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5,10-Dimethyl[13]annulenone: The First Monocyclic Annulenone Larger Than Tropone

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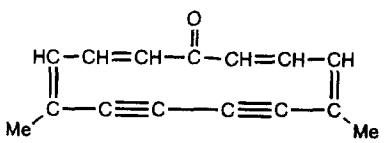
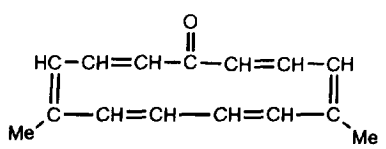
Abstract: 5,10-Dimethyl[13]annulenone, the first monocyclic annulenone larger than tropone, was synthesized by catalytic partial hydrogenation of 5,10-dimethylbisdehydro[13]annulenone. The ^{1}H NMR data indicate that the compound is completely atropic. Molecular mechanics studies suggest the nonplanarity of the ring and thus the lack of peripheral conjugation.

Although a variety of bridged annulenones and dehydroannulenones up to a [25] annulenone is known, the largest monocyclic annulenone so far known is still [7]annulenone, tropone.[1] We have been much interested in the synthesis and spectroscopic studies of monocyclic annulenones larger than tropone. As we have succeeded in the synthesis of a series of bisdehydroannulenones,[2] among which 5,10-dimethylbisdehydro[13]annulenone **1** is the lowest member, we underwent the preparation of 5,10-dimethyl-[13]annulenone **2** by hydrogenation of **1**.



1



2

Catalytic hydrogenation of **1** over 5%-Pd/$BaSO_4$ at atmospheric pressure in benzene with the absorption of 2 molar equiv. of H_2 afforded a complex mixture of partially hydrogenated products, from which compound **2** was isolated in 2.3% yield together with two isomeric 5,10-dimethylmonodehydro[13]annulenones, **3** and **4**, in 36 and 16% yield, respectively.[3]

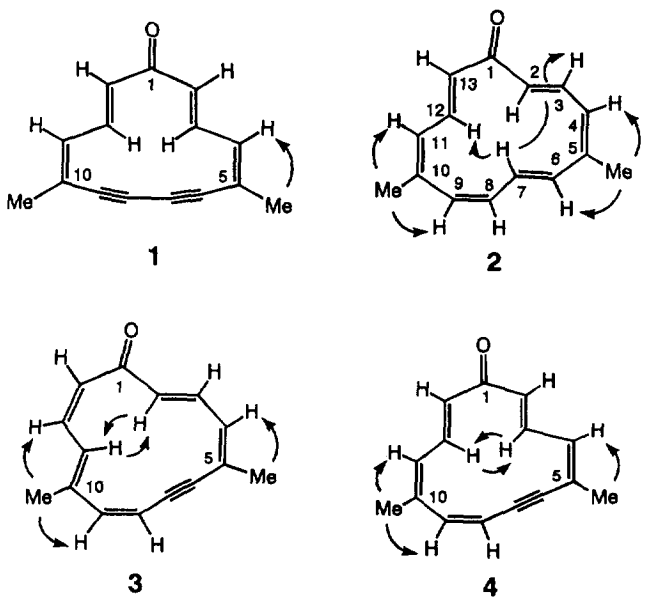
^{1}H NMR spectra of compounds **2**, **3**, and **4** in $CDCl_3$ at ambient temperature were fully analyzed and unambiguously assigned with the aid of decoupling and NOE experiments. The NMR data are compiled in Table 1 together with those for compound **1**, and the two-dimensional geometries of the compounds deduced from the NMR data are shown in Scheme 1 where the relevant NOE information is also given. Compounds **2**, **3**, and **4** each has three (*Z*)-double bonds as compared with the two (*Z*)-bonds in compound **1**.

Table 1. ^{1}H NMR Data of Compounds **1** - **4** in $CDCl_3$ at 24 °C.[a]

1[b]	1.752 (dt, 1.6, 0.6; 5/10-Me), 6.092 (d, 16.7; 2/13-H), 6.287 (ddq, 9.4, 0.9, 1.6; 4/11-H), 9.414 (ddq, 16.7, 9.4, 0.6; 3/12-H)
3	1.856 (d, 1.1; 10-Me), 1.911 (t, 1.1; 5-Me), 5.508 (d, 11.8; 8-H), 5.751 (d, 11.8; 13-H), 5.879 (d, 11.8; 9-H), 5.997 (dquint, 5.5, 1.5; 4-H), 6.778 (t, 12.0; 12-H), 6.922 (ddq, 15.7, 5.5, 1.1; 3-H), 8.536 (d, 15.7; 2-H), 9.428 (d, 12.2; 11-H)
4	1.883 (br s; 10-Me), 1.904 (br s; 5-Me), 5.703 (d, 13.2; 8-H), 5.725 (d, 15.8; 13-H), 5.785 (d, 13.2; 9-H), 5.860 (d, 16.7; 2-H), 5.910 (d, 11.8; 11-H), 6.330 (dquint, 8.9, 1.4; 4-H), 8.649 (dd, 15.8, 11.8; 12-H), 9.007 (ddq, 16.7, 8.9, 0.9; 3-H)
2	1.845 (br s; 5-Me), 1.925 (br s; 10-Me), 5.622 (d, 12.2; 9-H), 5.771 (d, 16.4; 6-H), 5.913 (d, 15.9; 13-H), 5.928 (dd, 16.6, 1.7; 2-H), 5.996 (dm, 6.6; 4-H), 6.018 (d, 11.5; 11-H), 6.032 (dd, 12.2, 11.0; 8-H), 7.043 (dd, 16.3, 11.0; 7-H), 7.963 (dd, 15.9, 11.7; 12-H), 8.184 (dd, 16.6, 6.6; 3-H)

