

STUDIES ON THE DIAMAGNETIC SHIFTS IN 4:7,10:13-DIOXIDO[15]ANNULENONE SYSTEMS

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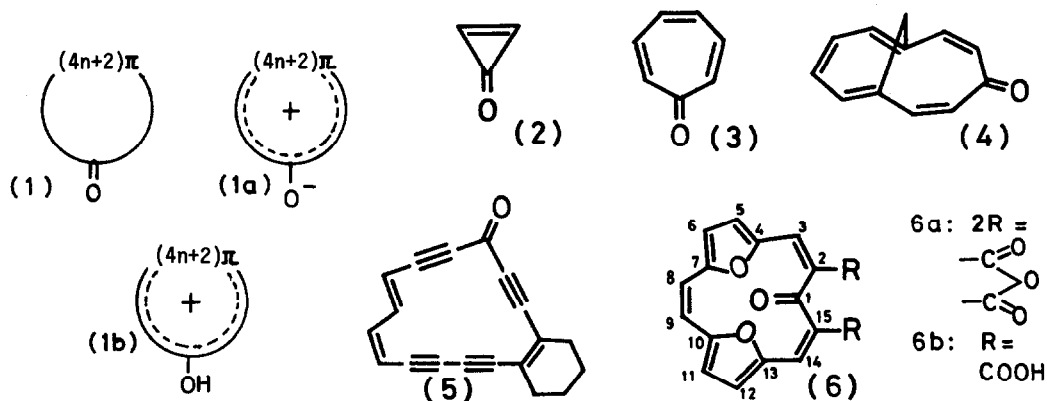
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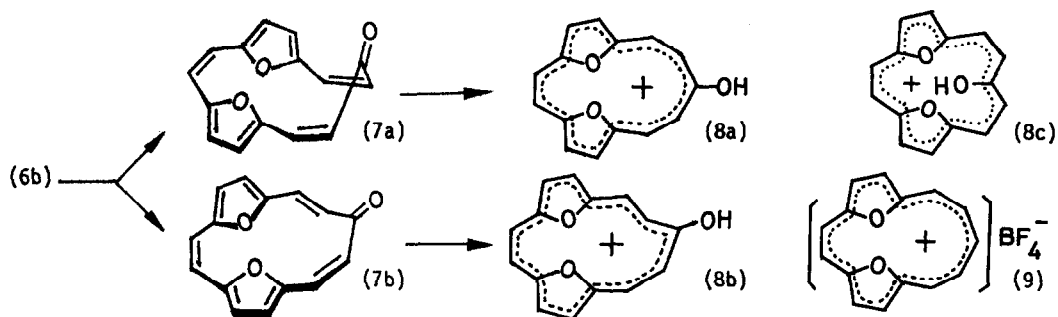
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THE experimental scrutiny of Hückel's rule has resulted in the synthesis of a number of novel aromatic $[4n+2]$ annulenes¹. When this rule is extended to annulenones² (monocarbocyclic conjugated ketones), there should exist a host of aromatic $[4n+3]$ annulenones (1), beginning with the $n = 0$ member. In this series of compounds, cyclopropenone ($n = 0$)³ (2), tropone ($n = 1$)⁴ (3), 4,9-methano[11]annulenone ($n = 2$)⁵ (4) and 4,5-tetramethylene-2,6,8,14-tetrahydro[15]-annulenone ($n = 3$)⁶ (5) are known.

If there is a high contribution of a dipolar structure (1a) in its ground state, the annulenone (1) should be aromatic, exhibiting a diamagnetic ring current; conversely, when there is no such contribution, (1) should be best fitted by a polyenone structure. However, even in the latter case, the completely delocalized 1-hydroxyannulenylum cation (1b) may be capable of existence, when (1) is protonated with some strong acids.

In a previous communication⁷, we showed that 2:3,8:9,14:15-tri-cis-4:7,10:13-dioxido[15]-annulenone 2,15-dicarboxylic acid anhydride (6a) fulfils the criteria for aromaticity in terms of ring current. We now report the synthesis of two isomeric 4:7,10:13-dioxido[15]annulenones (7a) and (7b), and show that these parent annulenones are best represented as nonaromatic poly-





enones. On the other hand, the corresponding 1-hydroxycyclopentadecaheptaenylium cations (8a) and (8b) were found to show a marked diamagnetic ring current.

