# Novel Monocation, Dication, and Dianion of a Cage Molecule, Trithienylmethanophane

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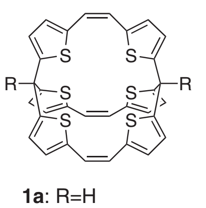
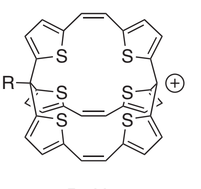
The McMurry coupling of tris(5-formyl-2-thienyl)methane afforded an unsubstituted, etheno-bridged trithienylmethanophane which was in turn transformed to novel cage-molecular monocation, dication, and dianion of substantial stability. The latter two species are the first examples of fully conjugated ionic cyclophane cage molecule.

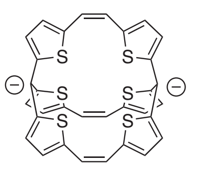
Multiple carbocations and carbanions of cage molecules have been rarely known.[1] We have recently reported the synthesis of trithienylmethanophane (TTMP), **1b** and **1c**, novel etheno-bridged cage molecule bicapped with tris(2-thienyl)methanes.[2,3] The EI mass spectra of these compounds suggested a considerable stability of monocations, **2b** and **2c**, and dication **3** by showing fragment peaks of $[M\text{-}R]^+$ and $[M\text{-}2R]^{2+}$. In view of stabilizing effect of 2-thienyl group upon not only carbocations but also carbanions,[4] dianion **4** would also be species of considerable stability. Di-ions **3** and **4** would be the first examples of fully conjugated ionic cyclophane cage molecule. Here we wish to report the synthesis of the parent cage molecule **1a**, monocation **2a**, dication **3**, and dianion **4**.



**1a**: R=H
**1b**: R=$CH_3$
**1c**: R=$C_6H_{13}$
**1d**: R=$Si(CH_3)_3$



**2a**: R=H
**2b**: R=$CH_3$
**2c**: R=$C_6H_{13}$
**3**: R=⊕

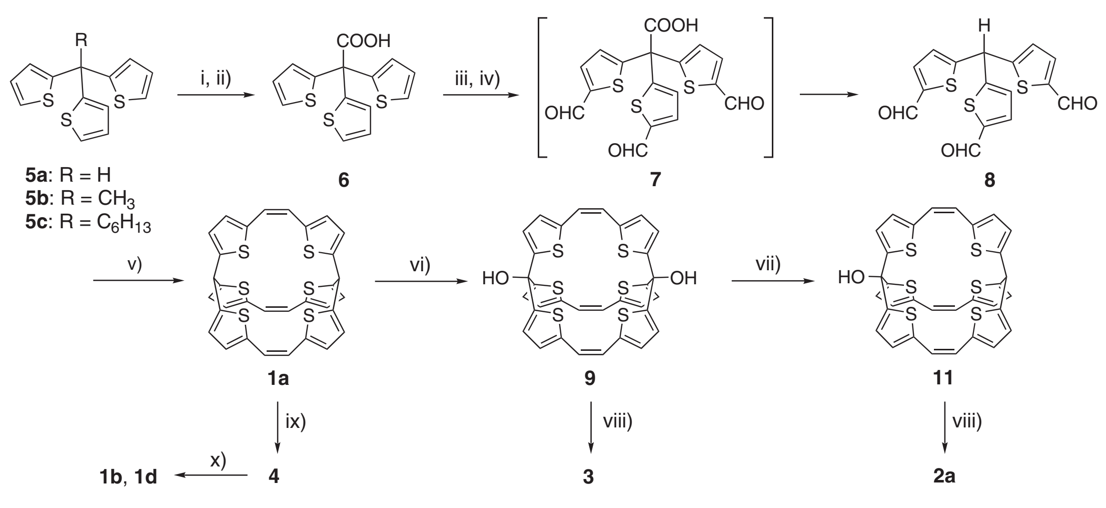


**4**

If we should employ the McMurry coupling[5] for **1a** as did for **1b** and **1c**, we need tris(5-formyl-2-thienyl)methane **8** or its derivative bearing a removable protecting group at the central methine carbon (Cα). Although sequential tri-lithiation and tri-formylation of derivatives of tris(2-thienyl)methane, **5b** and **5c**, at C-5 positions of the 2-thienyl groups have been successful, similar lithiation–formylation of **5a** was unsuccessful because of fairly high acidity of the Cα-proton.[6] Therefore, we looked for a proper protecting group at Cα and found that carboxyl group works for the purpose beyond expectation.

