

# Discreteness of $\pi$ conjugation of 1,6-methano[10]annulene by troponoid fusion at the 3,4- positions

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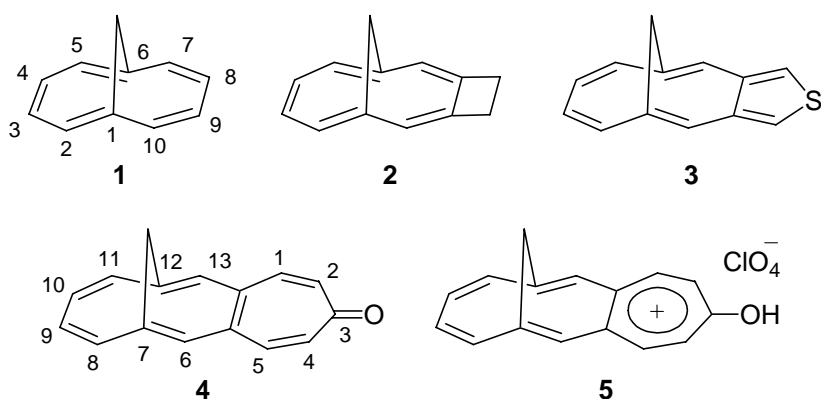
**Abstract:** The troponone-fused 1,6-methano[10]annulene **4** was synthesized from 3,4-bis(bromomethyl)-1,6-methano[10]annulene and protonation of **4** provided the hydroxytropylium ion-fused annulene **5**. <sup>1</sup>H NMR spectra of **4** and **5** exhibited an unequal shielding effect on the bridge hydrogens from the resulted  $\pi$  ring system, suggesting existence of the significant homoconjugative transannular interaction on the nonadjacent carbons at the bridge and discreteness of  $\pi$  conjugation of the annulene between two bonds at the C7-C8 and C11-C12 to separate the C8-C11 dienyl and the remaining parts. The X-ray crystallographic structures of **4** and **5** show relatively short atomic distance between those bridge carbons, and clear bond-alternation of the dienyl part and bond-convergence of the remaining part in these compounds, supporting the spectral properties.

*Keywords:* 1,6-Methano[10]annulene; Tropylium cation; Homoconjugation; Transannular interaction; X-ray crystallographic analysis.

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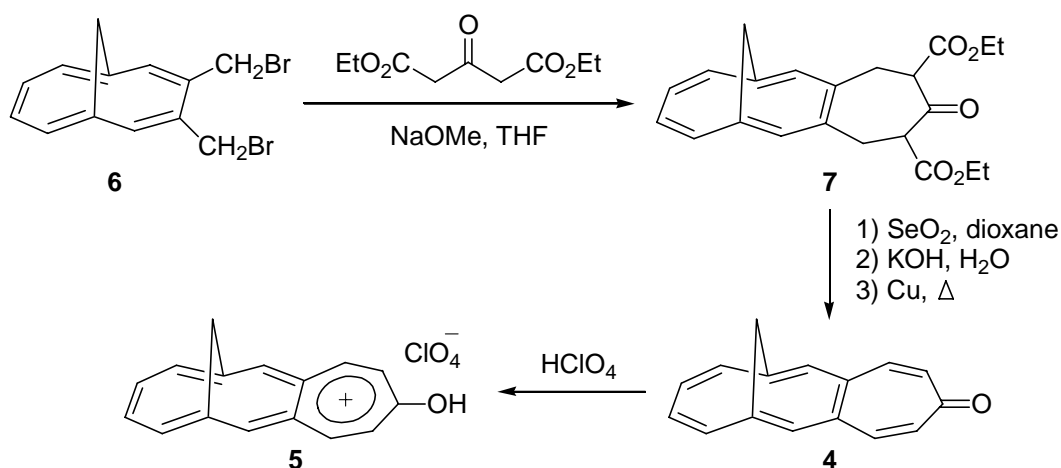
Since the first successful synthesis of the parent 1,6-methano[10]annulene (**1**) by Vogel and Roth,<sup>1</sup> bridged annulenes have long contributed to understanding cyclic conjugation and aromaticity in organic chemistry (Figure 1).<sup>2</sup> Importance of a bridge of annulenes was indicated not only by maintaining planarity of a large annulene ring but also by measuring aromatic character of the molecule by NMR spectroscopy.<sup>2,3</sup> Transannular overlap between p orbitals at the 1,6-positions in **1** is well established and, therefore, **1** is recognized as homonaphthalene.<sup>4</sup> We have