Decarbonylation of the [15]annulenone 2,15-dicarboxylic acid (6b) was carried out at 170° in quinoline for 15 min. in the presence of copper chromite. Chromatography of the reaction mixture on silica gel with CHCl_3 yielded (7a) and (7b) in 20% and 10% yield, respectively.

The tri-cis isomer (7a) was obtained as orange yellow prisms, mp 158-60° (from CCl_4), which decomposed gradually in the solid state on exposure to light and air; mass spectrum, molecular ion at m/e 238, base peak 210 ($\text{M}^+ - \text{CO}$); $\lambda_{\text{max}}^{\text{MeOH}}$ 232 (ϵ 21,700), 245 sh (19,900), 318 (39,200), 390 sh (5,000), 405 (5,300), 450 sh (4,200), 465 (4,500) and 495 nm (3,600) [see FIG. 2]; $\nu_{\text{max}}^{\text{KBr}}$ 1653, 1641, 1613, 1603 cm^{-1} ($>\text{C}=\text{O}$). The pmr spectrum in CDCl_3 does not indicate the existence of a diamagnetic ring current; the 4H AB system at δ 6.96 and 7.28 ppm with $J = 12$ Hz is assigned to the H_2, H_3 and $\text{H}_{14}, \text{H}_{15}$ protons, the 2H singlet at δ 7.04 ppm to the H_8, H_9 olefinic protons, and the sharp 4H singlet at δ 7.24 ppm to the furan protons, respectively [see FIG. 1].

The mono-trans-di-cis isomer (7b) was obtained as a reddish oil from the well separated upper band of the same chromatogram; mass spectrum, molecular ion at m/e 238; $\lambda_{\text{max}}^{\text{MeOH}}$ 232 (ϵ 14,800), 316 (27,300), 400 (4,450), 440 (3,300) and 500 nm (2,700); $\nu_{\text{max}}^{\text{CHCl}_3}$ 1658, 1621, 1601 cm^{-1} ($>\text{C}=\text{O}$). The pmr spectrum in CDCl_3 again exhibited no sign of a diamagnetic ring current, and this molecule should also be regarded as a nonaromatic polyenone; a 2H AB system at δ 7.06 and 7.35 ppm with $J = 12$ Hz is assigned to the $\text{H}_{14}, \text{H}_{15}$ protons, the 2H singlet at δ 7.14 ppm to the H_8, H_9 protons, the somewhat broadend signal at δ 6.85 ppm to the trans protons, and the 2H singlet at δ 7.31 ppm as well as the two 1H doublets at δ 7.21 and 7.37 ppm with $J = 4$ Hz to the furan protons [see FIG. 3A].

We consider that the nonaromaticity of (7a) or (7b) can reasonably be explained by their noncoplanar conformations in which the carbonyl groups are tilted away from the other double bonds. These conformations would seem to be likely, as coplanar conformations suffer from

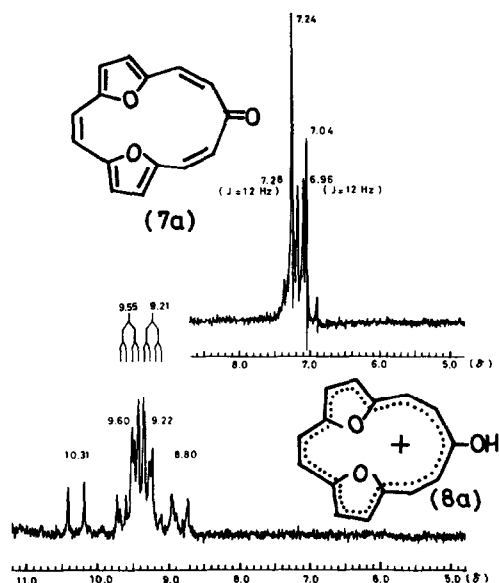


FIG. 1. PMR spectra of (7a) in CDCl_3 (upper spectrum) and of (8a) in CF_3COOH (lower spectrum) at 25° [60 MHz].

