Acknowledgments. This investigation was supported by the National Science Foundation and the U. S. Public Health Service.

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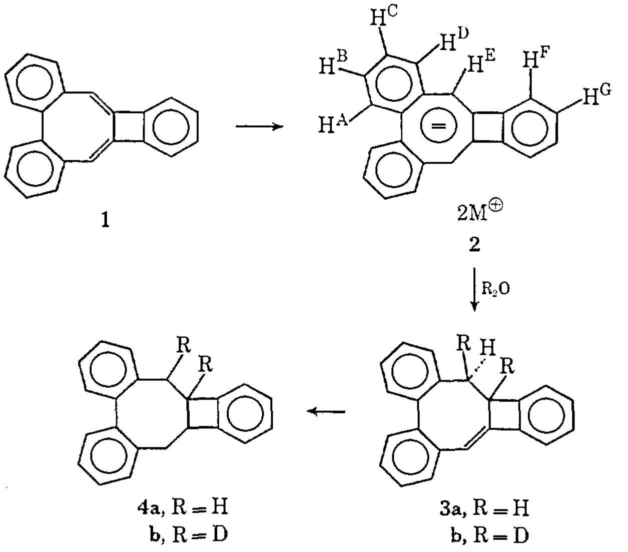
Received September 9, 1969

The 3,4:5,6:9,10-Tribenzobicyclo[6.2.0]decapentaenyl Dianion

Sir:

3,4:5,6:9,10-Tribenzobicyclo[6.2.0]decapentaene (**1**), a $(4n + 4n)$-π-electron system, is a nonplanar, nonaromatic molecule.[1] By analogy with cyclooctatetraene,[2] reduction of **1** with alkali metals could give a planar, aromatic dianion. Two factors might be expected to render this reduction less likely: namely, that annelation will increase the compression energy required to flatten the eight-membered ring,[3] and that the cyclobutadienyl character of the four-membered ring will be increased in the delocalized dianion.

We now report that **1** reacts with alkali metals to give eventually, through a series of intermediates, the 3,4:5,6:9,10-tribenzo[6.2.0]decapentaenyl dianion (**2**), the first analog of a biphenylene in which one of the phenyl rings has been replaced by a ten-π-electron system.[6]



A 0.2 *M* solution of **1** in dry THF reacts *in vacuo* with distilled potassium to give a dark green solution.[7] The assignment of **2** to the dianion in solution is based on its spectral and chemical properties. The nmr spectrum (THF-d_8, 35°, see Figure 1e) shows multiplets at τ 2.52 (4.0 H, H^A, H^D) and 3.90 (4.2 H, H^B, H^C), a singlet at τ 4.23 (1.8 H, H^E), and multiplets at τ 4.51 (1.9 H, H^G) and 4.87 (2.1 H, H^F). The low-field multiplet (4 H) consists of two doublets (J = 8 Hz), as expected for aromatic protons coupled to only one *ortho* proton (H^A, H^D). The multiplet at τ 3.9 is composed of two bands centered at τ 3.76 (2 H) and 4.06 (2 H), both consisting of an overlapping double doublet ($J = J'$ = 8 Hz), with further small couplings, as expected for aromatic protons coupled to two *ortho* protons (H^C, H^B). The two high-field multiplets appear as overlapping double doublets (J = 4, J = 3 Hz), consistent with the H^F, H^G protons having a small *ortho* and a relatively large *meta* coupling. The attribution of the τ 4.51 band to H^G and that at τ 4.87 to H^E is based on the expected effect of charge localization on these positions, and the relative chemical shift of the equivalent protons in biphenylene (see below and footnotes 9, 10). The

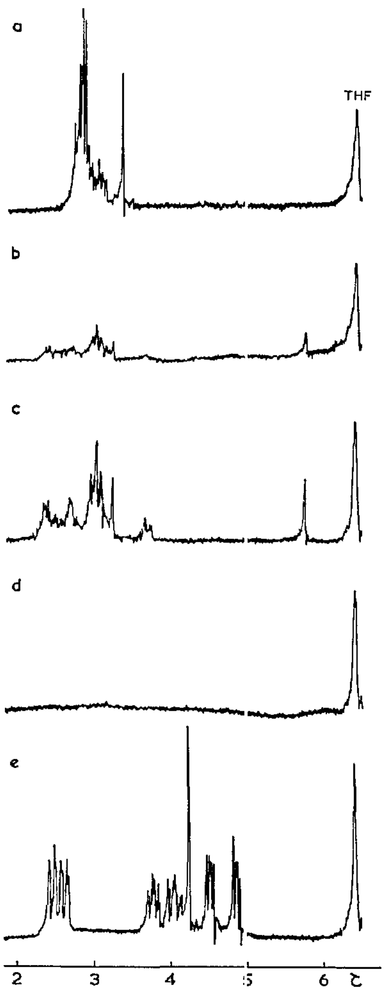


Figure 1. Nmr spectra (100 MHz, 35°) of a 0.2 *M* solution of **1** in THF-d_8 taken at different time intervals after contact with a potassium mirror.