[a] Chemical shifts are given in δ. In parentheses are the splitting pattern, coupling constants in Hz, and the assignment. [b] Re-examined. See also Ref. 2.

All of these four compounds are expected to be paratropic because they would constitute a 12π-electron peripherally conjugated system by polarization of the carbonyl group. The bisdehydro[13]annulenone **1** clearly shows paratropicity, judging from the large chemical shift difference (ca. 3.2 ppm) between the inner and outer olefinic protons. The dehydro[13]annulenones **3** and **4** are also paratropic: The chemical shift difference between the inner and outer olefinic protons are comparable to that in **1**, but the methyl proton signals appear at considerably lower field than that of **1**. This suggests that **3** and **4** are less paratropic than **1**, although quantitative discussion is difficult because other factors such as the steric compression effect and the anisotropy effect of the acetylenic bonds may contribute to the chemical shifts.



Scheme 1. Arrows represent NOE enhancements

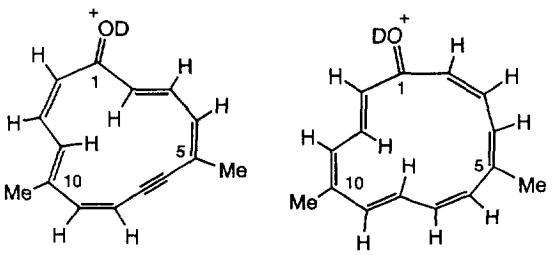
On the other hand, the [13]annulenone **2** is considered to be completely atropic. Two signals assigned to 3-H and 12-H resonate at low field of ca. δ 8.0, although 3-H should be located outside of the ring according to the NMR spectral analysis (Table 1). As these protons are located β to the carbonyl, the low-field appearance of these protons can be ascribed to the electron-density and anisotropy effects of the carbonyl group. In addition, the steric compression effect may partly be responsible for the chemical shifts of 7-H and 12-H which are close to each other.

Tropicity of annulenones is generally enhanced in acidic media

Table 2. ^{1}H NMR Data of Compounds **1** - **4** in Trifluoroacetic Acid-*d*.[a]

1D$^+$[b]	1.717 (d, 1.5; 5/10-Me), 6.163 (dm, 9.7; 4/11-H), 6.193 (d, 16.4; 2/13-H), 10.950 (dd, 16.4, 9.7; 3/12-H)
3D$^+$	1.840 (s), 1.879 (s), 5.271 (d, 11.7; 8-H), 5.665 (d, 11.7; 9-H), 5.772 (d, 11.3; 13-H), 5.801 (d, 6.1; 4-H), 7.037 (t, 11.7; 12-H), 7.235 (dd, 15.6, 6.1; 3-H), 11.358 (d, 15.6; 2-H), 11.712 (d, 12.1; 11-H)
2D$^+$[c]	1.860 (s, 5-Me), 2.581 (s, 10-Me), 4.946 (dd, 13.7, 11.8; 8-H), 6.210 (d, 10.9; 2-H), 6.254 (d, 8.3; 4-H), 6.359 (dd, 14.1, 11.3; 12-H), 6.644 (dd, 10.9, 8.3; 3-H), 6.980 (dd, 11.8, 10.1; 7-H), 7.003 (d, 13.7; 9-H), 7.152 (d, 10.1; 6-H), 7.236 (d, 14.1; 13-H), 7.279 (d, 11.3; 11-H)

[a] Obtained at 24 °C unless otherwise stated. Chemical shifts are given in δ. In parentheses are the splitting pattern, coupling constants in Hz, and the assignment. [b] Re-examined. See also Ref. 2. [c]Obtained at -10 °C.



Scheme 2.

such as trifluoroacetic acid (TFA) and sulfuric acid because the polarization of the carbonyl group is promoted by protonation on the carbonyl oxygen, as has been demonstrated for compound **1**.[2]

Dissolution of either **3** or **4** in TFA-*d* gave rise to a single species **3D**$^+$ which had the same geometry as **3** in $CDCl_3$ (Scheme 2 and Table 2).[4] Species **3D**$^+$ was quite unstable and rapidly decomposed but clearly exhibited enhanced paratropicity, as typically shown by the further low-field shifts of the inner protons (2-H: δ 11.36; 11-H: δ 11.71). As compound **2** was also unstable in TFA-*d* at ambient temperature, the NMR spectrum was obtained at -10 °C, where the protonated species survived long enough to afford sufficient spectra. Analysis of the ^{1}H NMR spectrum of **2** in TFA-*d* indicated that **2** existed in a conformation given as **2D**$^+$ in Scheme 2 by two-dimensional representation, which was different from that in $CDCl_3$, and this species showed no tropicity at all in this medium; the "inner" protons 8-H and 12-H appeared at δ 4.95 and 6.36, respectively.

