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

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Abstract

The tropone-fused 1,6-methano[10]annulene **4** was synthesized from 3,4-bis(bromomethyl)-1,6-methano[10]annulene and the protonation of **4** provided the hydroxytropylium ion-fused annulene **5**. ^{1}H NMR spectra of **4** and **5** exhibited an unequal shielding effect on the bridge hydrogens from the resulted π ring system, suggesting the existence of the significant homoconjugative transannular interaction on the nonadjacent carbons at the bridge and the discreteness of π-conjugation of the annulene between two bonds at the C7–C8 and C11–C12 to localize the C8–11 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 the 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

Since the first successful synthesis of the parent 1,6-methano[10]annulene (**1**) by Vogel and Roth,[1] bridged annulenes have long helped to understand cyclic conjugation and aromaticity in organic chemistry. The significance of a methylene bridge for annulenes was indicated not only by maintaining the planarity of a large annulene ring but also by measuring the aromatic character of the molecule by NMR spectroscopy.[2,3] Transannular overlap between p orbitals at the 1,6-positions in **1** is well established and, therefore, **1** is recognized as a homonaphthalene.[4] We have earlier reported that cyclobutene-fused 1,6-methano[10]annulene (**2**) is observed to have a relatively longer distance between its 1,6-carbons than that of **1** and shows comparatively poor transannular interaction affecting tropicity.[5] In addition, we recently reported the synthesis of thiophene-fused 1,6-methano[10]annulene (**3**), which was characterized not as a peripheral 14π-aromatic system but as an aromatic thiophene annulated by an olefinic 8π-component; that is, the thiophene destroys the aromaticity of the 1,6-methano[10]annulene part in **3**.[6] In this

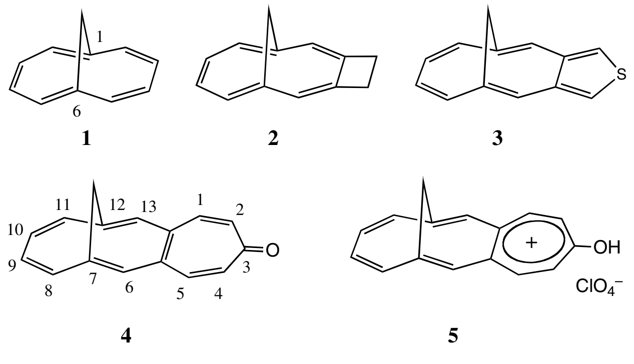

Fig. 1. Methano[10]annulenes.

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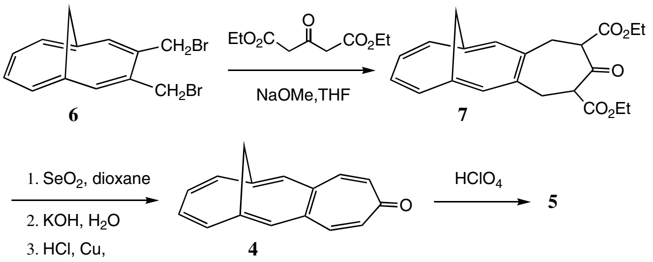
Letter, we describe an effect of troponoid-fusion on the spectroscopic and structural properties of **1** in the title compounds **4** and **5**, which exhibit unprecedented separation of π conjugation in the annulene ring (Fig. 1).

The troponoid-fused 1,6-methano[10]annulenes, **4** and **5**, were synthesized from 3,4-bis(bromomethyl)-1,6-methano[10]annulene (**6**)[6] as shown in Scheme 1. The reaction of **6** with diethyl acetonedicarboxylate under basic conditions gave **7** in 58% yield.[7] Oxidation of **7** with SeO_2 under reflux in dioxane, followed by the hydrolysis of the ester groups, and acidic decarboxylation, provided **4** as faintly yellow prisms in 32% yield based on **7**.[8] Hydroxytropylium ion **5** was obtained as slightly unstable green needles by the treatment of **4** with 60% $HClO_4$ aqueous solution in 78% yield.



Scheme 1. A synthetic method of **4** and **5**.

