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Synthesis and properties of 1,6-methano[10]annuleno-[3,4-*c*]thiophene and its 1,3-dicyano derivative

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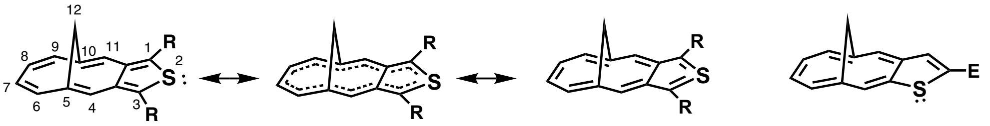
Abstract—New thiophene-annulated 1,6-methano[10]annulene **1** and **2** were synthesized. The anisotropic deshielding effect from the π-electron system, based on the chemical shift values of the bridged methylene protons, is reduced compared with that of **3**, and their crystal structures show clear bond alternation.

Condensation of thiophene at the 3,4-positions and annulene provides new π-electron systems known as an *o*-quinodimethane type of heterocyclic compounds, which have been investigated from the viewpoints of conductive materials,[1] and basic interest in an effect of the thiophene fusion on the ring current. Since the sulfur atom can contribute to the peripheral conjugation either by two π-electron moieties with its lone pair electrons or by π-sulfurane type conjugation, the ring current is expected in such systems.[2] Although 1,6-methano[10]-annulene condensed with thiophene at the 2,3-positions, **3**,[3] has been synthesized and shows a similar aromatic ring current to that of 1,6-methanobenzo[3,4-*a*][10]-annulene,[4] the titled compound of 1,6-methano[10]-annuleno[3,4-*c*]thiophene **1** is not known so far. It is of interest to know whether it is an aromatic as **3** or not, that is, which resonance form shown in Scheme 1 is dominant. Here, we report the first synthesis of the title compounds, **1** and **2**, and their physical and chemical properties including X-ray crystallographic structures.

The reaction of 3,4-bis(bromomethyl)-1,6-methano-[10]annulene **4**[5] with NaCN in THF–H_2O solution at rt for 18 h gave 3,4-bis(cyanomethyl) derivative **5** in 75% yield. Then, the reaction of **5** with thionyl chloride in the presence of triethylamine[2,6] gave **2** as pale yellow needles in 34% yield (see Scheme 2).

The structure of **2** was confirmed based on the spectral data and further was elucidated by X-ray crystallographic analysis. The IR spectrum of **2** showed the absorption at 2215 cm^{-1} as a typical conjugated cyano group. And the ^1H NMR spectrum of **2** showed the ring



1 : R=H
2 : H=CN

1a
2a

1b
2b

3 : E=COOEt

Scheme 1.

Keywords: Thiophene; 1,6-Methano[10]annulene; *o*-Quinodimethane; Ring current; X-ray crystallographic analysis.

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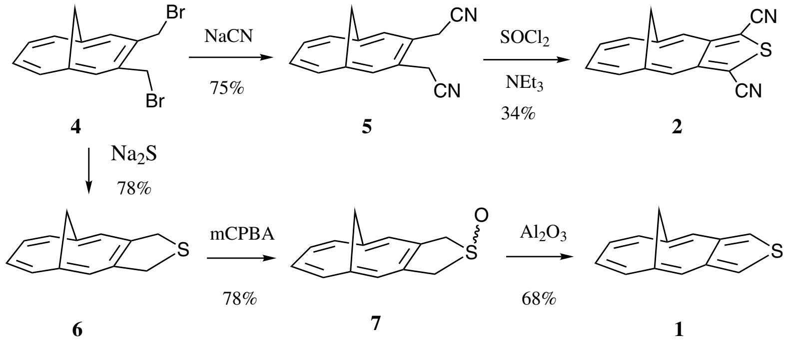


Scheme 2.

