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CYCLOOCTA[def]FLUORENYL ANION A PERTURBED ANTIAROMATIC [15]ANNULENYL ANION

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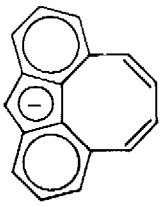
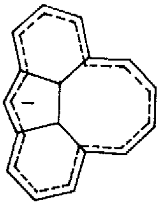
Perturbation theory[1] predicts that a fused conjugated system may be considered a peripheral π-electron system perturbed by a vinyl cross link Anions derived from odd-membered conjugated rings containing 4n +3 carbon atoms should be "antiaromatic '[2] An adequate substrate for a study of perturbed systems bearing antiaromatic" properties is the anion 1 derived from cycloocta[def]fluorene 2 In this system the double bonds of the eight membered ring are remote from the site of deprotonation and represent a sensitive probe for delocalization of the negative charge over the whole framework, e g 1 or 1a

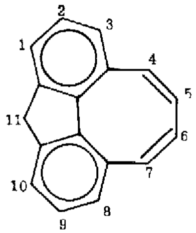
We wish to report the synthesis of cycloocta[def]fluorene 2 and the anion 1 derived from it Photocycloaddition of 4 5-methylenphenanthrene 3 with maleic anhydride, using benzil as sensitizer,[3] followed by hydrolysis gave 4 (70% yield)[4] ν_{max}^{nujol} (cm^{-1}) 1720 (C=O stretching) Oxidative bisdecarboxylation of 4 with lead tetraacetate[5] afforded after chromatography 5 (18% yield) m p 98°, mass spectrum m/e 217 (M + 1) 216 (M, 100%), 215 191, 190, 189, 108, ν_{max}^{KBr} (cm^{-1})



1



1a

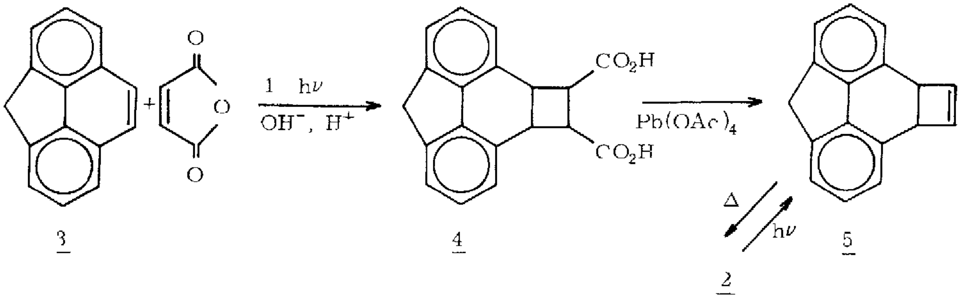


2

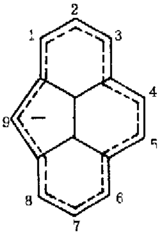
2909, 1630, 1455, 1260, 750 (s), $\lambda_{max}^{cyclohexane}$ 244 (ϵ 18,800) 231 (16,200) 238 (12,200) 254 (10,800), 263^{s} (10,400) 276 (11,500), 284 (9,300) 300^{s} nm (3000), pmr[6] (CDCl$_3$) δ = 3.84 ppm (s, 2H, methylen protons), 4.44 (s, 2H, benzylic) 6.10 (s, 2H, vinylic), 7.12-7.77 (m, 6H, aromatic). Pyrolysis of 5 (400°, 20 cm glass tubing, filled with glass chips) afforded 2 (85% yield after chromatography, red oil)[4]. Mass spectrum, m/e 217, 216 (M, 100%), 215, 191, 190, 189, 109, 108. ν_{max} (cm^{-1}) 3050, 1425, 1160, 770 (s), 730, $\lambda_{max}^{cyclohexane}$ 255 (ϵ 29,500) 273^{s} (21,200), 300 (4,600), 346^{s} nm (1360), pmr δ (CDCl$_3$) 3.63 ppm (s, 2H, H_{11}), 5.68 (d,d, 2H, H_5 and H_6, $J_{4,5} = J_{7,6} = 10$ Hz, $J_{4,6} = J_{7,5} = 2$ Hz), 5.90 (d,d, 2H, H_4 and H_7, $J_{5,4} = J_{6,7} = 10$ Hz, $J_{6,4} = J_{5,7} = 2$ Hz) 6.83-7.85 (m, 6H aromatic). Irradiation of 2 afforded 5 as predicted by the Woodward-Hoffman rules.[7]

