

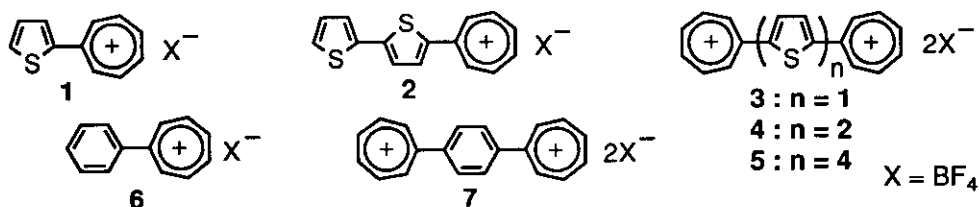
SYNTHESIS AND PROPERTIES OF THIENYL AND OLIGOTHIENYL SUBSTITUTED TROPYLIUM IONS

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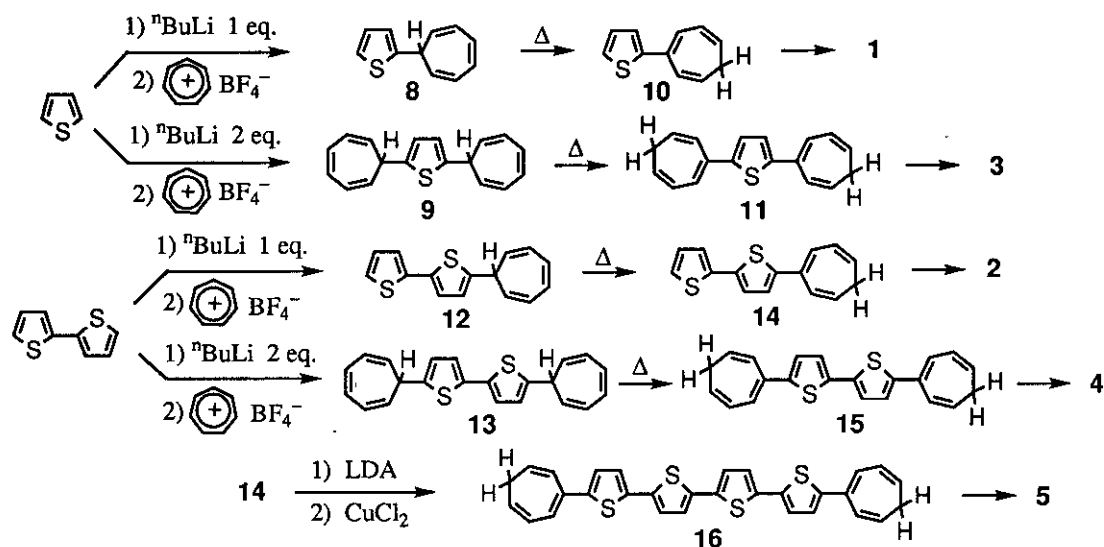
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Abstract – 2-Thienyl- and 2,2'-bithienyl-5-yltropylium ions, as well as 2,5-thienylenebis(tropylium), 2,2'-bithienyl-5,5'-diylbis(tropylium), and 2,2':5',2'':-5'',2'''-quaterthienyl-5,5'''-diylbis(tropylium) ions have been synthesized and their electronic structures in the ground and excited states have been clarified.

Thienyl-substituted carbonium ions such as 2-thienyl- and tris(2-thienyl)methyl cations,¹⁻⁴ and tris(2-thienyl)cyclopropenium ion^{5,6} have been synthesized and their properties have been investigated based on their spectroscopic data. On the other hand, heteroaromatic ring-substituted tropylium ions have not been known so far, whereas alkyl and aryl-substituted tropylium ions have been studied extensively.⁷ Thienyl and oligothieryl tropylium ions appear to be useful to get fundamental insight on the substitution effect of heteroaryl groups on carbonium ions, because they have neither strained ring carbons nor significant difference in hybridization character, and may exist in a coplanar conformation. To this end we have now synthesized thienyl and oligothieryl-substituted tropylium ions (1–5) and clarified their electronic structures at the ground and excited states based on their spectroscopic data, reduction potentials, and theoretical calculations, which are reported herein.



