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THE 1,5-BISDEHYDRO[12]ANNULENYL AND 1,5,9-TRIDEHYDRO[12]ANNULENYL RADICAL ANIONS AND DIANIONS[1]

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Abstract—The reduction of 1,5-bisdehydro[12]annulene (1) and 1,5,9-tridehydro[12]annulene (4) with potassium proceeds by a one electron addition to give the corresponding 1,5-bisdehydro[12]annulenyl and 1,5,9-tridehydro[12]annulenyl radical anions (2, 5). Further reduction converts the radical anions into the 1,5-bisdehydro[12]annulenyl and 1,5,9-tridehydro[12]annulenyl dianions (3, 6). The properties of these ions are described.

THE conversion of the nonplanar, nonaromatic 8 π-electron cyclooctatetraene molecule into the corresponding planar, aromatic 10 π-electron cyclooctatetraenyl dianion by reduction with alkali metals is well authenticated,[2] and the dianion has been used as a synthetic intermediate.[3] The reduction occurs by two discrete one electron processes, with the planar, 9 π-electron radical anion as an observable intermediate.[4] The similar reduction of [16]annulene has also been reported,[5a] and this again proceeds by two one electron additions. [16]Annulene, unlike cyclooctatetraene, is a paratropic system,[5b,*] and the reduction to the [16]annulenyl dianion thus converts a paratropic molecule into an 18 π-electron diatropic* system. The internal protons, which were at τ −0·56 in the low temperature NMR spectrum of [16]annulene, appear at τ 18·17 in the dianion, whereas the outer protons experience a downfield shift from τ 4·67 to τ 1·17 and τ 2·55.[5]

These observations indicate that there is a series of $(4n + 2)$ π-electron diatropic dianions which should be obtained on reduction of the corresponding [4*n*]annulenes.† A similar series of diatropic $(4n + 2)$ π-electron dehydrodianions may also be available if the corresponding dehydroannulenes containing 4*n* out-of-plane π-electrons could also be reduced. Two factors may interfere with such a reduction: (i) the acetylene groups might preferably undergo anion polymerisation reaction;[8] (ii) the in-plane π-electrons might seriously perturb both the π and σ-electron framework. Since the known $(4n + 2)$ π-electron dehydroannulenes are more stable than the corresponding annulenes, anion polymerisation appeared to be the most serious potential difficulty. The reduction of the paratropic, near planar 1,5-bisdehydro[12]annulene (1)[9] and 1,5,9-tridehydro[12]annulene (4)[9,10,11] systems, containing 12

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* We define as paratropic those molecules which sustain a paramagnetic ring current,[6] as diatropic those molecules which sustain a diamagnetic ring current,[7] and as atropic those molecules which do not sustain a ring current.

† Professor J. F. M. Oth has informed us privately that [12]annulene is reduced to the [12]annulenyl dianion with potassium.

out-of-plane π-electrons, to the corresponding radical anions and dianions is now described.*

Treatment of a tetrahydrofuran (THF) solution of **1** with a potassium mirror at *ca* 0° in vacuo gave an immediate red solution. The ESR spectrum (Figure 1) shows the presence of the radical anion **2**. The complex spectrum has not been analysed in detail, but the complexity indicates that interaction between the anion and the K^{39} counterion occurs. The g-value obtained, 2·0025, is close to that for the free electron. The electronic spectrum of the solution showed absorption maxima at 425 sh (ε 2100), 486 (2600) and 566 nm (4000), attributed to **2**. The extinction coefficients are minimal values, being based on the complete conversion of **1** into **2** (however, other absorption maxima assigned to the dianion **3** were already present). An NMR spectrum (THF-d_8), taken after a similar period of reduction, showed no signals for either **1** or **2**, although the signals for the residual protons of the THF were virtually unaffected.