already reported that cyclobutene-fused 1,6-methano[10]annulene (**2**) has a relatively longer distance between the 1,6-carbons than that of **1** and shows the poor transannular interaction affecting tropicity.<sup>5</sup> Also, we recently reported the synthesis of thiophene-fused 1,6-methano[10]annulene (**3**) which was characterized not as a peripheral 14 $\pi$ -aromatic system but an aromatic thiophene annulated by an olefinic 8 $\pi$ -component; *i.e.* the thiophene destroys aromaticity of the 1,6-methano[10]annulene part in **3**.<sup>6</sup> In this letter, we describe an effect of troponoid-fusion on spectroscopic and structural properties of 1,6-methano[10]annulene in the title compounds, **4** and **5** which exhibit unprecedented discreteness of  $\pi$  conjugation in the annulene ring.



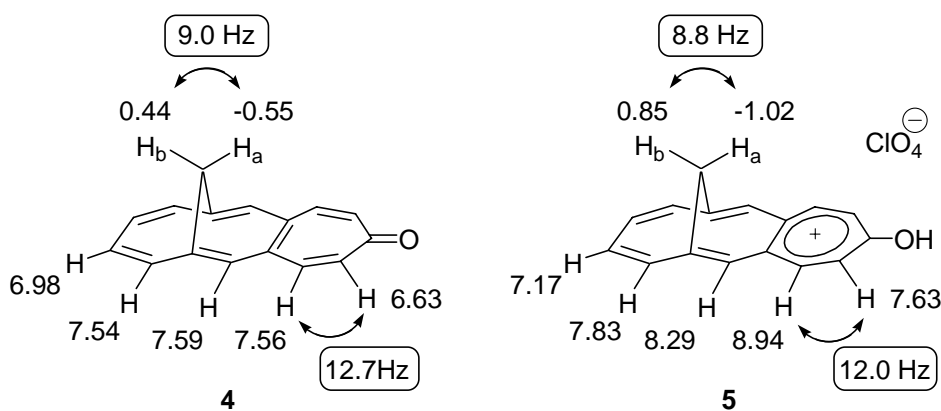
**Figure 1.**

Troponoid-fused 1,6-methano[10]annulenes, **4** and **5**, were synthesized from 3,4-bis(bromomethyl)-1,6-methano[10]annulene (**6**)<sup>6</sup> as shown in Scheme 1. Reaction of **6** with diethyl acetonedicarboxylate under basic conditions gave **7** in 58% yield. Oxidation of **7** with SeO<sub>2</sub> under reflux in dioxane, followed by hydrolysis of the ester groups and acidic decarboxylation, provided **4** in 32% yield based on **7**.<sup>8</sup> Hydroxytropylium ion **5** was obtained by treatment of **4** with 60% HClO<sub>4</sub> aqueous solution in 78% isolated yield.