The synthetic routes for 1–5 are outlined in Scheme 1. Thiophene was smoothly tropyliated on treatment first with 1 equiv. of *n*-BuLi in ether and then with 1 equiv. of tropylium fluoroborate to give **8** in 85% yield. Similarly, thiophene was ditropyliated by treating successively with 2 equiv. of *n*-BuLi⁸ and then with 2 equiv. of tropylium fluoroborate at 0 °C, affording **9** in 65% yield. Treatment of 2,2'-bithiophene with 1 equiv. and 2 equiv. of *n*-BuLi in ether followed by addition of the ether solution of the resulted mono and dilithiated bithiophene to the tropylium fluoroborate suspended in ether gave **12** (40% yield) and **13** (60% yield), respectively. Thermal isomerization of **8**, **9**, **12**, and **13** by heating in refluxing xylene for 7 h gave **10**, **11**, **14**, and **15**, which were then treated with trityl fluoroborate in dichloromethane to give stable cations **1** (90% yield), **3** (80% yield), **2** (92% yield), and **4** (89% yield), respectively. The compound (**14**) was lithiated with 1 equiv. of LDA in THF at –78 °C and then submitted to an oxidative



Scheme 1

homo-coupling reaction by treating with CuCl_2 to give **16** (27% yield). Hydride abstraction of **16** with trityl fluoroborate yielded cation (**5**) (73% yield).⁹

Spectroscopic data and reduction potentials of **1**–**5** determined by cyclic voltammetry, along with those of reference cations (**6**) and (**7**) measured under the same conditions, are summarized in Table 1. The ΔAr in ^1H nmr data implies the difference in the averaged chemical shifts for the thienyl (phenyl) protons of the cations from ring protons of thiophene: δ 7.00 (benzene: δ 7.30). The ΔTr in ^1H nmr data implies the difference in the averaged chemical shift for the 7-membered ring protons (H-2–5) of the cations from ring protons of tropylium ion (δ 9.49). Similarly, ΔAr and ΔTr values in ^{13}C nmr data imply averaged chemical shift differences for the thienyl (phenyl) and 7-membered ring carbons of the cations¹⁰ from ring carbons of thiophene (δ 125.3, phenyl: δ 128.5) and tropylium ion (δ 160.62), respectively. In ^1H nmr spectra, 7-membered ring proton signals of **1**–**7** are found at higher field than that of tropylium ion and the phenyl and thienyl ring proton signals of **1**–**7** are found at lower field than those of the ring protons of benzene and thiophene, respectively. There are, however, significant differences between the phenyl and

Table 1. ^1H and ^{13}C nmr Data, Electronic Spectra, and Reduction Potentials of Tropylium Ions (**1** – **7**)