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[1] P. J. Garratt and R. H. Mitchell, *Chem. Commun.*, 719 (1968); P. J. Garratt, R. H. Mitchell, and K. P. C. Vollhardt, submitted for publication.

[2] T. J. Katz, *J. Amer. Chem. Soc.*, **82**, 3784, 3785 (1960).

[3] The barrier to ring flattening is overcome in both *sym*-dibenzocyclooctatetraene[4,5] and tetraphenylene,[5] which are reduced by alkali metals.

[4] T. J. Katz, M. Yoshida, and L. C. Siew, *J. Amer. Chem. Soc.*, **87**, 4516 (1965).

[5] A. Carrington, H. C. Longuet-Higgins, and P. F. Todd, *Mol. Phys.*, **8**, 45 (1964).

[6] Recently the biphenylene analog has been reported in which a phenyl ring has been replaced by the six-π-electron cyclopentadienyl anion: M. P. Cava, K. Narasimhan, W. Zeiger, L. J. Radonovich, and M. D. Glick, *J. Amer. Chem. Soc.*, **91**, 2378 (1969).

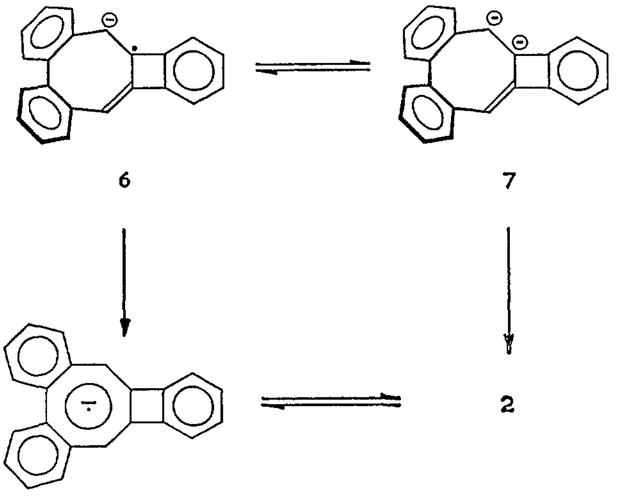
[7] Solutions of **1** also react with lithium, but the course of this reaction has been less well studied.

electronic spectrum (DME) shows maxima at 380 (*ca.* $\log \epsilon$ 4.12), 486 (*ca.* 3.66), and 625 nm (*ca.* 3.11).

Addition of a solution of 2 to water gave an 88% yield of 1,2-dihydro-3,4:5,6:9,10-tribenzobicyclo-[6.2.0]decapentaene (**3a**), as colorless crystals (mp 150–153°). The spectral properties [mass, *m/e* 280, base peak; nmr (CCl_4) τ 2.6–3.3 (m, 11.9 H) 3.58 (d, 0.95 H), 5.82 (d, 0.95 H), 7.4 (m, 2.1 H); uv 264 ($\log \epsilon$ 4.12), 294.5 (4.00), 301 nm (3.99)] were in accord with the assigned structure **3a**. Treatment of **2** with deuterium oxide gave a 93% yield of the corresponding dideuterio compound **3b**, in which the mass (*m/e* 282, base peak) and nmr [(CCl_4) τ 2.7–3.3 (m, 12.2 H); 3.57 (s, 0.9 H), 7.16 (bs, 0.9 H)] spectra confirmed the incorporation of two atoms of deuterium. Hydrogenation (Pd–C, EtOAc) of **3a** gave the known tetrahydro derivative **4a**.[1,8]

The nmr spectrum of **2** shows the same type of pattern as that of the *sym*-dibenzocyclooctatetraenyl dianion (**5**).[4] However, the proton chemical shifts of **2** are at higher field than the analogous protons of **5**, and, in particular, the singlet due to the proton H^E is now at higher field than the phenyl protons H^B, H^C. This displacement of the proton chemical shifts to higher field is due to the induced paramagnetic ring current of the four-membered ring.[9,10]