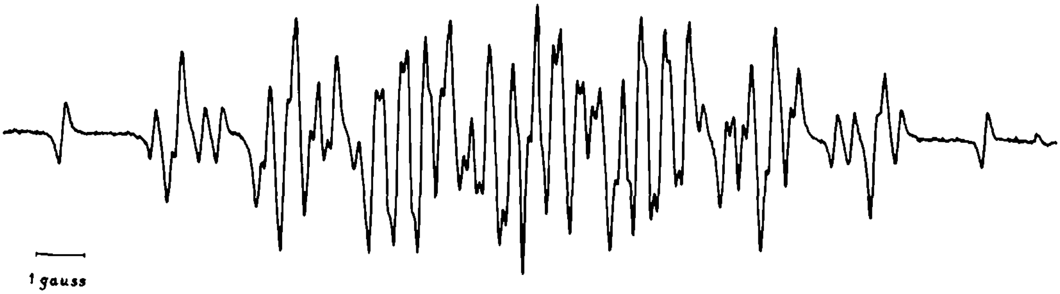
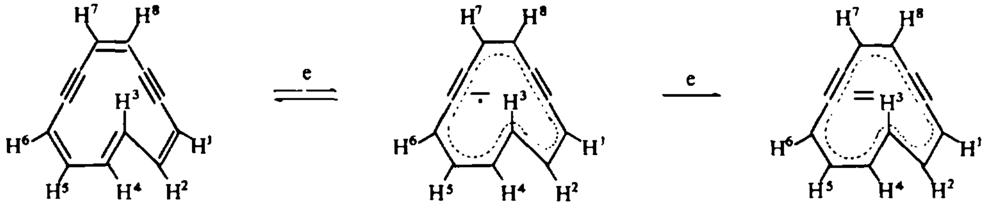


FIG 1. The ESR spectrum of the 1,5-bisdehydro[12]annulenyl radical anion (**2**) in THF.



It thus appears that **1** is readily converted into the radical anion **2**, and furthermore that these systems are in rapid equilibrium. This latter observation is in contrast with the observed behaviour of cyclooctatetraene and its radical anion,[2,4] and presumably reflects the fact that **1**, unlike cyclooctatetraene, does not have to overcome a barrier to ring flattening when it is reduced.

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[*] The radical anion of tribenzo-1,5,9-tridehydro[12]annulene has previously been reported [H. A. Staab and F. Graf, *Tetrahedron Letters* 751 (1966): *Chem. Ber.* **103**, 1107 (1970)]. The radical anion of 1,8-bisdehydro[14]annulene, a ($4n + 2$) π-electron system, has also been prepared [N. M. Atherton, R. Mason and and R. J. Wratten, *Mol. Phys.* **11**, 525 (1966)]. For the preparation of the radical anion and dianion of 1,3,7,9,13,15,19,21-octadehydro[24]annulene, see reference 1.

When the solution containing **2** was allowed to react further with the potassium mirror at *ca* 0° with intermittent shaking for 30 min, a solution of the dianion **3** was obtained. The electronic spectrum now showed absorption maxima at 313 (ε 38,000), 409 (3700) and 452 nm (6500), and the absorption bands due to **2** had disappeared. The extinction coeffients are again minimal values, being based on complete conversion of **1** into **3**.

The NMR spectrum of **3** was obtained by allowing a solution of **1** in THF-d_8 at *ca* − 35° to react with a potassium mirror, or preferably sodium-potassium alloy. The nmr spectrum at − 35° is shown in Figure 2. The low field 2H multiplet at τ 2·03–2·47 consists of two overlapping double doublets (J = 13·5, 14 Hz), which are assigned to H^2, H^4. The high field 1H double doublet at τ 16·88 (J = 14 Hz) is assigned to H^3, and the 5H multiplet at τ 3·31–4·01 is assigned to the remaining protons (H^1, H^5, H^6, H^7, H^8). The NMR spectrum was unchanged on warming to 30°, but above this temperature rapid polymerisation occurred and the spectrum due to **3** disappeared.

