

0040-4039(94)E0403-K

**SYNTHESIS AND STRUCTURAL PROPERTIES OF  
 2,7-METHANOCYCLODECA[a]AZULENE AND ITS DERIVATIVE**

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**Summary:** The title compounds were synthesized, and their <sup>1</sup>H NMR spectra revealed that they are composed of delocalized methano[10]annulene and localized azulene moieties.

1,6-Methano[10]annulene (1)<sup>1</sup> satisfies the Hückel (4n+2)π requirement and a variety of the derivatives, which are cata-condensed with aromatic<sup>2</sup> and hetero-aromatic<sup>3</sup> rings, have been studied in view of the degree of their aromaticity. In nearly every system studied, annulation of aromatic rings reduces the aromaticity of the parent ring, as measured by the loss of diatropicity in the <sup>1</sup>H NMR spectra. Among these investigations, compounds 2<sup>4</sup> and 3<sup>5</sup>, both of which are annulated with 1-azaazulene and azulene at the C2-C3 position of 1, respectively, have been synthesized. Their <sup>1</sup>H NMR spectra revealed that bond-length alternation of methano[10]annulene moieties is remarkable as compared with that of 1-azaazulene and azulene moieties. While a few 1,6-methano[10]annulenes condensed with hetero-aromatic rings at the C3-C4 position have been reported,<sup>6</sup> examples of 1 condensed with aromatic hydrocarbon at the C3-C4 position are scarce. Thus, our interests are focused on the synthesis and structural characteristics of 4 and 5.

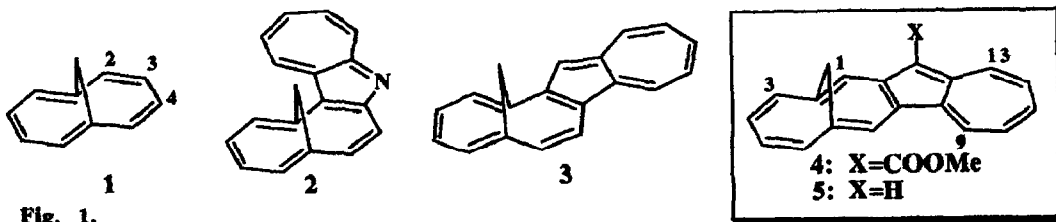
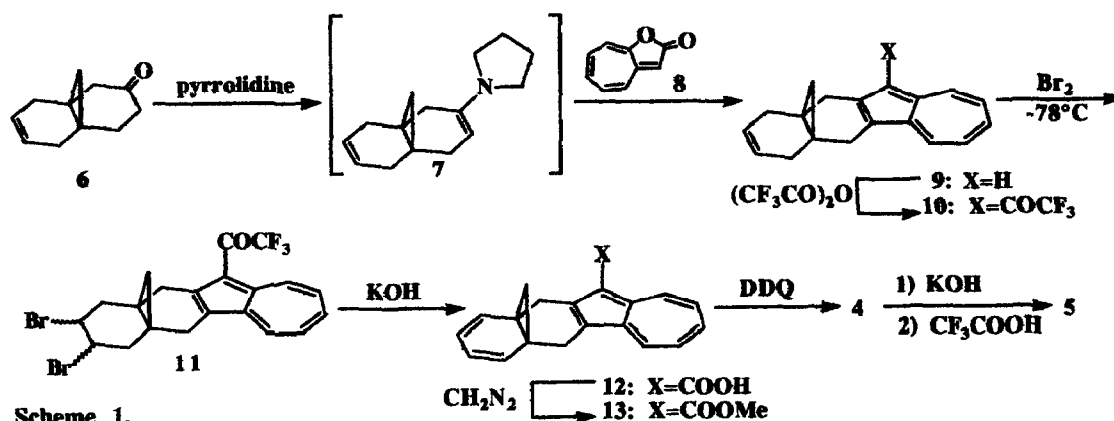


Fig. 1.