protons on the bridged annulene moiety at δ 7.31 ppm as a multiplet for H6, H9, δ 6.58 ppm as a singlet for H7, H8, δ 6.10 ppm as a multiplet for H4, H11, and the bridged methylene protons were observed at δ 1.70 and 0.76 ppm as a doublet for H12a and H12b, respectively, which were assigned by the W-letter type long-range coupling. The unsubstituted compound **1** was synthesized as follows. Treatment of sulfide **6**[5] with 1 equiv of *m*-chloroperbenzoic acid (*m*CPBA) in $CHCl_3$ at rt gave a stereo isomeric mixture of **7** in 37% and 41% yields, respectively. This mixture was treated with Al_2O_3[7] in refluxed benzene to give **1** as slightly unstable pale yellow needles in 68% yield. Allowing **1** to stand under air at room temperature causes color change from bright yellow to brown, suggesting its decomposition, but the compound is rather stable under inert gas atmosphere below 0 °C for a few months. The structure of **1** was also confirmed based on the spectral data.[8] The ^{1}H-chemical shifts are indicated and the ^{13}C-chemical shifts in parentheses in Figure 1. The assignment of the chemical shifts of the carbons was confirmed by the methods of C–H COSY, HMBC, and HMQC measurements. The protons at the 1,3-positions of **1** were observed at δ 7.77 ppm, the same as those of benzo[*c*]thiophene **9**.[7] The other ring protons of **1** observed at δ 7.16, 6.80, and 6.34 ppm are located in a little higher field than those of **2** and higher than those of **3** as shown in Figure 1. The bridged methylene protons of **1** were observed at δ 1.57 ppm for H12a and 1.23 ppm for H12b assigned by the same method as above. The lower ^{1}H-chemical shifts of H12a compared to that of H12b in both **1** and **2** must be due to the larger contribution of localized 6,8-diene form faced to H12a rather than peripheral conjugation, and the averaged chemical shift of **1** are slightly lower field than those of **2** and much lower field than those of **3** and **8**.[4] It clearly suggests that the anisotropic deshielding effect of the [10]annulene ring is reduced in **1**. These ^{1}H-chemical shifts of **1** and **2** indicate that contribution of the peripheral conjugation with 14 electrons is negligible.

The UV–vis spectra showed the longest absorption maximum of **1** was shown at a shorter wavelength region than that of **2** by 50 nm. Fluorescence was also observed at 500 nm for **1** and 572 nm for **2**. Single crystals were obtained for both **1** and **2** and X-ray crystallographic analyses were carried out.[9] The results are shown in Figures 2 and 3. The bond alternation in the bridged annulene moiety of **1** and **2** is clearly shown compared with the structure of 1,6-methano[10]annulene**10**[10] and naphtho[*c*]thiophene **11**.[11] The C–S bond lengths in **1** and **2** are similar to those of **11** and the distances between the bridgehead carbons C5–C10 in **1** and **2** are slightly longer than that of **10**.

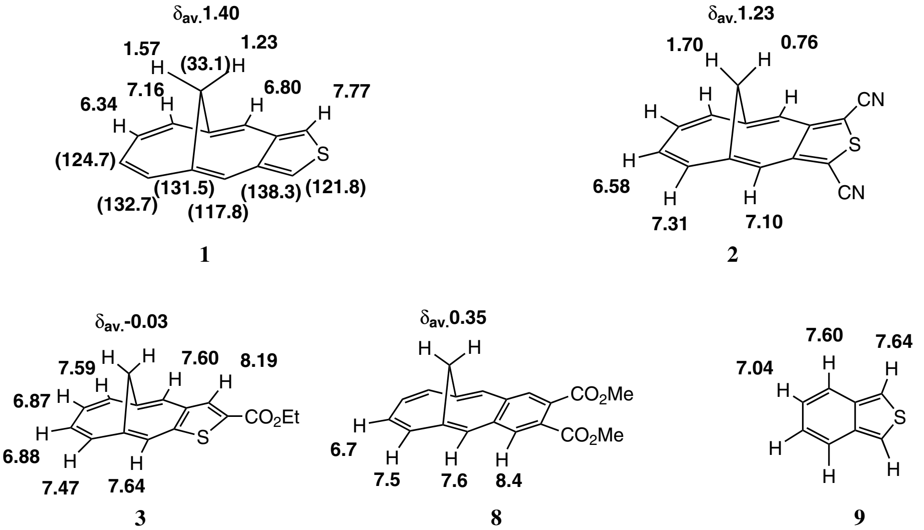
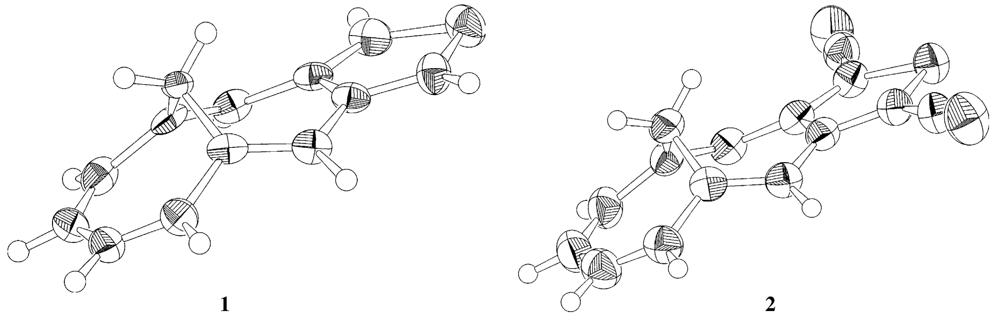
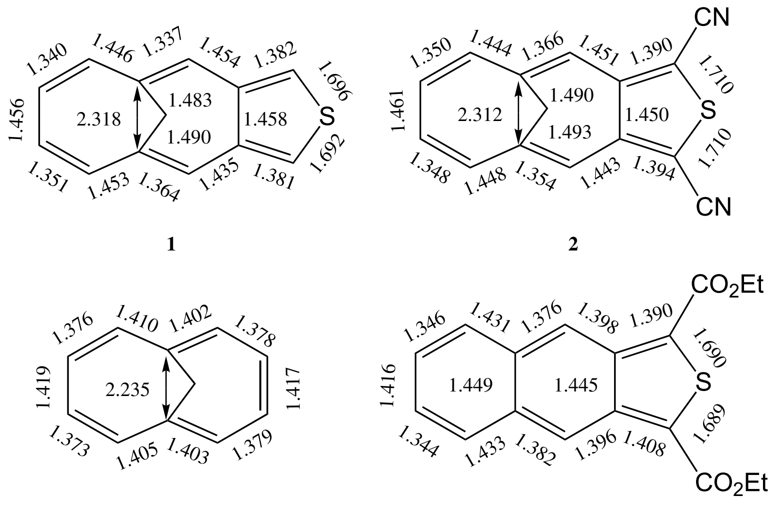