**Scheme 1.**

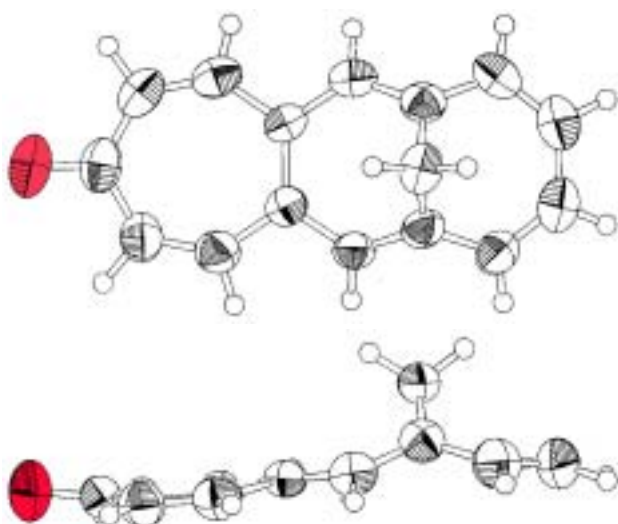
The structures of these compounds were confirmed by spectral data and X-ray crystallographic analysis (*vide infra*). Assigned proton signals<sup>9</sup> and coupling constants in their <sup>1</sup>H NMR spectra are shown in Figure 2. Although perimeter protons are observed in an aromatic region, hydrogens at the 9 and 10 positions of **4** appear slightly at high field compared with those of **1** (7.10 ppm) despite electron-withdrawing nature of tropone,<sup>10</sup> smaller coupling constant between the hydrogens at the seven-membered ring of **5** than that of **4** implies a less degree of bond-alternation in **5**. The most characteristic feature in their <sup>1</sup>H NMR spectra is that two bridge hydrogens appear apart from each other with shift differences of 0.99 ppm in **4** and 1.87 ppm in **5**. H<sub>b</sub> shifts to down field in both compounds. Particularly, H<sub>b</sub> of **5** appears at down field unusually as a bridge hydrogen of 1,6-methano[10]annulenes. These results clearly indicate that those hydrogens are exposed under entirely different deshielding effect from the annulene ring. To explain this unusual effect, we assumed that homoconjugative transannular interaction<sup>11</sup> on the nonadjacent carbons at the 7 and 12 positions of **5** became significant, and discreteness of  $\pi$  conjugation of diene part through C8-C11 in the annulene ring and the remaining parts occurred. Since homoconjugation is known to be observed more effectively in ionic species than a neutral compound<sup>11</sup>, a greater degree of the phenomenon in **5** can be reasonably accounted. Then, we accessed to structural details of these two compounds.



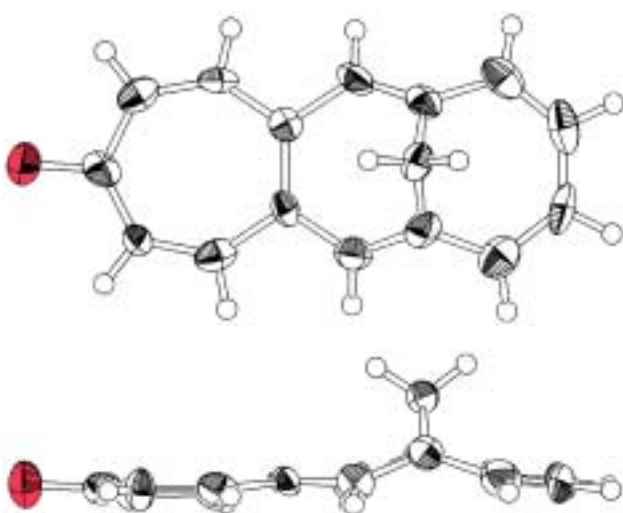
**Figure 2.** <sup>1</sup>H NMR chemical shifts in  $\delta_{\text{ppm}}$  of **4** and **5**

The solid-state structures of **4** and **5** were determined by X-ray crystallographic analysis (Figures 3 and 4).<sup>12</sup> Both structures are asymmetric. Whereas the tropone ring in **4** is slightly bended, the hydroxytropyl cation ring in **5** is nearly planar. Bond lengths and non-bonded atomic distances are summarized in Figure 5. The distances between the bridge carbons (C7 and C12) in crystal structures of **4** and **5** are shorter by ca. 0.05 Å than that of **1** (2.235 Å),<sup>13</sup> suggesting existence of the homoconjugative interaction in these compounds. Differences between two C–C bond lengths connecting to a [10]annulene perimeter carbon atom along the annulene ring in **4** and **5** are shown in Figure 6. While the dienyl part through C8-C11 in the annulene ring exhibits

