

TRIBENZO[a,c,f]CYCLOOCTYL ANION AND TETRABENZO[a,de,h,k1]BICYCLO[6,6,0]TETRADECYL DIANION AND THE QUESTION OF THEIR HOMOAROMATICITY. BENZANNELATED HOMOPENTADIENYL AND HOMOPENTALENYL ANIONS.

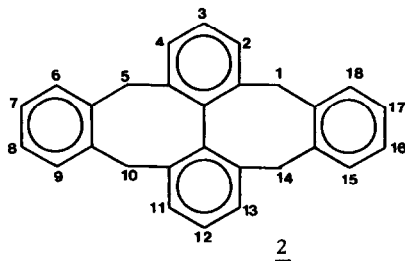
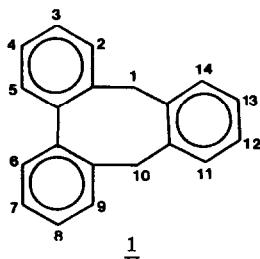
Arie Dagan, Daniel Bruck and Mordecai Rabinovitz*

Department of Organic Chemistry,
The Hebrew University of Jerusalem, Jerusalem, Israel

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The concept of homoaromatic systems as systems containing cyclic Hückeloid ($4n + 2$) arrays of π -electrons interrupted in one or more places by an intervening sp^3 hybridized carbon is by now a familiar one¹. Homoaromatic systems are characterized by a cyclic charge delocalization and have been treated in a number of studies². We report the preparation and properties of tribenzo[a,c,f]cyclooctyl anion and tetrabenzo[a,de,h,k1]bicyclo[6,6,0]tetradecyl dianion. The properties of these two anionic species can be explained in terms of the formation of homoaromatic systems viz. 3 and 4 respectively, so that 3 is a benzannelated homocyclopentadienyl anion and 4 is a tetrabenzannelated homopentalenyl dianion.

2,2'-Dihydroxymethyl biphenyl³ reacts with benzene in conc. sulfuric acid to form tribenzo[a,c,f]cyclooctane 1 in 70% yield⁴. Treatment of 1 with n-butyl lithium (T.H.F.-d₈, room temperature, 12 hrs.) gave a red solution. A new proton nmr spectrum was observed⁵ and assigned to a monoanion, δ ppm 3.10 (d, 1H, J = 12Hz), 3.87 (s, 1H), 5.47 (d, 1H, J = 12Hz) 5.59 (t, 1H, J = 7Hz), 5.90 (m, 2H, aromatic), 6.30 (m, 5H, aromatic) 6.90, (m, 4H, aromatic). The two doublets at 3.10 and 5.47 ppm, are mutually coupled, this was proved by double resonance experiments³. They are assigned therefore to the two protons on carbon atom 10. The triplet at 5.59 ppm is assigned to a benzene ring proton at a para position (H_4). The chemical shift difference of the two protons on carbon-10 $\Delta\delta = 2.37$ ppm needs further comment. A homoaromatic structure i.e. 3 can explain this significant difference of the protons on carbon-10 due to a paratropic shift on one proton and a

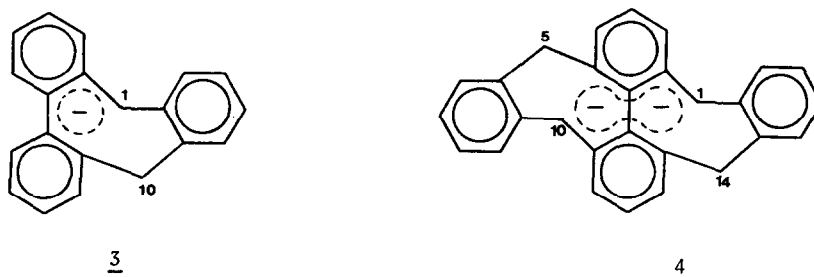


diatropic shift on the other. Some other facts assist the claim of homoaromatic character, among them is that there is only one proton in the para position which appears at 5.59 ppm. This observation means that the charge distribution on the two benzene rings attached to carbon atom 1 is quite different. (The assignment that the high field triplet at 5.59 ppm belongs to the proton (H_{12}) was confirmed by preparing the anion of 11,12,13,14-tetra deuteriotribenzo[*a,c,g*]cyclooctane. It should also be noted that in the anion 3 the biphenyl system is coplanar as shown by the relative low field absorption of protons 5 and 6 in contrast to the situation in 1 in which the biphenyl system is not coplanar.

Reaction of 2,2',6,6'-tetrahydroxymethyl biphenyl with benzene in conc. sulfuric acid forms tetrabenzo[*a,de,h,kl*]bicyclo[6,6,0]tetradecane⁴ 2 in 60% yield. Treatment of 2 with *n*-butyl lithium (T.H.F.- d_8 , room temperature, 12 hrs.) gave a dark red solution. In the nmr spectrum⁵ all bands of 2 have disappeared and a new spectrum was obtained assigned to an anion, δ ppm = 2.72 (d,2H, $J = 12$ Hz), 3.70 (s,1H). 4.67 (d,2H, $J = 12$ Hz), 5.38 (t,2H, $J = 7$ Hz), 5.87 (m,4H,aromatic), 6.11 (m,4H,aromatic), 6.40 (m,4H,aromatic). Here, too, the two protons on carbon atom 5 and the two protons on carbon atom 14 ($\Delta\delta = 1.95$ ppm) are mutually coupled. The triplet at 5.38 ppm which is assigned to protons in a para position i.e. H_7 and H_{16} is in accord with a symmetrical dianion in which one negative charge is formed on each eight membered ring.

The 1H nmr spectra of the anionic species 3 and 4 are very similar in their chemical shifts and coupling constants and should belong to similar structures. These structures can be interpreted in terms of the formation of homoaromatic anions. Anion 3 is therefore a benzannelated homopentadienyl anion and 4 is a benzannelated homopentalenyl dianion. These homoaromatic structures may also be the driving force for the rearrangement of systems 3 and 4 to the respective fluorenyl and pentalenyl anion derivatives⁴.

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References and Notes

1. For reviews see: (a) S. Winstein, Chem. Soc. special publication No. 21, 5 (1967): Quart. Rev. Chem. Soc., 23, 141 (1969); (b) P.J. Garratt and M.V. Sargent: Nonbenzenoid Aromatics, Vol. II, J.P. Snyder Ed., Academic Press New York, N.Y. 1971 p. 208.
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5. The nmr spectra were recorded at 100 MHz. Proton chemical shifts are reported in ppm downfield from $SiMe_4$. The decoupling experiments were carried out with the aid of a Hewlett-Packard 4204A oscillator.