Treatment of 2 with n-butyl lithium in THF-d_8 gave a dark red solution. The pmr spectrum[8] of the formed anion 1 clearly indicates the presence of a C_2 symmetry axis. The following spectrum was observed: δ ppm 7.08 (d, 4H, assigned to H_1, H_3, H_8 and H_{10}, $J_{2,1} = J_{2,3} = 8$ Hz) 6.38 (t, 2H assigned to H_2 and H_9, $J_{1,2} = J_{3,2} = 8$ Hz), 5.38 (s, 1H, H_{11}), 5.42 (dd, 2H, H_4 and H_7, $J_{5,4} = 10$ Hz, $J_{6,4} = 4$ Hz), 4.96 (dd, 2H, H_5 and H_6, $J_{4,5} = 10$ Hz, $J_{7,5} = 4$ Hz). It is surprising that in the spectrum of the anion 1, the H_1,H_{10}-protons resonate at exactly the same place as the H_3, H_8 protons.

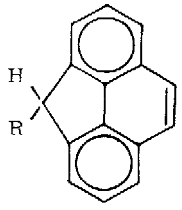
In order to gain further insight of the degree of the delocalization of the negative charge in 1, we prepared the cyclopenta[def]phenanthrene anion 6 from its parent hydrocarbon 3. This anion is closely related to 1, and it may be considered[1] as a peripheral perturbed aromatic [13]annulenyl anion. Treatment of 3 with n-butyl lithium in THF-d_8 yielded anion 6.[9] The pmr spectrum of 6 shows the following parameters: δ ppm 7.73 (s, 2H, H_4 and H_5), 7.41 (m, 4H, H_2, H_3, H_6 and H_7), 7.00 (dd, 2H, H_1 and H_8, $J_{2,1} = J_{7,8} = 8$ Hz, $J_{3,1} = J_{6,8} = 2$ Hz) 6.06 (s, 1H, H_9). In spite of the negative charge of 6, protons H_4 and H_5 are shifted downfield (ca. 0.5 ppm) relative to 3. The other aromatic protons are not affected. This observation reveals a paratropic character of 6. Quenching of 6 with D_2O or CH_3I yielded quantitatively 3a and 3b respectively.[4] The pmr spectrum of 3a is similar to the spectrum of 3 except for the H_9 which corresponds to one proton. The pmr spectrum of 3b is as follows: δ ppm (CDCl$_3$) 7.55-7.85 (m, 8H) 4.40 (1, 1H, J = 8 Hz), 1.65 (d, 3H, J = 8 Hz).



The pmr spectrum of 1 reveals an upfield shift of the vinylic protons (H_4, H_5, H_6, H_7) compared with the parent hydrocarbon 2 (H_4 and H_7 are shifted by 0.5 ppm, H_5 and H_6 by 0.7 ppm). The aromatic protons are also shielded and they are shifted upfield by ca. 0.8 ppm. It should be noted that protons H_1, H_3, H_8 and H_{10} are less shielded than H_2 and H_9, thus excluding a resonative shielding by the negative charge in the system. A comparison of the chemical shifts of 1 and 6 shows that in 6 protons H_4 and H_5 are deshielded (δ = 7.73 ppm) while the methylene proton H_{11} in 1 is shifted upfield by 0.23 ppm compared to H_9 in 6. These nmr data are consistent with the assumption that the negative charge in 1 is delocalized over the whole network, thus yielding a perturbed paratropic ("antiaromatic") [15]annulenyl anion 1a. This is the first example to our knowledge of a perturbed annulenyl anion showing "antiaromatic" properties. Anion 6, on the other hand, may be considered as a diatropic ("aromatic") perturbed [13]annulenyl anion.



6



3

3, R = H

3a, R = D

3b, R = CH_3

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References and Notes

1. a) M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, 1617 (1954).
   b) B. M. Trost, D. Buhner and G. M. Bright, *Tetrahedron Letters*, 2787 (1973).
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   b) I. Agranat in "M. T. P. International Reviews of Science, Organic Chemistry, Series One, Vol. 3", Butterworths, London, 1973, p. 139 and references cited therein.
3. A similar synthetic route has been carried out with phenanthrene. *Cf.* E. Vogel, W. Frass and J. Wolpers, *Angew. Chem.*, **75**, 979 (1963).
4. All new compounds gave satisfactory C, H analyses.
5. C. A. Grob, M. Ohta, E. Renk and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).
6. Proton spectra were recorded at 100 MHz (HA-100D spectrometer). Chemical shifts are reported in ppm downfield from Me_4Si.
7. R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry", Verlag Chemie, GmbH, Academic Press Inc., Weinheim/Bergstr.
8. The pmr spectrum did not change between (-20) – (20°C). It was stable for several days under nitrogen.
9. The reaction of 3 with potassium yielded two anionic species. *Cf.* R. H. Cox, E. G. Janzen and J. L. Gerlock, *J. Amer. Chem. Soc.*, **90**, 5906 (1968).