The structures of these compounds were confirmed by spectral data and X-ray crystallographic analysis (vide infra). Assigned proton signals[9] and coupling constants in their ^{1}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 at slightly higher field compared to those of **1** (7.10 ppm) despite the electron-withdrawing nature of tropone.[10] A smaller coupling constant between the vicinal hydrogens at the seven-membered ring of **5** than that of **4** implies a lower degree of bond alternation in **5**.[11] The most distinct feature in the ^{1}H NMR spectra of these compounds 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**. The outer hydrogen (Hb) shifts to the down field in both the compounds. The Hb of **5** rarely appears at the down field as a bridge hydrogen of 1,6-methano[10]annulenes. These results clearly indicate that these hydrogens are exposed to entirely different deshielding effects by the annulene ring (Fig. 3). To explain this unusual effect, we assumed that

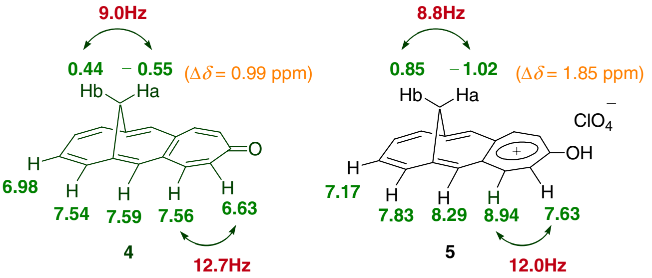


Fig. 2. ^{1}H NMR chemical shifts in δ_{ppm} of **4** and **5**.

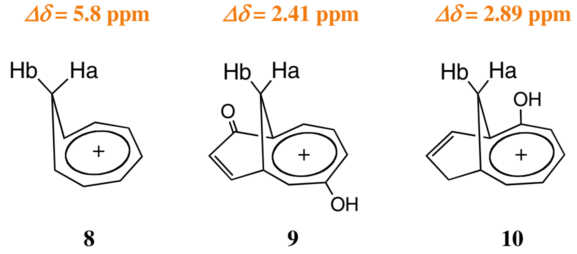


Fig. 3. Differences ($\Delta\delta = \delta_{Hb} - \delta_{Ha}$) in ^{1}H NMR chemical shifts between methylene bridge hydrogens of some homotropylium ions.

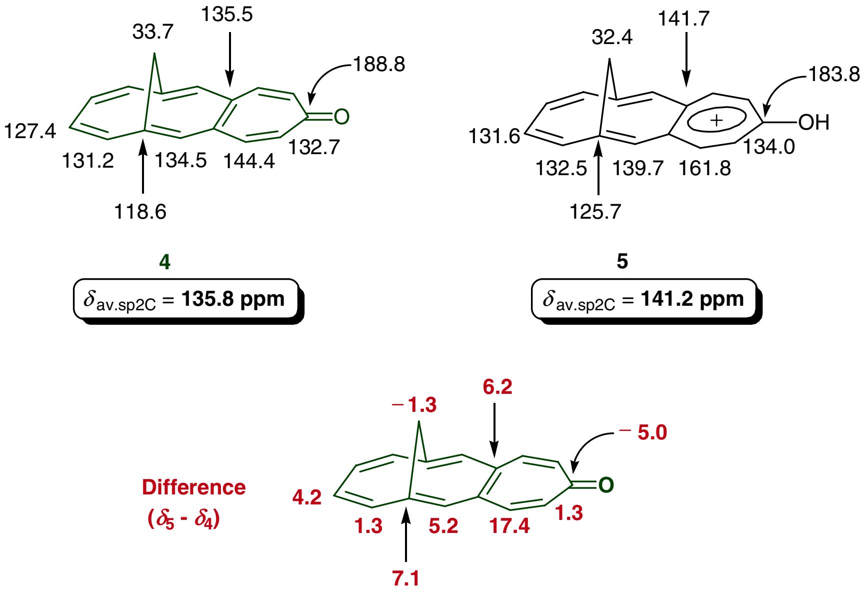


Fig. 4. ^{13}C NMR chemical shifts δ_{ppm} of **4** in CD_2Cl_2 and **5** in CF_3CO_2D.