The present results reveal that the paratropicity decreases with the decreasing number of triple bonds, **1** > **3**, **4** > **2**. Also, the longest-wavelength band in the UV spectra shifts toward longer wavelength on going from **2** to **4** to **1**,[2,3] indicating the increase in the degree of extended conjugation in this order. Molecular model considerations suggest that these trends can be ascribed to the decrease of planarity in this order, and preliminary molecular mechanics calculations support this view. In Fig. 1 is shown the calculated molecular structure of **2** optimized by MM2. The double bond planes are considerably

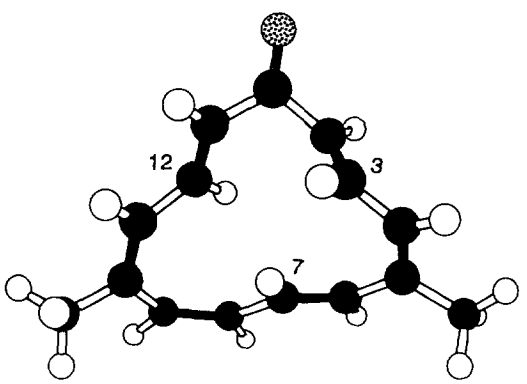


Fig. 1. MM2-optimized geometry of compound **2**.

distorted from the averaged plane of the ring, suggesting the lack of peripheral conjugation. The C2=C3–C4=C5 moiety has the dihedral angle of 68° and is thus considered to be *s*-cis rather than *s*-trans as given in Scheme 1. The calculated distances between 3-H and 7-H and between 7-H and 12-H are 2.72 and 2.39 Å, respectively, and these are compatible with the NOE data.

Further efforts to prepare monocyclic annulenones with a larger ring-size, especially those expected to exhibit diatropicity, are in progress.

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2. Cresp, T. M.; Ojima, J.; Sondheimer, F. *J. Org. Chem.*, **1977**, 42, 2130-2134; Ojima, J; Wada, K.; Terasaki, M. *J. Chem. Soc., Perkin Trans. 1*, **1982**, 51-58.
3. Compound **2**: orange prisms, mp 85.2–86.7 °C (from diethyl ether-hexane). Found: C, 84.78; H, 7.75%. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60%. IR (KBr): ν_{max} (cm^{-1}) 1627 (C=O), 1615, 1581 (C=C), 995, 962 ((*E*)-HC=CH), 695, 670 ((*Z*)-HC=CH). UV (THF): λ_{max} (nm) 263.5 (ε 31800), 348.5 (2600), 361sh (2600). ^{13}C NMR ($CDCl_3$): δ 194.54, 149.29, 143.20, 142.79, 140.71, 133.60, 131.37, 130.76, 130.38, 129.44, 128.39, 125.98, 123.77, 25.78, 24.08. Compound **3**: red needles, mp 64.4–65.2 °C (from diethyl ether-hexane). Found: C, 85.51; H, 6.73%. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71%. IR (KBr): ν_{max} (cm^{-1}) 2157 (C≡C), 1647 (C=O), 1604, 1585 (C=C), 980 ((*E*)-CH=CH), 670 ((*Z*)-CH=CH). UV (THF): λ_{max} (nm) 269 (ε 34200), 280.5sh (28400), 341sh (4600). ^{13}C NMR ($CDCl_3$): δ 191.27, 142.10, 140.45, 138.00, 135.28, 133.49, 129.03, 127.76, 125.08, 124.05, 109.14, 99.00, 95.12, 24.35, 17.91. Compound **4**: orange plates, mp 95.2–96.4 °C (from diethyl ether-hexane). Found: C, 85.83; H, 6.68%. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71%. IR (KBr): ν_{max} (cm^{-1}) 2159 (C≡C), 1625 (C=O), 1577, 1565 (C=C), 976 ((*E*)-CH=CH), 685 ((*Z*)-CH=CH). UV (THF): λ_{max} (nm) 270 (ε 41100), 276sh (40300), 372 (1700). ^{13}C NMR ($CDCl_3$): δ 198.12, 150.64, 141.55, 141.31, 137.82, 132.72, 129.40, 128.11, 127.76, 126.35, 110.46, 99.32, 97.06, 26.22, 21.29.
4. In annulenones facile occurrence of cis-trans isomerization of double bonds in acidic media has often been observed. See for example: Yamamoto, G.; Higuchi, H.; Yamamoto, H.; Ojima, J. *J. Chem. Soc., Perkin Trans. 2*, **1992**, 479-487; *Bull. Chem. Soc. Jpn.*, **1992**, 65, 2388-2393.

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