Figure 1. The ^{1}H- (and ^{13}C-) chemical shifts of **1**, **2**, **3**, **8**, and **9**.



1 **2**

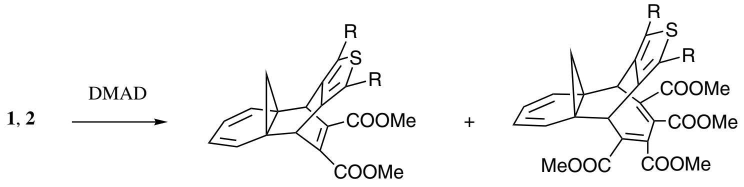
Figure 2. The ORTEP drawing of **1** and **2**.



1 **2**

10 **11**

Figure 3. The distances between C–C and C–S (Å) of **1**, **2**, **10**, and **11**.



12: R=H
14: R=CN

13: R=H

Scheme 3.

These data indicate that the thiophenes stay as aromatic and the methano[10]annulene parts are olefinic. The reaction of **1** with dimethyl acetylenedicarboxylate (DMAD) at 140 °C gave two adducts, **12** (34%) and **13** (31%) and that of **2** provided a single product **14** (46%). Although the formation of **13** implies ionic intermediate,[12] and that of **12** and **14** can be rationalized by a sequence involving the [8+2] cycloaddition and the following 6π-electrocyclization (Scheme 3).[13]

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8. Selected spectral data of the new compounds are as follows:

   Compound **7**: one of the stereoisomers: pale yellow needles, mp 42–44 °C. IR (KBr) $\nu_{\max}$ 2941m, 1441w, 1866m, 1247m, 1120s, 1036vs, 847m, 808s, 750m, 720s, 537s cm^{-1}. ^{1}H NMR (CDCl$_3$–TMS): δ ppm = 7.55 (s, 2H), 7.42 (m, 2H), 7.11 (m, 2H), 4.36 (d, $J = 16.4$ Hz, 2H), 4.15 (d, $J = 16.4$ Hz, 2H), −0.31 (d, $J = 9.2$ Hz, 1H), −0.35 (d, $J = 9.2$ Hz, 1H). ^{13}C NMR (CDCl$_3$–TMS): δ ppm = 131.8, 129.4, 128.7, 127.2, 112.6, 62.9, 35.4. MS *m/z* (rel. int.) 216 (M^{+}, 13), 197 (34), 184 (36), 167 (100), 152 (56), 141 (21), 139 (18), 128 (23), 115 (30).