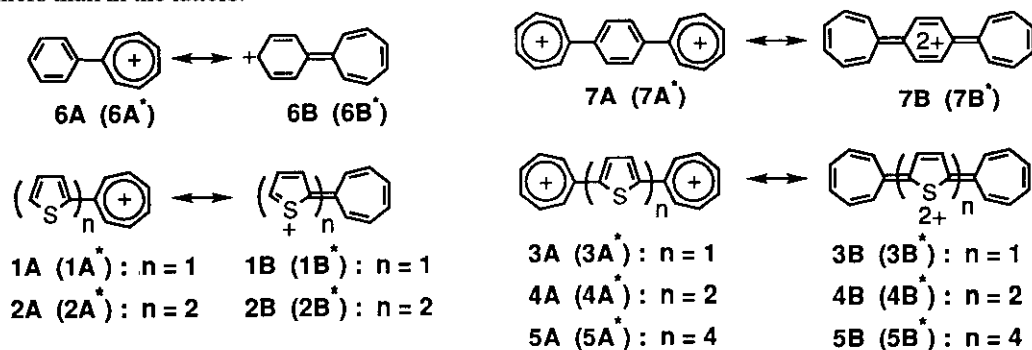
Compd.	^1H nmr Data (δ_{av}) ^a				^{13}C nmr Data (δ_{av}) ^{a,b}				UV-vis (1st Band)		$E_{\text{pred}}^{\text{red}}$ V ^c
	Ar	Tr	ΔAr	ΔTr	Ar	Tr	ΔAr	ΔTr	λ_{max} nm (log ϵ)	ΔE (eV)	
6	7.81	9.22	+0.51	-0.27	131.3	154.1	+2.8	-6.5	368 (4.43)	3.37	-0.24
1	8.02	8.79	+1.02	-0.70	138.7	151.5	+13.4	-9.1	426 (4.42)	2.91	-0.21
2	7.60	8.40	+0.60	-1.09	132.8	149.5	+7.5	-11.1	534 (4.55)	2.35	-0.19
7	8.20	9.48	+0.90	-0.01	132.1	155.4	+3.6	-5.2	382 (4.45)	3.25	—
3	8.43	9.10	+1.43	-0.39	139.2	154.2	+13.9	-6.4	498 (4.41)	2.49	-0.21
4	7.99	8.78	+0.99	-0.71	136.5	153.3	+11.2	-7.3	568 (4.55)	2.18	-0.15
5	7.76	8.41	+0.76	-1.08	—	—	—	—	652 (4.17)	1.90	-0.09

^a δ in $\text{CF}_3\text{CO}_2\text{D}$. ^b The chemical shift of the ipso carbon was excluded in averaging chemical shifts.

^c V vs. SCE: 1.0 mM solution in MeCN with 0.1 M Et_4NClO_4 ; 100 mV/sec.

the thienyl derivatives in the ΔTr and ΔAr values. ΔTr values of **1** and **2** are 2.6 and 4 times larger than that of **6**, respectively. The ΔTr values of **3** and **4** are much larger than that of **7**, and ΔTr values become larger in the order of $3 < 4 < 5$. Similar phenomena are observed in ^{13}C nmr spectra as shown in Table 1. Moreover, the terminal thienyl ring proton (H-5) signals of **1** (δ 8.18) and **2** (δ 7.58) are found at particularly lower field than those of the corresponding protons of **10** and **14** (δ ca. 7.00). ^{13}C nmr chemical shifts of C-5 carbons of **1** (δ 142.98) and **2** (δ 130.91) are at very lower field than those of the corresponding carbons of **10** and **14** (δ 122.4). These facts demonstrate that the positive charge is delocalized over the thienyl groups especially on the sulfur atom of the terminal ring. Indeed, the total charge densities of **1–5** obtained by MNDO-PM3 calculations¹¹ are very high on the sulfur atoms. Whereas the A-type of resonance structures contribute preferably to the ground state of **1–7**, it is now clarified that the contribution extent of **1B** and **2B** to **1** and **2** is higher than that of **6B** to **6** and those of **3B–5B** to **3–5** are higher than that of **7B** to **7** at the ground state, which is quite reasonable in considering that the positive charge can delocalize easier on the weakly aromatic and sulfur containing thienyl moiety than on the phenyl moiety.