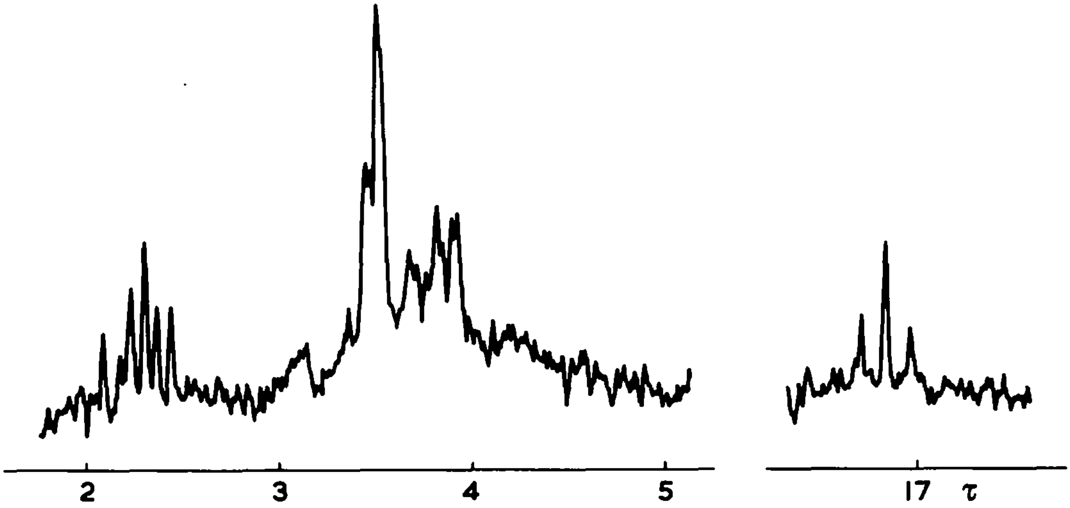


FIG 2. The NMR spectrum of the 1,5-bisdehydro[12]annulenyl dianion (3) in THF-d_8 at −35°.

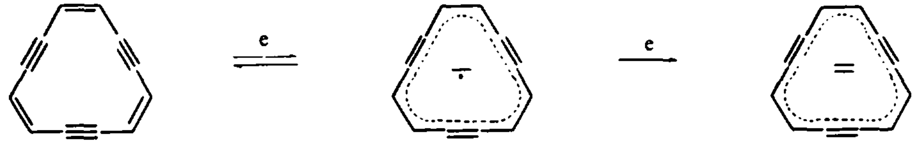
Treatment of a THF solution of **4** with a potassium mirror at *ca* 0° in vacuo also gave an immediate deep red solution. The ESR spectrum of this solution is shown in Fig 3. The simple 7 line hyperfine spectrum expected for a system with 6 equivalent protons is complicated by the presence of further coupling with the K^{39} counterions, which produces 4 equally spaced hyperfine lines. However, these are sufficiently different in line width to allow for measurement of the hyperfine splitting. The proton hyperfine splitting a^H = 2·98 gauss, and the splitting due to K^{39} is 0·7 gauss. The C^{13} satellites can also be observed in Fig 3, and the spectral lines are narrower than those observed for potassium cyclooctatetraenide in either THF or dimethoxyethane.

FIG 3. The ESR spectrum of the 1,5,9-tridehydro[12]annulenyl radical anion (5) in THF.

The g-value obtained was 2·0023, again close to the value for the free electron. Applying the McConnell relationship[12]

$$a^{H} = Q_{CH}{}^{H}\rho^{\pi}$$

and taking the value for Q as − 25·67 gauss (the value obtained for the cyclooctatetraenyl anion radical[4]), then the excess electron density of each of the sp^2 carbon atoms



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is 0·12, and that on each sp carbon atom is, by difference, 0·05. If the value of Q is varied between −20 and −30 gauss, the calculation always predicts that the excess electron density is greater on the sp^2 than on the sp carbon atoms.

