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TRIBENZO[a,c,g]CYCLOUNDECA-2,12-DIENE AND THE NATURE OF ITS [11]ANNULENYL ANION

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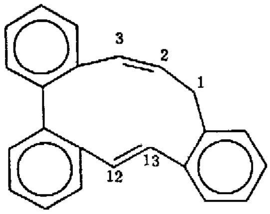
[11]Annulene is a potential precursor of the aromatic [11]annulenium cation and the antiaromatic [11]annulenyl anion. Previously we have reported the preparation of a dehydro-derivative of dibenzoannelated [11]annulene which failed to yield the corresponding aromatic cation.[1] We wish to report the preparation of two isomers of tribenzo[11]annulene, viz. cis,trans- and trans,trans-tribenzo[a,c,g]cycloundeca-2,12-diene 1 and 2 respectively, and the nature of their anion 3. Anion 3 should behave prima facie as an antiaromatic ion but it does not show any evidence for antiaromaticity, viz. paratropic ring current.

Wittig reaction[2a] of homophthaldialdehyde[2b] and biphenyl-2,2'-bis(triphenylphosphonium bromide), (NaOMe, DMF, 80°, 16 hrs) afforded 10% of a product which was separated by fractional recrystallizations (cyclohexane) into isomer 1[3] and isomer 2[3]. These isomers are stable to light, air and prolonged heating and show an identical mass spectrum: m/e = 295 (M+1, 12%), 294 (M, 43%), 178 (100%). Isomer 1 (m.p. 135°, 70%) showed the following spectra: $\lambda_{max}^{CH_3CN}$ 240 (ϵ 31,200), 297 nm (16,800); ν_{max}^{KBr} (cm^{-1}) 3060, 3020, 1485, 1440, 985, 755, 735, 700; pmr ($CDCl_3$)[4,5] ppm 3.30 (dt, 1H, J_1 = 16.3, $J_2 = J_3$ = 2.8 Hz, H_1), 4.00 (dd, 1H, J_1 = 16.3, J_2 = 11.9, $J_3 < 0.5$ Hz, allylic, $H_{1'}$), 5.38 (ddd, 1H, J_1 = 11.9, J_2 = 10.9, J_3 = 2.8 Hz, H_2), 6.07 (d, 1H, J = 16.6 Hz, H_{12}), 6.20 (dd, 1H, J_1 = 10.9, J_2 = 2.8, $J_3 < 0.5$ Hz, H_3), 6.74 (d, 1H, J = 16.6 Hz, H_{13}), 7.00-7.63 (m, 12H, aromatic protons). Pmr and ir spectra show the presence of a cis and a trans double bonds. From the pmr spectrum it can be seen that $C_2 - C_3$ bond is a cis and $C_{12} - C_{13}$ bond is a trans double bond. (J_{cis} = 10.9 Hz, J_{trans} = 16.6 Hz). Isomer 2 (m.p. 128°, 30%), $\lambda_{max}^{CH_3CN}$ 250 (ϵ 43,500) 295^S (32,900) ν_{max}^{KBr} (cm^{-1}) 2930, 1470, 1440, 980, 960, 755; Pmr ($CDCl_3$)[4,5] ppm 3.39 (broad d, 2H, J_1 = 7.5, $J_2 < 0.7$ Hz, allylic H_1, $H_{1'}$), 5.50 (dt, 1H, J_1 = 16, J_2 = 7.5 Hz, H_2), 6.07 (d, 1H, J_1 = 16, $J_2 < 0.7$ Hz, H_3), 6.08 (d, 1H, J = 16 Hz, H_{12}), 6.62 (d, 1H, J = 16 Hz, H_{13}), 7.05-7.60 (m, 12H, aromatic protons). Treatment of either 1 or 2 with $\bar{C}H_2SOCH_3$ gave a blue solution of anion 3. δ (DMSO - d_6)[4,5] ppm 5.15 (d, 1H, J = 10 Hz, H_{12}), 6.00 (t, 1H, $J_1 = J_2$ = 7 Hz, H_6), 6.24 (t, 1H, $J_1 = J_2$ = 7 Hz, H_{15}), 6.62 (t, 1H, $J_1 = J_2$ = 7 Hz, H_5), 6.72 (d, 1H, J = 10 Hz, H_{13}), 6.74 (m, 3H, H_{14}, H_{16}, H_{17}), 6.96 (d, 1H, J = 7 Hz, H_4), 7.06 (m, 5H, H_1, H_2, H_3, H_9, H_{10}), 7.31

(d, 1H, J = 7 Hz, H_{11}), 7.42 (d, 1H, J = 7 Hz, H_7), 7.70 (m, 1H, H_8). Experiments to prepare the [11]annulenium cation failed

The nmr spectrum of 3 shows that no paratropic system was obtained since none of the vinylic protons was shifted to high field. However, the nmr spectrum can be interpreted in terms of the formation of a homoaromatic system containing nine carbon atoms, i. e. a homocyclononatetraenyl anion. Nonaromatic or localized systems are ruled out since there is a downfield shift of the vinylic protons and the aromatic protons do not appear at a high field as has been observed in linear analogs.[6] The coupling constants of H_{12} and H_{13} (10 Hz) show that these protons bear a delocalized charge. It should also be noted that the biphenyl moiety of 3 is not coplanar since there are no low field protons that would be expected in such a planar system. Our suggestion, supported by molecular models, is that in anion 3 ring B sticks out of the plane of the rest of the molecule, and thus H_{12} which is an inner ring proton should not show a paratropic shift.



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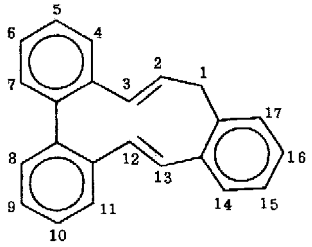

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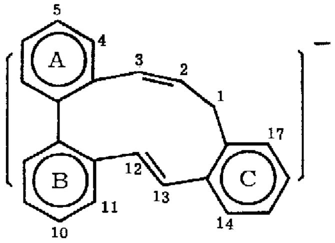

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References and Notes

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2. (a) K. P. Vollhardt, Synthesis, 765 (1975).
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3. All new compounds gave satisfactory elementary analysis.
4. ^{1}H NMR spectra were recorded at 100 MHz on a Varian HA 100D spectrometer, Me_4Si served as internal standard.
5. The assignments were supported by double resonance experiments with a Hewlett-Packard 4204A oscillator.
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