Interrupting the reaction by removing the solution of **1** from the potassium surface allows the course of the reduction to be followed. The sequence of events which occurs at 35° to the nmr spectrum of the solution is shown in Figure 1.[12] After initial contact with the potassium, the spectrum of **1** broadens and completely disappears, and a new spectrum (b) *which is not that of* **2**, develops. This spectrum slowly increases in intensity on additional contact with potassium until it reaches a maximum resolution (c). On further contact the signal diminishes in intensity and disappears (d), and the final signal due to **2** appears (e).[13] This behavior is *completely different* from that observed in the reduction of cyclooctatetraene[2] and *sym*-dibenzocyclooctatetraene,[4] and is most readily explained by assuming that the initial reduction occurs to give a *nonplanar* anion radical **6**, which undergoes a rapid electron-exchange reaction with the hydrocarbon **1**. Disproportionation or reduction of **6** then gives the *nonplanar* dianion **7**, the spectrum of which is now observed (b, c). The high-field singlet (τ 5.76, 0.8 H) in the spectrum of **7** is attributed to the proton on the reduced double bond. Finally ring flattening occurs to give **2**, which is assumed to undergo rapid electron exchange with the planar anion radical **8**, since **2** does not appear until the spectrum of **7** has disappeared.[14]



This is the first observation of the formation of a nonplanar, nonaromatic dianion in the reduction of a cyclooctatetraenyl system. Whereas in the previous systems studied[3-5] the addition of the first electron was the rate-determining step,[4,15,16] the reduction of **1** appears to occur by two discrete one-electron additions in the nonplanar conformation. The changed course of reduction in this system we attribute to the increased barrier to ring flattening arising from the antiaromaticity of the cyclobutadienyl ring.

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[8] Hydrogenation of **3b** gave **4b**.

[9] H. P. Figeys, *Chem. Commun.*, 495 (1967).

[10] Taking the value of the paramagnetic ring current of the cyclobutadienyl ring to have the same value, but opposite sign to the diamagnetic ring current of benzene,[9] then a correction for the proton chemical shifts for the ring currents of directly adjacent rings was made using a modification[4] of the method of Shaefer and Schneider.[11] Calculations of the charge densities of the carbon atoms bonded to the protons using this method overestimated the electronic charge (sum >2). If the value for the paramagnetic ring current is increased threefold, then the following values for the excess charge densities are obtained. C^A 0.09, C^B 0.18, C^C 0.15, C^D 0.11, C^E 0.19, C^F 0.10, C^G 0.14. This is a minimal estimate for the paramagnetic effect, since some charge is certainly localized on the carbons bearing no protons.

[11] T. Schaefer and W. G. Schneider, *Can. J. Chem.*, 41, 966 (1963).

[12] (Preliminary studies (with Dr. B. P. Roberts) have also shown that changes occur to the esr spectrum during the course of the reaction.

[13] The signals due to the protonated solvent remain relatively sharp throughout the experiment. Hydrolysis of the solution when the spectrum was at stage c gave a 43% yield of **3a**.

[14] When the experiment is carried out at −40°, the spectrum of a further intermediate, *not* **7**, is observed, together with the spectrum of **2**. When the experiment is carried out at −70°, the spectrum of the intermediate **7** is not well developed, and the signals of **2** are the first to be well resolved. However, if, after the spectrum of **2** has partially developed, the sample is allowed to warm to room temperature without further contact with the potassium, then a reexamination of the spectrum at −70° shows the spectrum of **7** appearing coincidently with that of **2**.

[15] T. J. Katz, W. Reinmuth, and D. E. Smith, *J. Amer. Chem. Soc.*, **84**, 802 (1962).

[16] R. D. Allendoerfer and P. H. Rieger, *ibid.*, 87, 2336 (1965).

[17] SRC Predoctoral Fellow, 1967 to present.

[18] Recipient of a fellowship of the Studienstiftung des deutschen Volkes (German National Fellowship Foundation), 1968–1969.

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Received September 17, 1969

Driven Equilibrium Fourier Transform Spectroscopy. A New Method for Nuclear Magnetic Resonance Signal Enhancement[1]

Sir:

Fourier transform spectroscopy has attracted considerable attention as a means of attaining very significant improvements in the signal:noise ratio of high resolution nuclear magnetic resonance (nmr) spectra.[2] The technique consists of the application to the sample of a short, intense pulse of radiofrequency energy and the measurement as a function of time of the resulting free induction signal from the nuclear spins in the

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[1] A preliminary report of this work was given at the 5th Western Regional Meeting of the American Chemical Society, Anaheim, Calif., Oct 7, 1969.

[2] R. R. Ernst and W. A. Anderson, *Rev. Sci. Instrum.*, 37, 93 (1966).