Our synthetic strategy at first was to prepare the azulene skeleton 9, which would be expected from the thermal reaction of the enamine 7 with 2H-cyclohepta[b]furan-2-one 8, according to the method explored by Yasunami, Takase, and co-workers.<sup>7</sup> Compound 7 derived from ketone 6<sup>8</sup> in a usual manner reacted with 0.5 molar equivalents of 8 in BuOH under reflux for 5 h to give 9<sup>11,12</sup> in a 42% yield after purification by column chromatography (silica gel, Hexane) (Scheme 1). For protection toward electrophilic attack onto the C1 of azulene nucleus, 9 was treated with trifluoroacetic anhydride<sup>13</sup> in CH<sub>2</sub>Cl<sub>2</sub> at 0 °C for 10 min to give 10<sup>11,12</sup> quantitatively. Bromination of 10 was carried out at -78 °C to give 11<sup>11,12</sup> in a 93% yield. Treatment of 11 with

5.7% KOH in EtOH-H<sub>2</sub>O (5/1) under reflux for 1 h underwent hydrolysis of trifluoroacetyl group and dehydrobromination simultaneously to afford 12,<sup>11</sup> which was treated with CH<sub>2</sub>N<sub>2</sub> to give 13<sup>11,12</sup> in a 34% yield after purification by TLC (silica gel, Hexane-AcOEt:10/1). Treatment of 13 with DDQ in PhH at room temperature for 5 min afforded the expected dehydrogenation product 4<sup>11,12</sup> in an 85% yield, while that with Pd/C in 1,2-dimethylbenzene under reflux for 23 h gave 4 in a 37% yield, after purification by TLC (silica gel, Hexane-AcOEt:10/1). Compound 4 was easily hydrolyzed with 5.7% KOH in EtOH-H<sub>2</sub>O (5/1) under reflux to give 14-carboxy-2,7-methanocyclodeca[a]azulene (14), which was subsequently treated with trifluoroacetic acid in CH<sub>2</sub>Cl<sub>2</sub> at 40 °C for 1 h to give 2,7-methanocyclodeca[a]azulene (5)<sup>11,12</sup> in a 32% yield (based on 4 used) after purification by TLC (alumina, Hexane-AcOEt:10/1).



Scheme 1.

The <sup>1</sup>H NMR spectra of 4 and 5 revealed that the mean chemical shift of peripheral protons of methano[10]annulene moiety of 4 ( $\delta_{av} = 7.52-7.62$ ) and 5 ( $\delta_{av} = 7.59$ ) was slightly shifted to the lower field than those of 1 ( $\delta_{av} = 7.10$ ), 2 ( $\delta_{av} = 7.45$ ), 3 ( $\delta_{av} = 7.35$ ), and 2,3-benzo-1,6-methano[10]annulene (15) ( $\delta_{av} = 7.20$ ).<sup>2a</sup> Similarly, the mean chemical shift of azulene moiety of 5 ( $\delta_{av} = 7.55$ ) was slightly shifted to the lower field than that of azulene ( $\delta_{av} = 7.47$ ), while that of 4 ( $\delta_{av} = 8.26$ ) was largely shifted to the lower field because of the electron-withdrawing methoxycarbonyl group, which also causes a drastic low-field shift of H-13 ( $\delta = 9.60$ ). The weakening of the diamagnetic ring current in the methano[10]annulene ring of 2 and 3 was most clearly manifested in the signals of the bridge methylene of 2 ( $\delta_{av} = 0.75$ ) and 3 ( $\delta_{av} = 0.54$ ) for they were shielded similarly to that of 15 ( $\delta_{av} = 0.66$ ), but less shielded than that of 1 ( $\delta_{av} = -0.50$ ). On the other hand, the mean values of chemical shifts of the bridge methylene of 4 ( $\delta_{av} = -0.07$ ) and 5 ( $\delta_{av} = -0.34$ ) were greatly shielded than those of 2, 3, and 15. The feature indicates the diamagnetic ring current in the methano[10]annulene ring of 4 and 5 is similar to that of 1. More finding such as the similar vicinal coupling constants of methano[10]annulene moieties of 4 ( $J_{3,4} = 8.59$ ,  $J_{4,5} = 8.52$ , and  $J_{5,6} = 8.50$ ) and 5 ( $J_{3,4} = 8.93$ ,  $J_{4,5} = 8.66$ , and  $J_{5,6} = 8.70$ ) suggests that double bonds of