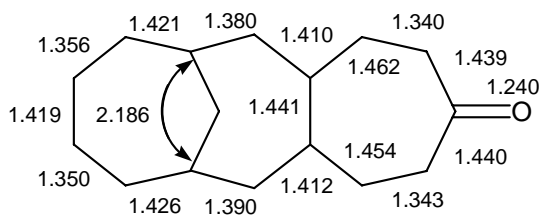
bond-alternation, the remaining part of C7-C6-C5a-C13a-C13-C12 shows rather bond-convergence.<sup>14</sup> Based on these structural facts, sufficient cyclic  $\pi$ -conjugation can be found only at the part of C7-C6-C5a-C13a-C13-C12 in **4** and at the same part and tropylium ion part in **5**, supporting the spectral properties, particularly the unequal shielding effect on the bridge hydrogens and the unusual low field shift of one of the hydrogens. Thus, the compound **5** does not exist as a  $14\pi$  delocalized cation, **5a** shown in Figure 7, but as a homobenzotropylium ion associated with the dieny part without  $\pi$ -conjugation, **5b**. And this tendency can be observed in the neutral compound **4**.



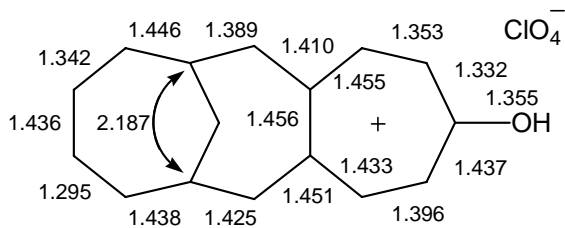
**Figure 3.** ORTEP drawings of **4** (top view and side view)



**Figure 4.** ORTEP drawings of **5**. The hydrogen of the hydroxy group can not be specified yet

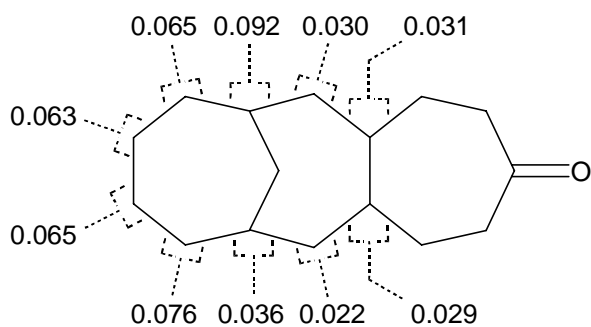


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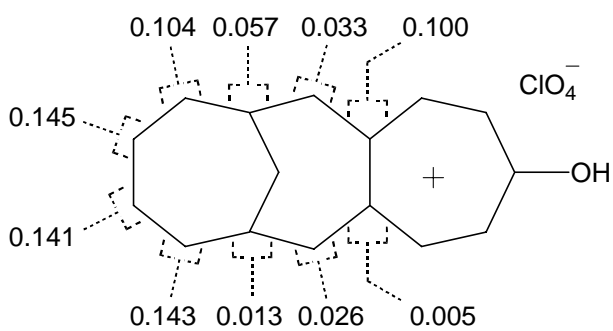


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**Figure 5.** Bond lengths and atomic distances in crystal structure of **4** and **5**

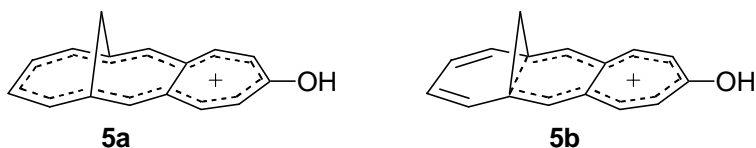


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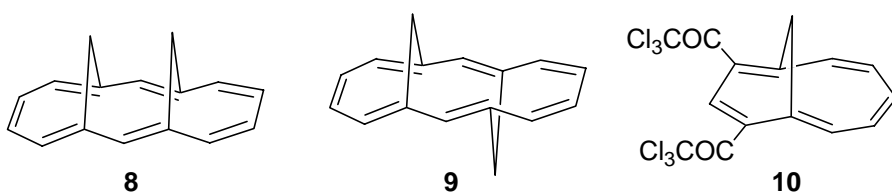
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**Figure 6.** Differences ( $\text{\AA}$ ) between two bond lengths connecting to the [10]annulene perimeter carbon atoms along the annulene ring in crystal structures of **4** and **5**



