CHEMISTRY LETTERS, pp. 1273-1274, 1977. Published by the Chemical Society of Japan

2,3:6,7:8,9:12,13-TETRABENZO[13]ANNULENYL ANION

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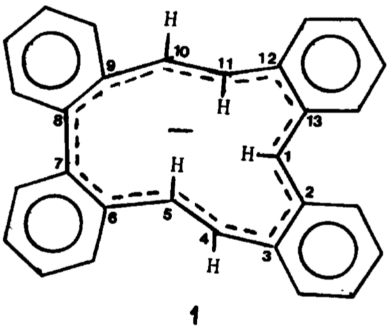
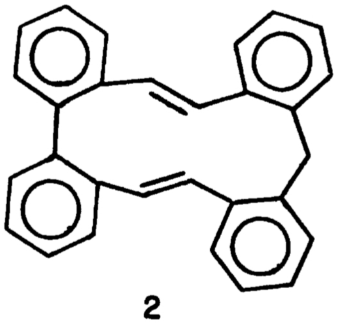
2,3:6,7:8,9:12,13-tetrabenzo[13]annulenyl anion 1 was prepared from the corresponding hydrocarbon 2. The effect of benzannelation and the spatial structure of the anion is derived from its proton nmr spectrum.

Benzannelated nonbenzenoid aromatic compounds evoked interest in recent years.[1] Benzene rings fused to the annulene moiety force the molecule to share a common link with what has been recognized as "ultimate aromatic systems".[1b] In addition, steric repulsions may arise in fused frameworks.[2] It has previously been shown that medium sized all *cis*-benzocyclononatetraenyl anion isomerized to *cis*, *trans*-benzocyclononatetraenyl anion.[3] This transformation was attributed to relief of steric strain. Interestingly, 3,4:5,6 dibenzocyclononatetraenyl anions did not experience such isomerization.[4] However, all benzannelated cyclononatetraenyl anions proved to be strongly diatropic. In contrast, benzannelated large annulenes had a lower diatropic character.[1a,5] This was recently examplified by Staab who pointed out the difference in diatropic character between benzo[18]annulene and the parent non-annelated annulene.[5b] In the [13]annulene series the influence of configuration on aromaticity of hetero[13]annulene was discussed.[1c] In addition, reduced paratropicity of benzannelateddehydro[13]annulenones was recognized.[6] We wish to report the preparation and properties of 2,3:6,7:8,9:12,13 tetrabenzo[13]annulenyl anion 1, the first [13]annulenyl anion containing only double bonds[7] and to discuss the influence of tetra-benzannelation upon the structure and diatropic character of 14π aromatic [13]annulenyl anion.



1



2

Treatment of 2,3:6,7:8,9:12,13-tetrabenzo[13]annulene[8] 2 with t-BuLi in d_8-THF furnished a dark red solution with the following ^{1}H-NMR parameters[9]: δ (ppm) 3.42 (d,1H,J = 13Hz,H_{11}) 3.49 (s,1H,H_1) 4.25 (d,1H,J = 13Hz,H_5) 6.30-7.40 (m,18H aromatic and H_4, H_{10}). The two high-field doublets as well as coupling constants implicate the presence of two "inner" protons bound to two distinct *trans* bonds, while the high field singlet can only be attributed to H_1 in an "inner" position. On the basis of the chemical shifts and coupling constants we assign this spectrum to the planar delocalized aromatic anion 1.[10] Quenching of 1 with water yielded 2.

The observed difference in chemical shifts of the "inner" protons H_5, H_{11} between 1 and 2 (*ca*. 3 ppm) compared with those of the nonbenzanelated[13]annulenyl anion (*ca*. 11 ppm)[7] should be noted. We conclude that benzannelation reduces the diatropic character of the [13]annulenyl moiety. However, more interesting is the clear demonstration of "molecular spatial arrangement to relieve steric strain". The flexible *trans* proton of 2[8] are forced into distinct opposite *trans* bond configurations in order to reduce steric overcrowding, while the H_1 proton is forced int the [13]annulenyl frame in order to prevent two peri non-bonded H-H repulsions at the ring juncture These results provide evidence for the powerful influence of the steric factors and of the benzannelation exerted on the development of the aromatic character in [13]annulenyl anion.

Acknowledgement. This work was supported by the "Ben-Gurion Fund for the Encouragement of Research" - Histadrut - Israel.

References and Notes

1. (a) R.T. Weavers and F. Sondheimer, Angew. Chem., 1974, 86, 167; Angew. Chem. Internat. Edit. 1974, 13, 141.
   (b) M. Nakagawa, Pure Appl. Chem., 1975, 4, 885.
   (c) A.G. Anastassiou, Accounts of Chem. Research, 1976, 9, 453 and references cited therein.
2. Peripheral H-H repulsions were theoretically recognized by H.E. Simmons and J.K. Williams, J. Amer. Chem. Soc., 1964, 86, 3222.
3. A.G. Anastassiou and E. Reichmanis, Angew. Chem., 1974, 86, 784; Angew. Chem. Internat. Edit. 1974, 13, 728.
4. (a) P.J. Garratt and K.A. Knapp, J. Chem. Soc., Chem. Comm., 1970, 1215;
   (b) M. Rabinovitz and I. Willner, Tetrahedron Letters 1975, 3211.
5. (a) M. Morigaki, M. Iyoda and M. Nakagawa, Tetrahedron Letters 1975, 2311;
   (b) V.E. Meissner, A. Gensler and H.A. Staab, ibid, 1977, 3.
6. (a) J. Ojima, Y. Yokoyama and T. Yokoyama, Chemistry Letters, 1975, 487;
   (b) J. Ojima, M. Miyako, A. Kimura and Y. Yokoyama, Tetrahedron Letters, 1975, 1909.
7. Didehydro[13]annulenyl anion has been prepared Cf. E. LeGoff and F. Sondheimer, Angew.Chem. 1972, 84, 996; Angew. Chem. Internat. Edit., 1972, 11, 926.
8. A. Gamliel, I. Willner and M. Rabinovitz, Synthesis, 1977, 410.
9. ^{1}H NMR spectra were recorded at 100 MHz on a varian HA-100D spectrometer. Chemical shifts are reported downfield from TMS.
10. The ^{1}H-NMR spectrum did not change upon cooling to -50°C, thus excluding an averaging of a dynamic process in 1 at this temperature range.

(Received August 4, 1977)