methano[10]annulene moieties are delocalized as indicated in the canonical structures 4A and 5A in Fig. 2. On the contrary, a remarkable difference of the vicinal coupling constants of the azulene moiety of 4 ( $J_{9,10} = 8.80$ ,  $J_{10,11} = 10.27$ ,  $J_{11,12} = 8.80$ ,  $J_{12,13} = 11.04$ ) and 5 ( $J_{9,10} = 8.43$ ,  $J_{10,11} = 10.99$ ,  $J_{11,12} = 8.43$ , and  $J_{12,13} = 10.85$ ), respectively, also indicates a bond-length alternation of the azulene moieties as indicated in 4A and 5A in Fig. 2. No contribution of 4C and 5C is also suggested. Furthermore, if peripheral  $18\pi$ -electron conjugation mainly contributes in 4 and 5 as indicated in the canonical structures 4B and 5B, much lower chemical shift of the peripheral protons should be expected.<sup>14</sup> Thus, the contribution of peripheral  $18\pi$ -electron conjugation seems to be less important. Regarding the spectral data described above, one may consider a possibility of a rapid equilibrium between X and Y (Fig. 2) in the compounds 4 and 5. However, the  $^1\text{H}$  NMR spectra of 5 recorded in the temperature range between 25 °C and -100 °C exhibited no change. The electronic spectrum of 4, which has an electron-withdrawing substituent, is shifted to shorter wave-length as compared to that of 5. The feature is in good accordance with annulated azulene ring system.<sup>15</sup>

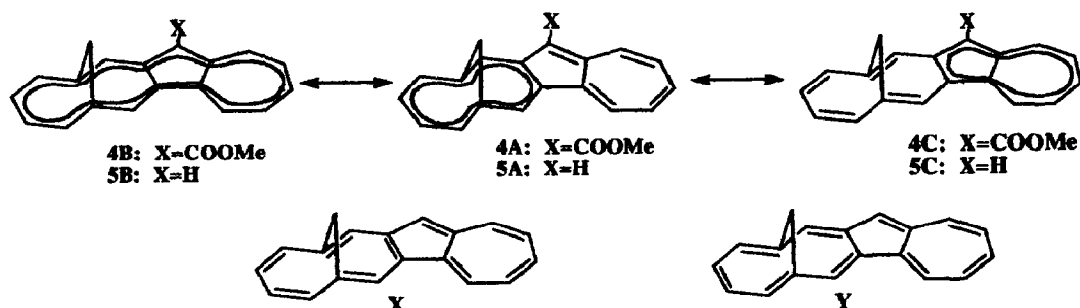


Fig. 2.

Regarding the resonance energy of azulene (12.8 kcal/mol) and methano[10]annulene (17.5 kcal/mol),<sup>16</sup> the electronic feature of 4 and 5 seems to be reasonable. On the contrary, a double-bond fixation is remarkable in the methano[10]annulene moiety rather than the azulene moiety of 3. Thus it is interesting that an interpretation of inherent  $\pi$ -electronic system as a result of condensation of aromatic ring is much dependent on the position of condensation.

**Acknowledgement:** This work was financially supported by Waseda University Grant for Special Research Project.

#### References

1. E. Vogel and H. D. Roth, *Angew. Chem.*, **76**, 145 (1964); E. Vogel and W. A. Böll, *Angew. Chem. Int. Ed. Engl.*, **3**, 228 (1964); E. Vogel and W. A. Boll, *Angew. Chem.*, **76**, 784 (1964).
2. (a) S. Tanimoto, R. Schafer, J. Ippen, and E. Vogel, *Angew. Chem. Int. Ed. Engl.*, **15**, 613 (1976). (b) R. K. Hill, C. B. Giberson, and J. V. Siluerton, *J. Am. Chem. Soc.*, **110**, 497 (1988).
3. R. Neidlein and G. Hartz, *Chem. Zeit.*, **108**, 366 (1984); R. Neidlein and G.