homoconjugative transannular interaction[11] on the nonadjacent carbons at the 7 and 12 positions became significant, and the separation of π-conjugation of the annulene between the C8–11 diene and the remaining parts occurred. Since homoconjugation is observed more effectively in ionic species than in a neutral compound,[12] a greater degree of the phenomenon in **5** can be reasonably assumed. Although the difference in the chemical shift between the bridge hydrogens ($\Delta\delta = 1.87$ ppm) in **5** is far less than that of the homotropylium ion **8** ($\Delta\delta = 5.8$ ppm),[13] the value is close to those of the bicyclic homotropylium ions **9** ($\Delta\delta = 2.41$ ppm) and **10** ($\Delta\delta = 2.89$ ppm),[14] which are perturbed by the hydroxy group of the homotropylium ion part and the double-bond groups in the six-membered ring part as **5** is. Chemical shift data of **4** and **5** obtained by ^{13}C NMR analysis are shown in Figure 4. Average shifts of the sp^2 carbons of **4** and **5** are 135.8 and 141.2 ppm, respectively. The cation **5** indicates the down-field shift by 5.4 ppm with respect to **4**. When the difference of carbon chemical shifts at the same positions in **4** and **5** is compared, carbon atoms at the 5a, 6, and 7 positions show larger down-field shift than the average, and carbon atoms at the 8 and 9 positions show lower shifts. Based on this result, the positive charge in **5** is expected to be localized at the right part of this molecule. We then studied the structural details of these two compounds.

The solid-state structures of **4** and **5** were determined by X-ray crystallographic analysis (Figs. 5 and 6).[15] Both crystallographic structures are asymmetric. The tropone ring in **4** is slightly bent, whereas the hydroxytropylium ring in **5** is almost planar. Bond lengths and non-bonded atomic distances are summarized in Figure 7. The distances between the bridge carbons (C7 and C12) in the crystal structures of **4** and **5** are shorter by approximately 0.05 Å than that of **1** (2.235 Å),[16] suggesting the existence of the homoconjugative interaction in these compounds. Differences between the 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 8. While the dienyl part through C8–C11 in the annulene ring exhibits bond alternation, the remaining part, C7–C6–C5a–C13a–C13–C12, shows bond convergence.[17] Based on these structural results, sufficient cyclic π-conjugation can be found at the C7–C6–C5a–C13a–C13–C12 part in **4** and at the same part and the tropylium ion moiety in **5**. This supports the observed spectral properties, particularly the unequal shielding effect on the bridge hydrogens and the unusual low-field shift of one of the hydrogens. Thus, compound **5** does not exist as a 14π delocalized cation **5a** (Fig. 9) but as a homobenzotropylium ion associated with the dienyl part **5b**, which does not exhibit π-conjugation. This tendency can also be observed in the neutral compound **4**.

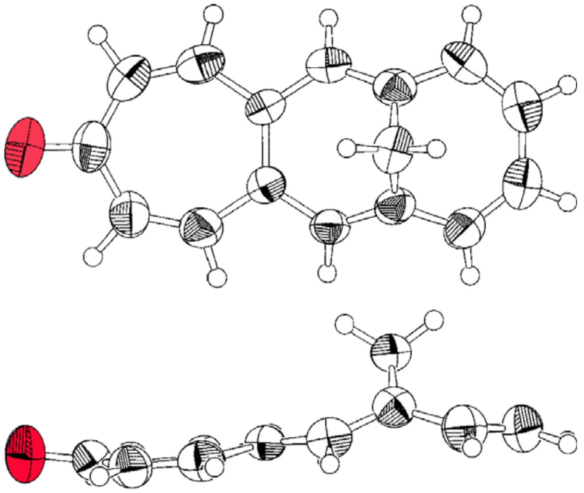


Fig. 5. ORTEP drawings of **4**.

