$, Me_4Si) 2.98(1H, t, *J* = 5.4 Hz, seven-membered ring), 5.40(2H, dd, *J* = 5.4, 8.9 Hz, seven-membered ring), 6.20-6.26(2H, m, seven-membered ring), 6.65-6.75(2H, m, seven-membered ring), 7.08(1H, dd, *J* = 1.3, 5.1 Hz, thiophene-4'), 7.15(1H, dd, *J* = 1.2, 2.9 Hz, thiophene-2'), 7.23(1H, d, *J* = 5.3 Hz, thiophene-4), 7.26(1H, dd, *J* = 3.0, 4.9 Hz, thiophene-5'), 7.28(1H, d, *J* = 5.2 Hz, thiophene-5); MS(70 eV, direct injection) 256(M^+), 223, 221, 179, 165, 91, 45; Anal. Calcd for $C_{15}H_{12}S_2$: C,70.27; H, 4.72. Found: C, 70.55, H, 4.56.

Preparation of 3-cycloheptatrienyl-2,2'-thiophene (14)

In a similar manner as described above, **14** was prepared from 3-bromo-2,2'-thiophene (**13**) as a colorless oil in 70.0 % yield; δ_H (250 MHz, $CDCl_3$, Me_4Si) 3.11(1H, t, *J* = 5.4 Hz, seven-membered ring), 5.39(2H, dd, *J* = 5.4, 9.0 Hz, seven-membered ring), 6.20-6.29(2H, m, seven-membered ring), 6.71(2H, t, *J* = 3.1 Hz, seven-membered ring), 6.95-7.01(2H, m, thiophene-2' or 5'), 7.21-7.24(1H, m, thiophene-2' or 5'), 7.25(1H, d, *J* = 5.4 Hz, thiophene-4), 7.31(1H, d, *J* = 5.4 Hz, thiophene-5); MS(70 eV, direct injection) 256(M^+), 221, 179, 149,111, 97, 83, 71; Anal. Calcd for $C_{15}H_{12}S_2$: C,70.27; H, 4.72. Found: C, 70.44, H, 4.52.

Thermal isomerization of 10 and 14 to 10' and 14', respectively

The xylene solution (30 mL) of **10** (2.2g, 8.6 mmol) was refluxed for 5 h. The solvent was evaporated in vacuo and the residue was short-chromatographed over silica gel to give the isomeric mixture (**10'**) in almost quantitative yield. In a similar manner, **14** was thermally isomerized to the isomeric mixture **14'**.

Preparation of 3-tropilio-2,3'-bithiophene tetrafluoroborate (11)

A solution of **10'** (678 mg, 2.60 mmol) in 5 mL of dry acetonitrile was added to a solution of triphenylmethyl tetrafluoroborate (879 mg, 2.60 mmol) in 15 mL of dry acetonitrile at ambient temperature and the mixture was stirred for 10 min. After addition of 150 mL of dry ether, the resulting precipitates were collected, washed thoroughly with dry ether, and dried in *vacuo* to yield **11** as a bright orange powder; 776 mg (86.0 %); mp 124-128 ˚C (from CH_2Cl_2) (decomp); δ_H (250 MHz, CD_3CN, Me_4Si) 6.97(1H, d, *J* = 4.6 Hz, thiophene-4'), 7.40-7.55(2H, m, thiophene-2',5'), 7.49(1H, d, *J* = 5.4 Hz, thiophene-5), 7.66(1H, d, *J* = 5.4 Hz, thiophene-4), 8.70-9.04(6H, m, tropylium); Anal. Calcd for $C_{15}H_{11}BF_4S_2$: C,52.65; H, 3.24. Found: C, 52.84, H, 3.12.

Preparation of 3-tropilio-2,2'-bithiophene tetrafluoroborate (15)

In a similar manner as described above, **15** was obtained as a reddish-brown powder in 78.2 % yield; mp 116-120 ˚C (from CH_2Cl_2) (decomp); δ_H (250 MHz, CD_3CN, Me_4Si) 7.01-7.06(2H, m, thiophene-3',4'), 7.48(1H, d, *J* = 5.4 Hz, thiophene-5), 7.54(1H, d, *J* = 4.8 Hz, thiophene-5'), 7.70(1H, d, *J* = 5.3 Hz, thiophene-4), 8.70-9.06(6H, m, tropylium); IR (KBr, cm^{-1}) 1060Anal. Calcd for $C_{15}H_{11}BF_4S_2$: C,52.65; H, 3.24. Found: C, 52.72, H, 3.28.

Preparation of cyclohepta[e]thieno[2,3-g]benzodithiophenylium ion (12)

From ***10'***. A solution of **10'** (170 mg, 0.66 mmol) in 5 mL of dry acetonitrile was added to a solution of triphenylmethyl tetrafluoroborate (442 mg, 1.32 mmol) in 10 mL of dry acetonitrile at 10 ˚C for 10 min, and then 30 mL of dry acetonitrile was added. The mixture was stirred for 30h at ambient temperature. After addition of 100 mL of dry ether, the resulting precipitates were collected, washed thoroughly with dry ether, and dried in *vacuo* to yield **12** as a brown powder; 154 mg (68.5%); mp 208-220 ˚C (from CH_2Cl_2) (decomp); IR (KBr, cm^{-1}) 1060 (BF_4^-, broad); Anal. Calcd for $C_{15}H_9BF_4S_2$: C,52.96; H, 2.67. Found: C, 53.12, H, 2.52.

From ***11***. To a solution of **11** (100 mg, 0.29 mmol) in 10mL of dry acetonitrile a solution of triphenylmethyl tetrafluoroborate (95 mg, 0.29 mmol) in 3 mL of dry acetonitrile was added at 10 ˚C for 10 min, and then 20 mL of dry acetonitrile was added. The mixture was stirred for 30h at ambient temperature. After addition of 50 mL of dry ether, the resulting precipitates were collected, washed thoroughly with dry ether, and dried in *vacuo* to yield **12**; 61 mg (62.0%).

Preparation of cyclohepta[e]thieno[3,2-g]benzodithiophenylium ion (16)

From ***14'***. A solution of **14'** (360 mg, 1.41 mmol) in 30 mL of dry 1,2-dichloroethane was added to a solution of triphenylmethyl tetrafluoroborate (940 mg, 2.82 mmol) in 30 mL of dry 1,2-dichloroethane at 10 ˚C for 10 min. The mixture was refluxed for 30 h. After cooling, 250 mL of dry ether was added. The resulting precipitate was collected, washed with dry ether, and dried in *vacuo* to yield **16** as a deep brown powder; 331 mg (68.9%); mp 210-220 ˚C (from CH_2Cl_2) (decomp); IR (KBr, cm^{-1}) 1070 (BF_4^-, broad); Anal. Calcd for $C_{15}H_9BF_4S_2$: C,52.96; H, 2.67. Found: C, 53.22, H, 2.58.

From ***15***. To a solution of **15** (100 mg, 0.29 mmol) in 10mL of dry acetonitrile a solution of triphenylmethyl tetrafluoroborate (95 mg, 0.29 mmol) in 3 mL of dry acetonitrile was added at 10 ˚C for 10 min, and then 60 mL of dry 1,2-dichloroethane was added. The mixture was refluxed for 20h. After addition of 100 mL of dry ether, the resulting precipitates were collected, washed thoroughly with dry ether, and dried in *vacuo* to yield **16**; 68 mg (68.9%).

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