Scheme 1 shows the synthesis of **1a**, **2a**, **3**, and **4**. The reaction of trithienylmethyl anion obtained from **5a** with carbon dioxide gave trithienylacetic acid **6** in good yield. To our surprise, treatment of **6** with *n*-BuLi (5 equiv.) in THF at 0 °C followed by addition of DMF and usual work-up afforded **8** involving spontaneous decarboxylation. This easy decarboxylation of the intermediate **7** may be due to electron-withdrawing properties of the formyl groups. Compound **6** begins to decarboxylate above 180 °C. The McMurry coupling of **8** afforded **1a**[9] as a stable, pale yellow, crystalline substance in 2–4% yield. Although the yield of **1a** was poor,[10] its isolation from the major oligomeric materials was easy by chromatography on silica gel. TTMP **1a** is sparingly soluble in benzene and a little more soluble in $CH_2Cl_2$ and $CHCl_3$. $^1H$-NMR spectrum of **1a** is similar to those of **1b** and **1c** except for the appearance of bridgehead protons (Cα-H) as a singlet at δ 6.06 which is at slightly higher field than Cα-H of **5a** (δ 6.11). Single-crystal X-ray analysis established the molecular structure of **1a** (Figure 1) where the sulfur atoms point inside the cage similar to those of **1b**.[11]

Although TTMP **1a** can be a direct precursor to dication **3** by hydride abstraction, diol **9** should be a better precursor for its



**Scheme 1.** i) 1.6 equiv. LDA–THF, rt, 1 h; ii) $CO_2$ (80%), iii) 5.0 equiv. *n*-BuLi/THF, 0 °C, 2 h; iv) excess DMF (80%); v) $TiCl_4$, Zn, CuI/DME, rt, overnight then reflux, 24 h (2–4%); vi) excess DDQ–5% wet benzene, reflux 2 h (82%), vii) addition of **1a**/$CH_2Cl_2$ to a $CF_3COOH$ solution of **9**, then addition of NaOH aq. after 2 h at rt (85%); viii) $CF_3COOH$, ix) excess *t*-BuLi/THF, −40 °C; x) excess $CH_3I$ or TMSCl (>90%).

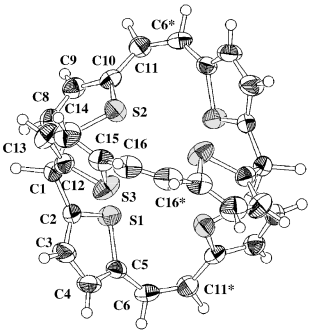


**Figure 1.** ORTEP drawing (50% thermal ellipsoids) of the cage molecule **1a**. Selected bond lengths (Å) and angles (°): C1–C2 1.529(6), C2–C3 1.351(6), C3–C4 1.405(7), C4–C5 1.351(6), C5–C6 1.464(6), C6–C11* 1.319(6), S1–C2 1.714(4), S1–C5 1.731(4), C5–C6–C11* 129.6(5), C6–C11*–C10 131.5(4), C2–C1–C12 110.4(3).

clean generation. The synthesis of **9** was attained by oxidation of **1a** with DDQ in 5% wet benzene at 80 °C. As expected, dissolution of **9** in trifluoroacetic acid (TFA) cleanly generated **3** in a deep orange solution where **3** remains unchanged more than ten days at room temperature. Its $^1$H- and $^{13}$C-NMR spectra are consistent with the dication structure showing a high symmetry of the molecule (only three signals for $^1$H and six signals for $^{13}$C) and appreciably low-field chemical shifts of $^1$H and $^{13}$C signals (averaged chemical shift of the thienyl and etheno groups: $^1$H; $\delta_{av}$ 7.81 vs 6.71 of **1a**, and $^{13}$C; $\delta_{av}$ 145.10 vs 134.79 of **1a**).[12] The cation-center carbons ($C\alpha^+$) resonate at $\delta$ 166.26 which is almost the same chemical shift as $C\alpha^+$ of tris(2-thienyl)methyl cation **10** ($\delta$ 166.27). Dication **3** exhibits a strong visible absorption at 495 nm that is red-shifted by 22 nm relative to that of **10** (Figure 2).[12]

Attempted mono-hydroxylation of **1a** using one equivalent of DDQ produced mono-ol **11** in only poor yield, and the major product was diol **9** together with a substantial recovery of **1a**. A consideration that dication **3** should be thermodynamically less stable than monocation **2a** owing to electrostatic repulsion led us to examine successfully disproportionation between **1a** and **3**: addition of a TFA solution of **3** to a dichloromethane solution of **1a** (1:1 molar ratio) at room temperature afforded **11** in 85% yield after quenching with water. Dissolution of **11** in TFA generated **2a** in a blue-green solution and its NMR spectra indicate considerable delocalization of the positive charge into all the thienyl groups.[12] The averaged $^1$H chemical shift ($\delta_{av}$ 7.22) is at almost the middle of those of **1a** and **3**.[13] The chemical shifts of $C\alpha$-H and $C\alpha$ opposite to $C\alpha^+$ are also down-shifted slightly relative to those of **1a** ($^1$H: $\delta$ 6.19 vs. 6.06; $^{13}$C: $\delta$ 43.57 vs 42.47). The UV-vis spectrum of **2a** is remarkably different from that of **3**, exhibiting a broad absorption at much longer wavelength of about 630 nm in accordance with the NMR observation (Figure 2).[12,14]