   Compound **7**: another isomer: pale yellow needles, mp 97–98 °C. IR (KBr) $\nu_{\max}$ 3022w, 2978w, 2940m, 1402w, 1306m, 1259m, 1052vs, 924m, 808s, 728w, 701m cm^{-1}. ^{1}H NMR (CDCl$_3$–TMS): δ ppm = 7.44 (m, 2H), 7.34 (s, 2H), 7.12 (m, 2H), 4.41 (s, 4H), −0.29 (d, $J = 9.19$ Hz, 1H), −0.33 (d, $J = 9.19$ Hz, 1H). ^{13}C NMR (CDCl$_3$–TMS): δ ppm = 130.4, 129.2, 127.1, 127.0, 114.9, 61.0, 35.1. MS *m/z* (rel. int.) 216 (M^{+}, 12), 197 (49), 184 (14), 167 (100), 152 (52), 141 (18), 128 (18), 115 (23).

   Compound **1**: pale yellow needles, mp 102.5–103 °C. IR (KBr) $\nu_{\max}$ 3079m, 2935m, 1563w, 1454w, 1256w, 923m, 850vs, 771s, 698s, 666s, 560s cm^{-1}. ^{1}H NMR (CDCl$_3$–TMS): δ ppm = 7.77 (s, 2H, H1, H3), 7.16 (m, 2H, H), 6.80 (s, 2H), 6.34 (m, 2H), 1.57 (d, $J = 10.4$ Hz, 1H, H12a), 1.23 (d, $J = 10.4$ Hz, 1H, H12b). ^{13}C NMR (CDCl$_3$–TMS): δ ppm = 138.3, 132.7, 131.5, 124.7, 121.8, 117.8, 33.1. UV–vis $\lambda_{\max}$ (MeOH) 214 ($\log\varepsilon = 4.12$), 266 (4.61), 379 nm (3.53). MS *m/z* (rel. int.) 198 (M^{+}, 74), 197 (100), 185 (13), 165 (20), 149 (50), 141 (14), 139 (12). HRMS calcd for $\mathrm{C_{13}H_{10}S}$: 198.0503, obsd: 198.0483.

   Compound **2**: orange needles, mp 172–176 °C. IR (KBr) $\nu_{\max}$ 2924m, 2210s, 1650m, 1383m, 1260m, 923m, 1025s, 794s, 668w cm^{-1}. ^{1}H NMR (CDCl$_3$–TMS): δ ppm = 7.31 (m, 2H, H6, H9), 7.10 (s, 2H, H4, H11), 6.56 (m, 2H, H7, H8), 1.70 (d, $J = 10.5$ Hz, 1H, H12a), 0.76 (d, $J = 10.5$ Hz, 1H, H12b). ^{13}C NMR (CDCl$_3$–TMS): δ ppm = 145.2, 134.5, 132.4, 127.1, 116.6, 115.3, 113.3, 33.1. UV–vis $\lambda_{\max}$ (MeOH) 231 ($\log\varepsilon = 4.12$), 259 (4.61), 292 (4.26), 430 nm (3.38). MS *m/z* (rel. int.) 248 (M^{+}, 95), 247 (84), 85 (94), 69 (100). HRMS (M^{+}) Obsd: 248.0411; Calcd for $\mathrm{C_{15}H_{8}N_{2}S}$: 248.0408.

   Compound **12**: pale yellow needles, mp 53–54 °C. IR (KBr) $\nu_{\max}$ 3032w, 3001w, 2953m, 2926m, 1726vs, 1625m, 1436s, 1275vs, 1129m, 1060m, 830w cm^{-1}. ^{1}H NMR (CDCl$_3$–TMS): δ ppm = 6.93 (s, 2H), 6.18 (m, 2H), 5.84 (m, 2H), 4.48 (s, 2H), 3.74 (s, 6H), 1.37 (d, $J = 5.60$ Hz, 1H), −0.16 (d, $J = 5.60$ Hz, 1H). ^{13}C NMR (CDCl$_3$–TMS): δ ppm = 166.4, 148.4, 141.0, 128.5, 121.1, 116.7, 52.3, 45.3, 40.3, 20.9. MS *m/z* (rel. int.) 340 (M^{+}, 59), 325 (20), 308 (49), 279 (76), 253 (72), 219 (100), 115 (46).