**Figure 7.**

Vogel *et al.* previously synthesized the *syn* and *anti* bismethno[14]annulenes, **8** and **9** (Figure 8). While **8** showed a diatropic property in the  $^1\text{H}$  NMR spectrum, **9** is atropic and, thus exhibits an olefinic property.<sup>15</sup> The *anti* bismethnoannulene **9** has a distorted  $\pi$  system and loses total and partial  $\pi$ -conjugations; the maximum torsion angle along perimeter carbons is  $75^\circ$  which is large enough to break a  $\pi$ -bond.<sup>13b,16</sup> It should be pointed out that our result described in this letter is apart from the case of **9**. The torsion angles through C6-C7-C8-C9 and C10-C11-C12-C13 in **5** are  $38.7^\circ$  and  $42.1^\circ$ , respectively. Scott claimed that aromatic  $\pi$ -system can tolerate dihedral twists in excess of  $42^\circ$  without losing their aromaticity based on the crystal structure of a derivative of 1,5-methano[10]annulene (**10**).<sup>17</sup> Therefore, **5** favors smaller homoconjugative  $10\pi$ -system although **5** could be constituted of a  $14\pi$ -peripheral system.



**Figure 8.**

In summary, we have synthesized the 1,6-methano[10]annulenes fused by tropone and hydroxytropylium ion, **4** and **5**. Based on analysis of their  $^1\text{H}$  NMR spectra and X-ray crystal structures, the sufficient homoconjugative transannular interaction separates  $\pi$ -conjugation of the [10]annulene part at the C7-C8 and C11-C12 positions. Therefore, the compound **5** does not exist as a  $14\pi$  delocalized cation but as a homobenzotropylium ion associated with the dienyl part without  $\pi$ -conjugation.

### Acknowledgements

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12. The X-ray data for **4**: C<sub>16</sub>H<sub>12</sub>O, Mw = 204.27, 0.50 x 0.20 x 0.50 mm<sup>3</sup>, monoclinic, space group *P2<sub>1</sub>/n* (#14), *a* = 9.677(3), *b* = 10.198(5), *c* = 11.649(2) Å,  $\beta$  = 103.09(2) deg, *V* = 1119.7(6) Å<sup>3</sup>, *Z* = 4, *D*<sub>calc</sub> = 1.212 g cm<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 0.68 cm<sup>-1</sup>, 3270 independent reflections, 202 parameters, *R* = 0.093, *wR* = 0.070, *T* = 298 K. Those for **5**: C<sub>16</sub>H<sub>13</sub>ClO<sub>5</sub>, Mw = 320.73, 0.50 x 0.40 x 0.30 mm<sup>3</sup>, monoclinic, space group *C2/c* (#15), *a* = 20.524(4), *b* = 8.149(4), *c* = 17.926(3) Å,  $\beta$  = 105.04(1) deg, *V* = 2895.0(1) Å<sup>3</sup>, *Z* = 6, *D*<sub>calc</sub> = 1.104 g cm<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 2.14 cm<sup>-1</sup>, 4237 independent reflections, 198 parameters, *R* = 0.079, *wR* = 0.100, *T* = 298 K. Some comments are required for the data for **5**. The hydrogen of the hydroxy group was not specified yet. Perchlorate anion nearby the hydrogen shows disorder. The unusually short C-C double bond length (C8-C9) was observed. In order to discuss the phenomenon more precisely, we are planning to carry out the analysis at low temperature. The result will be presented in a full account. Crystallographic data excluding structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 654622 for **4** and CCDC 654623 for **5**, 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](mailto:linstead@ccdc.cam.ac.uk); [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].
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