The electronic spectrum of solutions of **5** have absorption maxima at 344 sh (ε 2100), 398 sh (1000), 409 (1300), 423 (1600), 445 (1800) and 530 nm (2900), the extinction coefficients again being minimal values. Examination of an NMR sample in THF-d_8 at this stage of reduction showed no signals for **4** or **5**, but relatively unchanged signals for the residual THF protons, which indicates that **4** and **5** are also in rapid equilibrium.

Further reduction of the solution of **4** with a potassium mirror with intermittent shaking at *ca* 0° for 30 mins gave the dianion **6**. The electronic spectrum of the solution has absorption maxima at 307 (ε 30,700) and 432 nm (4100), the extinction coefficients again being based on complete conversion of **4**. The simplicity of the electronic spectrum of the dianion compared to that of the anion radical is to be expected on theoretical grounds.[13]

Attempts to prepare samples of the dianion **6** at suitable NMR concentrations by this method were unsuccessful, as rapid polymerisation occurred and a black precipitate formed. However reduction with sodium-potassium alloy in THF-d_8 at *ca* 0°

proceeded smoothly, and a single sharp resonance signal at τ 3·26 was observed for the protons of **6**. An attempt to quench this solution with dilute hydrochloric acid gave **4** (10% yield) as the sole isolable product.

The NMR spectra of the dianions **3** and **6** clearly indicate that these are diatropic systems. The inner proton H^3 of **3** is shielded by the induced diamagnetic ring current and appears at τ 16·88, whereas the estimated position of the inner proton in **1**, which is deshielded by the induced paramagnetic ring current, is *ca* τ −7·5.[14] The chemical shift difference of the outer protons is less dramatic, the outer protons in **3** ranging from τ 2·03–4·01, whereas those in **1** are in the range τ 4·97–5·82. The upfield shift of H^3 is accentuated by the increased electron density in the dianion, which also serves to restrict the down field shift of the outer protons. In the cyclooctatetraenyl dianion the effects of ring current and change in electron density balance,[2] whereas in the present case the ring current effect is greater. Presumably, this difference partially arises from the different magnetic properties of the neutral hydrocarbons (cyclooctatetraene being atropic and **1** paratropic), and partially from the lower electron density of the carbon atoms of **3** compared to those of the cyclooctatetraenyl dianion. The position of the proton resonance in **6** (τ 3·26) is also at lower field than the position of this resonance in **4** (τ 5·58), again demonstrating the change from a paratropic to a diatropic system.

The dianion **3** appears to be in a 'frozen' conformation and no interconversion between the protons H^3 and H^4 is observed up to 30°. This behaviour is in marked contrast to that of the hydrocarbon **1**, which exhibits conformational mobility between H^3 and H^4 down to − 130°.[15] This observation parallels that made with [16]annulene, where it was found that the [16]annulenyl dianion was 'frozen'[5a] whereas the hydrocarbon is configurationally and conformationally mobile.[5b] The barrier height for the interconversion of inner and outer protons in [14]annulene, which is isoelectronic with **3**, was calculated[16] as $\Delta G\ddagger = 10{\cdot}8$ kcal mole^{-1}. Since [14]annulene is conformationally mobile at 30°, the barrier height in **3** must be greater than this, which further supports the general observation that charged systems have energetically more to gain by delocalisation than do neutral molecules.

EXPERIMENTAL

NMR spectra were taken on a Varian HA-100 spectrometer fitted with a variable temperature probe. Peak separations were measured directly from calibrated paper, using the residual peaks of THF-d_8 at τ 6·40 as an internal standard. Electronic spectra were recorded on a Cary-14 spectrophotometer. ESR spectra were taken on a Varian V-4500 spectrometer, and the spectra were calibrated using Fremy's salt, assuming a *g* value of 2·0055.