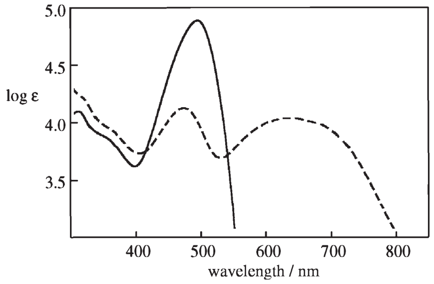


**Figure 2.** UV-vis spectra of monocation **2a** (dashed line) and dication **3** (solid line) in trifluoroacetic acid.

On the other hand, treatment of **1a** with *t*-BuLi in THF below −40 °C generated dianion **4** in a deep red solution and its reaction with iodomethane or chlorotrimethylsilane afforded **1b** or **1d** in more than 90% yield. Dianion **4** seems less stable than tris(2-thienyl)methyl anion because its red solution turns to a blackish solution at around 0 °C; however, its clean generation indicates a fair stability.

In conclusion, we have generated novel dication **3** and dianion **4** from TTMP **1a**. These di-ionic species can be used as synthons for novel molecular systems containing cage-structure of **1a**, although improvement of the yield will be needed for such applications.

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**References and Notes**

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3 IUPAC nomenclature for **1a**: 33,34,35,36,37,38-hexathiaoctacyclo-[10,10,10,$1^{2,5}$,$1^{8,11}$,$1^{13,16}$,$1^{19,22}$,$1^{23,26}$,$1^{29,32}$]octatriaconta[2,4,6,8,10,13,15,17,19,21,23,25,27,29,31]pentadecaene.

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6 Since bis(2-thienyl)methane (p*K*a 28.9[7]) is more acidic than diphenylmethane (p*K*a 32.3), tris(2-thienyl)methane should be more acidic than triphenylmethane (p*K*a 30.6[8]).

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9 **1a**: pale yellow prisms; mp >225 °C; MS (EI) $m/z$ 596 ($M^+$); $\delta_H$ (270 MHz, $CDCl_3$) 6.86 (dd, $J = 0.9$, 3.6 Hz, 6H), 6.79 (d, $J = 3.6$ Hz, 6H), 6.47 (s, 6H), 6.06 (s, 2H); $\delta_C$ (67.8 MHz, $CDCl_3$) 148.28, 136.84, 128.99, 125.05, 122.46,42.47; UV-vis ($CH_2Cl_2$) $\lambda_{max}$ nm 386sh, 327 (log ε 4.25), 271 (4.65); Anal. Calcd. for $C_{32}H_{20}S_6$: C 64.39, H 3.38. Found: C 64.18, H 3.28.

10 Existence of the enolizable $C\alpha$ proton in **1a** may be responsible for the poorer yield of **1a** than **1b** and **1c**.

11 Crystal data for **1a**: $C_{32}H_{20}S_6$, $M_r = 596.87$, monoclinic, space group *C2/c*(no. 15), $a = 18.373(5)$, $b = 9.819(2)$, $c = 15.718(4)$ Å, $\beta = 108.39(1)$, $V = 2690(1)$ Å$^3$, $Z = 4$, $D_{calcd} = 1.473$ Mgm$^{-3}$, 9476 reflections measured, 2928 unique ($R_{int} = 0.108$) used in refinement. $R1 = 0.061$ (1380 data, $I > 2\sigma(I)$), $wR = 0.151$ (all data). CCDC 199161.

12 **3**: $\delta_H$ (270 MHz, $CF_3COOD$) 8.45 (d, $J = 4.3$ Hz, 6H), 7.65 (d, $J = 4.3$ Hz, 6H) 7.32 (s, 6H); $\delta_C$ (67.8 MHz, $CF_3COOD$) 166.26, 159.36, 148.65, 146.74, 138.91, 131.86; UV-vis ($CF_3COOH$) $\lambda_{max}$ nm 495 (log ε 4.89); **2a**: $\delta_H$ (270 MHz, $CF_3COOD$) 8.10 (d, $J = 4.4$ Hz, 3H), 7.43 (d, $J = 4.4$ Hz, 3H), 7.14 (d, $J = 11.5$ Hz, 3H), 7.03 (d, $J = 3.8$ Hz, 3H), 6.85 (d, $J = 3.8$ Hz, 3H), 6.74 (d, $J = 11.5$ Hz, 3H), 6.19 (s, 1H); $\delta_C$ (67.8 MHz, $CF_3COOD$) 171.28, 153.45, 142.85, 140.47, 137.14, 133.59, 133.40, 132.18, 124.89, 118.10, 43.57; UV-vis ($CF_3COOH$) $\lambda_{max}$ nm 634 (log ε 4.06), 473 (4.15).

13 The averaged $^{13}$C chemical shift of **2a** is not certain at present because of missing one carbon signal by overlapping.

14 The broad absorption may be ascribed to intramolecular charge transfer.

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