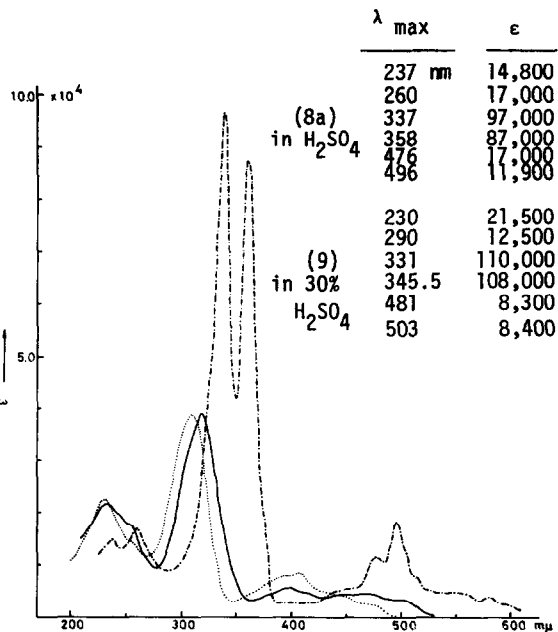


FIG. 2. UV and visible spectra of (7a) in (—MeOH) and in (..... cyclohexane); uv and visible spectrum of (8a) in (--- H_2SO_4).

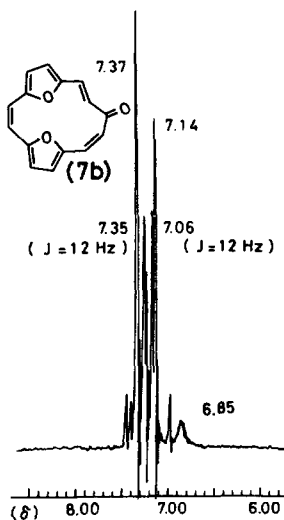


FIG. 3A. PMR spectrum of (7b) in CDCl_3 at 25° [60 MHz].

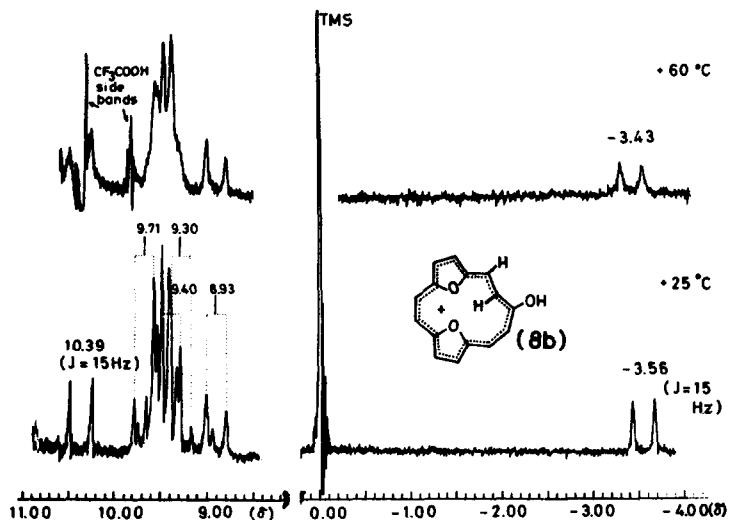


FIG. 3B. PMR spectra of (8b) in CF_3COOH at 25° (lower spectrum) and at 60° (upper spectrum) [60 MHz].

severe overcrowding [especially in (7b)] or from large angle strains.

The pmr spectra of (7a) and (7b) in CF_3COOH showed dramatic shifts, in accord with the expected formation of the aromatic 1-hydroxy-4:7,10:13-dioxido-cyclopentadecaheptaenylum cations (8a) and (8b). The ten outer protons of (8a) and the nine outer protons of (8b) resonated at δ 8.80 - 10.31 and 8.93 - 10.39 ppm, respectively. The one inner proton of (8b) now appeared at very high-field (a doublet at δ - 3.56 ppm at 25°, and δ - 3.43 ppm at 60°, J = 15 Hz). This high-field shift and the area integration of the inner hydrogen are exactly what was expected for (8b). The temperature dependence of the spectrum is not caused by a transformation product, because the original spectrum is regenerated on cooling the solution to 25°.

The uv spectra of (8a) and (8b) in H_2SO_4 , and their high absorption coefficients support well the formation of these aromatic cations, since these spectra are extremely similar to that of 2:3,8:9,14:15-tri-cis-4:7,10:13-dioxido[15]annulenyl tetrafluoroborate⁸ (9) [see FIG. 2]. Although the conformational mobility of the $>\text{C}=\text{O}$ group of (7a) may afford another cation (8c), we believe that high resonance stabilization would be unlikely in this structure as the internal OH group overlaps severely the oxygen atoms of the furan rings. The preferred geometry (8a) is similar, in part, to that of the cyclononatetraene anion, and it follows that (8a) is reasonably planar.

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* Author to whom correspondence should be addressed.

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