The cations (**1–6**) exhibit an irreversible reduction wave in their cyclic voltammograms.¹² The peak potential (E_p^{red}) of **1** is more positive than that of **6**, and the E_p^{red} of **2** is more positive than that of **1**. The same trend is observed for the dications, namely E_p^{red} values become more positive in the order of $3 < 4 < 5$, indicating that the electron affinity increases in this order. Interestingly, the orbital symmetry behavior of LUMO's of **1**, **3**, **4**, and **7** correlates with the HOMO of heptafulvene or that of heptafulvalene having bonding interactions in the intercyclic bonds, that is, the contribution of **B***-types is preferable to the excited states of **1–7**. Due to the same reason mentioned for the ground states, the contribution extent of **1B*** and **2B*** to the excited state of **1** and **2** would be higher than that of **6B*** to the excited state of **6**, and that of **3B*** is higher than that of **7B*** to the excited state of **3** and **7**, respectively. The contribution extent of **B***-types to the excited state would increase in the order of $3 < 4 < 5$. This means that the thienyl substituted tropylium ions with higher contribution of **B***-type resonance structure give more stable reduction products than the corresponding phenyl derivatives, resulting in higher electron affinities in the formers than in the latters.



We can also see in Table 1 significant differences in observed transition energies (ΔE) between the phenyl and thienyl derivatives. The ΔE values of **1** and **3** are smaller by 0.46 and 0.76 eV than those of **6** and **7**, respectively. The ΔE values decrease with an increase in the number of the thienyl groups, and the

decreasing extent is more significant in the mono cations (difference between **1** and **2**) than in the dications (differences between **3** and **4**, and between **4** and **5**). The MNDO¹¹ calculated HOMO's of **2** and **4** lie at 1.34 and 1.33 eV higher energy levels than those of **1** and **3**, respectively, although HOMO's of **6** and **1**, as well as **7** and **3**, are in almost similar energy levels. Therefore pronounced decreases in the observed ΔE values in **1** and **3** compared with **6** and **7**, respectively, can be ascribed to the stabilization of the LUMO levels of **1** and **3**, and the decreases in the ΔE values in **2** and **4** can be mainly ascribed to the destabilization of the HOMO levels of these cations.

We here conclude that there is a significant difference between thienyl- and phenyl-substituted tropylium cations and ditropylium dications in the electronic structures of both the ground and the excited states. The findings described here could be widely applicable to the design and synthesis of a variety of new functional materials involving heterocyclic ring systems.

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9. All new compounds (**1**–**5** and **8**–**16**) gave satisfactory elemental analyses and spectroscopic data. Selected physical data for **1** (BF₄⁻): Yellow powder, mp 145–147 °C; ir (KBr) 3050, 1605, 1500, 1400, 1350, 1270, and 1050 (br.) cm⁻¹. **2** (BF₄⁻): Dark violet powder, mp 188–189 °C; ir (KBr) 3040, 1600, 1520, 1495, 1470, 1415, 1265, 1050 (br.) cm⁻¹. **3** (2BF₄⁻): Violet powder, mp > 300 °C; ir (KBr) 3000, 1600, 1493, 1418, 1345, 1262, 1200, 1050 (br.) cm⁻¹. **4** (2BF₄⁻): Dark violet powder, mp > 300 °C; ir (KBr) 3000, 1600, 1490, 1412, 1320, 1260, 1066 (br.) cm⁻¹. **5** (2BF₄⁻): Black powder, mp > 300 °C; ir (KBr) 3020, 1605, 1511, 1490, 1408, 1355, 1265, 1070 (br.) cm⁻¹. **8**: Pale yellow oil. **9**: Pale yellow oil. **10**: Pale yellow oil. **11**: Pale yellow oil. **12**: Yellow needles, mp 43–45 °C. **13**: Orange needles, mp 104–105 °C. **14**: Yellow needles, mp 64–65 °C. **15**: Orange needles, mp 161–164 °C. **16**: Dark orange crystals, mp >250°C.
10. The ipso carbon was excluded from the average to avoid inductive or anisotropic effect; δ_{ipso} of the 7-mem. ring : **6** (171.1), **1** (164.1), **2** (162.4), **7** (168.4), **3** (161.0), **4** (162.5).
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12. The cation **7** fails to show clear reduction waves in the cyclic voltammogram, probably due to the instability of the resulting [7.6.7]quinarene.

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