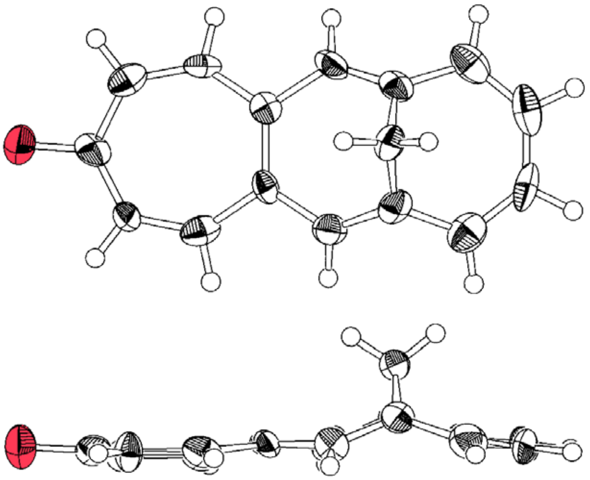
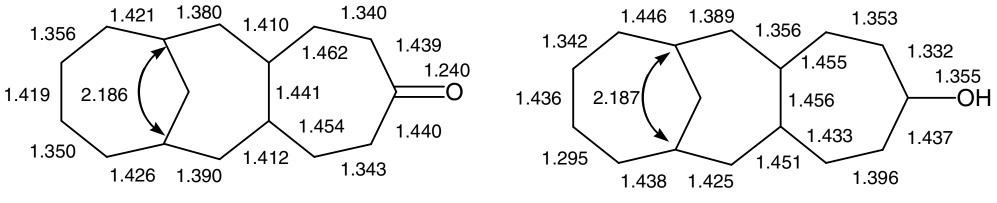


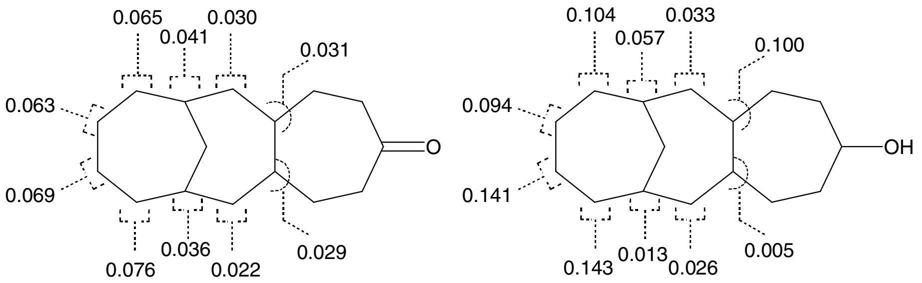
Fig. 6. ORTEP drawings of **5**. The hydrogen of the hydroxy group can not be specified yet.

Vogel et al. previously synthesized *syn*- and *anti*-bismethano[14]annulenes, **11** and **12** (Fig. 10). While **11** showed a



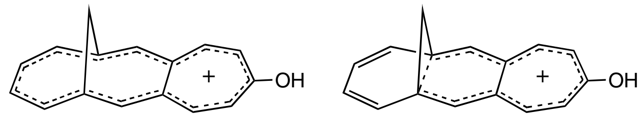
4 **5**

Fig. 7. Bond lengths and atomic distances in the crystal structures of **4** and **5**.



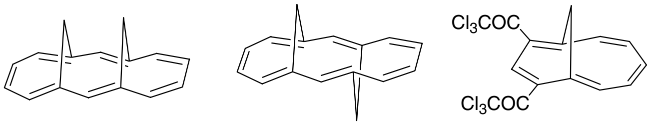
4 **5**

Fig. 8. Differences (Å) between two bond lengths connecting to the [10]annulene perimeter carbon atoms along the annulene ring in crystal structures of **4** and **5**.



5a **5b**

Fig. 9. Resonance structures of **5**.



11 **12** **13**

Fig. 10. Distorted and undistorted methanoannulenes.

diatropic property in the ^1H NMR spectrum, **12** was atropic, and therefore exhibits an olefinic property.[18] The *anti*-bismethanoannulene **12** has a distorted π-system and loses total and partial π-conjugations; the maximum torsion angle along the perimeter carbons is 75°, which is large enough to break a π-bond.[16b,19] It should be noted that our result described in this Letter is different from this case. The angles through C6–C7–C8–C9 and C10–C11–C12–C13 in **5** are 38.7° and 42.1°, respectively. Scott et al. claimed that the aromatic π-system can tolerate dihedral twists in excess of 42° without losing its aromaticity, based on the crystal structure of a derivative of 1,5-methano-[10]annulene (**13**).[20] Therefore, **5** favors a smaller homoconjugative 10π-system, although it could contain a 14π peripheral system.

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

Acknowledgments

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