- Lautenschlager, *Chem. Ber.*, **122**, 493 (1989); U. H. Brinker and W. N. Jones, *Tetrahedron Lett.*, 577 (1976); M. W. Jones, R. A. La Bar, U. H. Briker, and P. H. Gebert, *J. Am. Chem. Soc.*, **99**, 6379 (1977); N. Kanomata, H. Kawaji, and M. Nitta, *J. Org. Chem.*, **57**, 618 (1992).
4. M. Nitta, H. Kawaji, and N. Kanomata, *Tetrahedron Lett.*, **33**, 251 (1992).
  5. S. Kuroda, J. Yazaki, S. Maeda, K. Yamazaki, M. Yamada, I. Shima, and M. Yasunami, *Tetrahedron Lett.*, **33**, 2825 (1992).
  6. R. Neidlein and L. Tadesse, *Chem. Ber.*, **119**, 3862 (1986); R. Neidlein and G. Schröder, *Helv. Chim. Acta*, **75**, 825 (1992).
  7. P.-W. Yang, M. Yasunami, and K. Takase, *Tetrahedron Lett.*, 1971, 4275; Y. Kitamori, M. Yasunami, C. Kabuto, and K. Takase, *Bull. Chem. Soc. Jpn.*, **66**, 245 (1993); M. Yasunami, S. Miyoshi, N. Kanegae, and K. Takase, *Bull. Chem. Soc. Jpn.*, **66**, 892 (1993); M. Yasunami, T. Hioki, Y. Kitamori, I. Kikuchi, and K. Takase, *Bull. Chem. Soc. Jpn.*, **66**, 2273 (1993).
  8. The ketone **6**<sup>o</sup> was prepared through the reaction of a known mixture of syn and anti 4-oxatetracyclo[5.4.1.0.<sup>1,7</sup>0<sup>3,5</sup>]undec-9-en<sup>o</sup> with LiAlH<sub>4</sub> followed by Swern oxidation.<sup>10</sup>
  9. R. Neidlein and P. Bronner, *Chem. Ber.*, **122**, 1499 (1989).
  10. A. J. Mancuso and D. Swern, *Synthesis*, 165 (1981).
  11. Elemental analyses or high resolution mass spectral data are satisfactory for all new compounds except **12** and **14**-carboxy-2,7-methanocyclodeca[10]azulene (**14**).
  12. Physical data: **4**: dark green prisms; mp 130–132 °C (from MeOH); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ = -0.55 (1H, d, 9.54 Hz, -CH<sub>2</sub>-), 0.42 (1H, d, 9.54 Hz, -CH<sub>2</sub>-), 4.13 (3H, s, OMe), 6.86–6.96 (2H, dd, 8.52, 8.59 Hz, H-4, 5), 7.50–7.70 (2H, m, H-3, 6), 7.53 (1H, dd, 8.80, 11.04 Hz, H-12), 7.56 (1H, dd, 8.80, 10.27 Hz, H-10), 8.14 (1H, s, H-8), 8.24 (1H, s, H-1), 8.91 (1H, d, 8.80 Hz, H-9), 9.60 (1H, d, 11.04 Hz, H-13); IR (CHCl<sub>3</sub>) 3009, 2951, 1678, 1530, 1455, 1438, 1415, 1223, 1153, 1100, 1012 cm<sup>-1</sup>; λ<sub>max</sub> (log ε) in EtOH, 241 (3.96), 280 (3.95), 314 (4.17), 361 (4.09), 578 (2.71), 691 (2.61), 745 (2.28), 772 (1.89). **5**: dark green prisms; mp 166–167 °C (from EtOH); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ = -0.76 (1H, d, 9.53 Hz, -CH<sub>2</sub>-), 0.08 (1H, d, 9.53 Hz, -CH<sub>2</sub>-), 6.91 (1H, dd, 8.43, 10.85 Hz, H-12), 6.97 (1H, dd, 8.66, 8.70 Hz, H-5), 7.04 (1H, dd, 8.66, 8.93 Hz, H-4), 7.12 (1H, dd, 8.43, 10.99 Hz, H-10), 7.25 (1H, dd, 8.43, 10.99 Hz, H-11), 7.54 (1H, br. s, H-14), 7.71 (1H, d, 8.93 Hz, H-3), 7.73 (1H, d, 8.70 Hz, H-6), 7.77 (1H, br. s, H-1), 7.99 (1H, d, 10.85 Hz, H-13), 8.34 (1H, br. s, H-8), 8.46 (1H, d, 8.43 Hz, H-9); λ<sub>max</sub> (log ε) in EtOH, 239 (4.16), 340 (4.59), 412 (3.55), 480 (2.81), 565 (2.33), 580 (2.39), 616 (2.51), 664 (2.56), 712 (2.45), 721 (2.44), 845 (1.89). **6**: colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 60 MHz) δ = 0.48 (1H, d, 4.0 Hz, cyclopropane), 0.73 (1H, d, 4.0 Hz, cyclopropane), 1.70–2.67 (6H, m, H-2, 3, 5, 8), 5.43–5.67 (2H, m, H-6, 7); IR (CHCl<sub>3</sub>) 2969, 2861, 2841, 2811, 1710, 1400, 1194 cm<sup>-1</sup>. **9**: blue prisms; mp 113–114 °C (from EtOH); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz) δ = 0.23 (1H, d, 4.18 Hz, cyclopropane), 0.56 (1H, d, 4.18 Hz, cyclopropane), 2.20–2.73 (4H, m, H-1, 8), 2.82–3.70 (4H, m, H-3 and 6), 5.50–5.73 (2H, m, H-4, 5), 6.90–7.60 (4H, m, H-10, 11, 12, 14), 8.00–8.27 (2H, m, H-9, 13). **10**: reddish oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz) δ = 0.19 (1H, d, 3.95 Hz, cyclopropane), 0.61 (1H, d, 4.17 Hz, cyclopropane), 2.10–2.70 (4H, m, H-1, 8), 2.70–3.83 (4H, m, H-3 and 6), 5.45–5.80 (2H, m, H-4, 5), 6.90–8.60 (3H, m, H-10, 11, 12), 8.31 (2H, d, 9.67 Hz, H-9), 9.22 (2H, d, 9.67 Hz, H-13); IR (CHCl<sub>3</sub>) 2970, 2895, 2840, 1640, 1430, 1410, 1330, 1145, 1030 cm<sup>-1</sup>. **11**: reddish purple oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 60 MHz) δ = 0.34 (1H, d, 5.0 Hz, cyclopropane), 0.74 (1H, d, 5.0 Hz, cyclopropane), 2.10–4.05 (8H, m, H-1, 3, 6, 8), 4.28–4.65 (2H, m, H-4, 5), 7.15–7.92 (3H, m, H-10, 11, 12), 8.21 (1H, d, 9.0 Hz, H-9), 9.41 (1H, d, 10.0 Hz, H-13); IR (CHCl<sub>3</sub>) 2910, 2840, 1640, 1430, 1260, 1140, 1030 cm<sup>-1</sup>. **13**: dark purple oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 60 MHz) δ = 0.48 (1H, d, 7.0 Hz, cyclopropane), 2.41 (1H, d, 7.0 Hz, cyclopropane), 3.42–4.68 (7H, m, H-1, 8, and OMe), 6.05–6.48 (4H, m, H-3, 4, 5, 6), 7.08–7.65 (3H, m, H-10, 11, 12), 8.21 (1H, d, 9.0 Hz, H-9), 9.32 (1H, d, 9.0 Hz, H-13); IR (CHCl<sub>3</sub>) 3000, 2960, 2870, 1675, 1580, 1440, 1410, 1305, 1283, 1105, 1100 cm<sup>-1</sup>.
  13. A. G. Anderson, Jr. and R. G. Anderson, *J. Org. Chem.*, **27**, 3578 (1962).
  14. L. M. Jackman, F. Sondheimer, Y. Amiel, D. A-Ren-Efrain, Y. Gaoni, R. Wolovsky, and A. A. Bosner-By, *J. Am. Chem. Soc.*, **84**, 4307 (1962); Z. Yoshida, M. Shibata, E. Ogino, and T. Sugimoto, *Tetrahedron Lett.*, **25**, 3343 (1984).
  15. M. Nitta, K. Nishimura, and Y. Iino, *Tetrahedron Lett.*, **34**, 2157 (1993); M. Nitta, Y. Iino, T. Sugiyama, and A. Toyota, *Tetrahedron Lett.*, **34**, 835 (1993).
  16. W. R. Roth, O. Adamczak, R. Breuckmann, H-W. Lennartz, and R. Boese, *Chem. Ber.*, **124**, 2499 (1991).

(Received in Japan 27 September 1993; accepted 27 December 1993)