   Compound **13**: pale yellow needles, mp 104–105 °C. IR (KBr) $\nu_{\max}$ 3031w, 3000w, 2953m, 2925m, 2853m, 1721vs, 1436s, 1267vs, 1121s, 1062m, 1037m, 802w cm^{-1}. ^{1}H NMR (CDCl$_3$–TMS): δ ppm = 7.61 (s, 2H), 6.20 (m, 2H), 5.87 (m, 2H), 4.61 (s, 2H), 3.91 (s, 6H), 3.74 (s, 6H), 1.13 (d, $J = 6.0$ Hz, 1H), −0.13 (d, $J = 6.0$ Hz, 1H). ^{13}C NMR (CDCl$_3$–TMS): δ ppm = 167.8, 165.8, 147.6, 142.8, 128.0, 124.8, 121.5, 52.7, 52.4, 49.1, 38.1, 30.9. MS *m/z* (rel. int.) 482 (M^{+}, 2), 450 (20), 419 (27), 391 (100), 390 (87), 331 (59), 149 (85).

   Compound **14**: pale yellow needles, mp 215–219 °C. IR (KBr) $\nu_{\max}$ 3032w, 2956m, 2225m, 1721s, 1272s, 1235s, 1121m, 1055m, 757m cm^{-1}. ^{1}H NMR (CDCl$_3$–TMS): δ ppm = 6.18 (m, 2H), 5.92 (m, 2H), 4.75 (s, 2H), 3.80 (s, 2H), 3.91 (s, 6H), 1.16 (d, $J = 6.6$ Hz, 1H), 0.10 (d, $J = 6.6$ Hz, 1H). ^{13}C NMR (CDCl$_3$–TMS): δ ppm = 164.7, 151.2, 147.0, 126.8, 122.3, 110.9, 52.9, 44.9, 38.3, 21.0. MS *m/z* (rel. int.) 390 (M^{+}, 7), 358 (26), 330 (63), 271 (100), 247 (33), 221 (14). HRMS (M^{+}) Obsd: 390.0662; Calcd for $\mathrm{C_{21}H_{14}N_{2}O_{4}S}$: 390.0674.
9. The X-ray data for **1**: $\mathrm{C_{13}H_{10}S}$, $M_{\mathrm{w}} = 198.28$, $0.50 \times 0.30 \times 0.30\ \mathrm{mm}^3$, orthorhombic, space group $P2_12_12_1$(#19), $a = 9.989(2)$, $b = 16.491(2)$, $c = 5.974(2)$ Å, $V = 984.1(3)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.338\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo\ K_\alpha}) = 0.28\ \mathrm{mm^{-1}}$, 1672 independent reflections, 128 parameters, $R = 0.052$ ($I > 2\sigma(I)$, 724 reflections), $wR = 0.062$, $S = 1.310$, $T = 223$ K. Those for **2**: $\mathrm{C_{15}H_{8}N_{2}S}$, $M_{\mathrm{w}} = 248.30$, $0.50 \times 0.40 \times 0.30\ \mathrm{mm}^3$, monoclinic, space group $P2_1/c$(#14), $a = 6.163(2)$, $b = 15.507(1)$, $c = 12.233(1)$ Å, $\beta = 92.87(2)°$, $V = 1167.8(3)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.412\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo\ K_\alpha}) = 0.26\ \mathrm{mm^{-1}}$, 3404 independent reflections, 163 parameters, $R = 0.040$ ($I > 3\sigma(I)$, 1861 reflections), $wR = 0.108$, $S = 1.277$, $T = 296$ K. Estimated standard deviations for the bond lengths and angles are 0.004 (angstrom) and 0.2–0.3 (degrees), respectively, for the nonhydrogen atoms. Crystallographic data excluding structure has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC275147 for **1** and CCDC 275146 for **2**, respectively. A copy of the data can be obtained free of charge from CCDC, 12 Union road, Cambridge CB2 1EZ, UK [Direct line: +44 1223 762910, fax: +44 (0)1223 336033 or e-mail: linstead@ccdc.cam.ac.uk; deposit@ccdc.cam.ac.uk].
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13. Preliminary theoretical study by semi-empirical molecular orbital calculations is as follows. We obtained a transition state (TS$_1$) for [8+2] addition of **1** and DMAD with activation enthalpy of 47.0 kcal/mol. The process is exothermic with the enthalpy difference of 37.9 kcal/mol at 0 °K. Attempts to obtain a transition state for the [2+2+2] addition have failed to provide the above-mentioned TS$_1$ only. We also obtained a transition state from the [8+2] adduct to **12** with the activation enthalpy of 10.9 kcal/mol. The process is slightly exothermic with 2.1 kcal/mol and is supported to be in equilibrium between them.