1,5-Bisdehydro[12]annulene (**1**) and 1,5,9-tridehydro[12]annulene (**4**) were prepared by the method of Wolovsky and Sondheimer.[9] THF and THF-d_8 were dried over K on a vacuum line. All samples were prepared on a vacuum line using essentially the type of apparatus described by Okamura and Katz[17] (without the sinters or break seal side arms). The K mirror was formed by distilling K into the NMR tube from a bulb side-arm. Na-K alloy (1:5)[18] was added from a side-arm under vacuo. The concentrations of the ESR and electronic spectrum samples were *ca* 10^{-4} M, and the concentrations of the NMR samples were *ca* 2×10^{-2} M.

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REFERENCES

[1] Unsaturated Macrocyclic Compounds LXXVI. For part LXXV, see R. M. McQuilkin, P. J. Garratt and F. Sondheimer, *J. Am. Chem. Soc.* **92**, 6682 (1970)

[2] T. J. Katz, *Ibid.* **82**, 3784, 3785 (1960)

[3] For a review, see P. J. Garratt and M. V. Sargent, *Nonbenzenoid Aromatics* Vol 2 (Edited by J. P. Snyder), Chap 4, Interscience, New York (1971)

[4] T. J. Katz and H. L. Strauss, *J. Chem. Phys.* **32**, 1873 (1960); H. L. Strauss, T. J. Katz and G. K. Fraenkel, *J. Am. Chem. Soc.* **85**, 2360 (1963); R. D. Allendoerfer and P. H. Rieger. *Ibid.* **87**, 2336 (1965); F. J. Smentowski and G. R. Stevenson, *Ibid.* **89**, 5120 (1967)

[5] [a] J. F. M. Oth, G. Anthoine, and J.-M. Gilles, *Tetrahedron Letters* 6265 (1968);
[b] J. F. M. Oth and J.-M. Gilles, *Ibid.* 6259 (1968)

[6] See J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.* **88**, 4811 (1966); T. Nakajima and S. Kohida, *Bull. Chem. Soc. Japan* **39**, 804 (1966); F. Baer, H. Kuhn, and W. Regel, *Z. Naturf.* **22a**, 103 (1967); H. C. Longuet-Higgins, *Special Publication* No 21, The Chemical Society London p 109 (1967)

[7] See J. A. Pople, W. G. Schneider and H. J. Bernstein, *High-resolution Nuclear Magnetic Resonance* pp 180, 247. McGraw-Hill, New York (1959)

[8] See T. F. Rutledge, *Acetylenes and Allenes* p 381. Reinhold, New York (1969)

[9] R. Wolovsky and F. Sondheimer, *J. Am. Chem. Soc.* **87**, 5720 (1965)

[10] K. G. Untch and D. C. Wysocki, *Ibid.* **88**, 2608 (1966)

[11] F. Sondheimer, R. Wolovsky, P. J. Garratt and I. C. Calder, *Ibid.* **88**, 2610 (1966)

[12] H. M. McConnell, *J. Chem. Phys.* **24**, 632, 764 (1956); H. M. McConnell and H. H. Dearman, *Ibid* **28**, 51 (1958); H. M. McConnell and D. B. Chestnut, *Ibid.* **28**, 107 (1958)

[13] For an example, see N. S. Hush and J. R. Rowlands, *Mol. Phys.* **6**, 317 (1963)

[14] K. G. Untch and D. C. Wysocki, *J. Am. Chem. Soc.* **89**, 6386 (1967); F. Sondheimer *et al.*, *Special Publication* No. 21, The Chemical Society London, p. 75 (1967)

[15] Unpublished experiments with Dr. J. E. Anderson

[16] I. C. Calder and P. J. Garratt, *J. Chem. Soc.* (B) 660 (1967)

[17] W. H. Okamura and T. J. Katz, *Tetrahedron* **23**, 2491 (1967)

[18] See L. F. Fieser and M. Fieser, *Reagents for Organic Synthesis* pp. 1102–1103, Wiley, New York (1967)