

from 95% ethanol it melted at 120–122 °C [lit.<sup>2a</sup> mp 121–122 °C (for enantiomer<sup>14</sup>)].

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**Registry No.** 2, 35903-48-1; 5, 687-47-8; 6, 86163-00-0; 7, 86163-01-1; 9, 86163-02-2; 2-(2-bromoethyl)-1,3-dioxane, 33884-43-4.

(13) Shriner, R. L.; Fuson, R. C.; Curtin, D. Y. "The Systematic Identification of Organic Compounds"; 5th ed.; Wiley: New York, 1964; p 253.

(14) Haines<sup>3</sup> encountered dimorphism and/or isomerism and reports various melting points. We did not experience this complication.

### The [12]Annulene Anion Radical

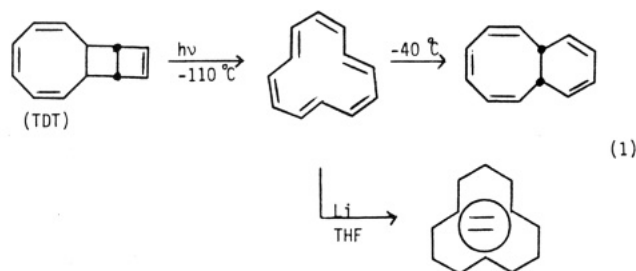
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There has been considerable interest in the addition of a single electron to annulenes that are antiaromatic in the Hückel sense. However, only two such anion radicals (containing  $4n + 1$   $\pi$  electrons) have been generated and observed. Both [8]annulene and [16]annulene readily accept an additional electron from either an alkali metal or an electrode to yield the respective anion radical.<sup>1,2</sup> Here, we report the preparation and ESR observation of the missing annulene anion radical that lies between the anion radicals of [8]annulene and [16]annulene.

Neutral [12]annulene has been observed at low temperature and was prepared via the photoirradiation of *syn*-tricyclo[6.4.0.0<sup>9,12</sup>]dodeca-2,4,6,10-tetraene (TDT) at -110 °C.<sup>3</sup> At -40 °C [12]annulene rearranges irreversibly to its bicyclic tautomer as shown in eq 1.



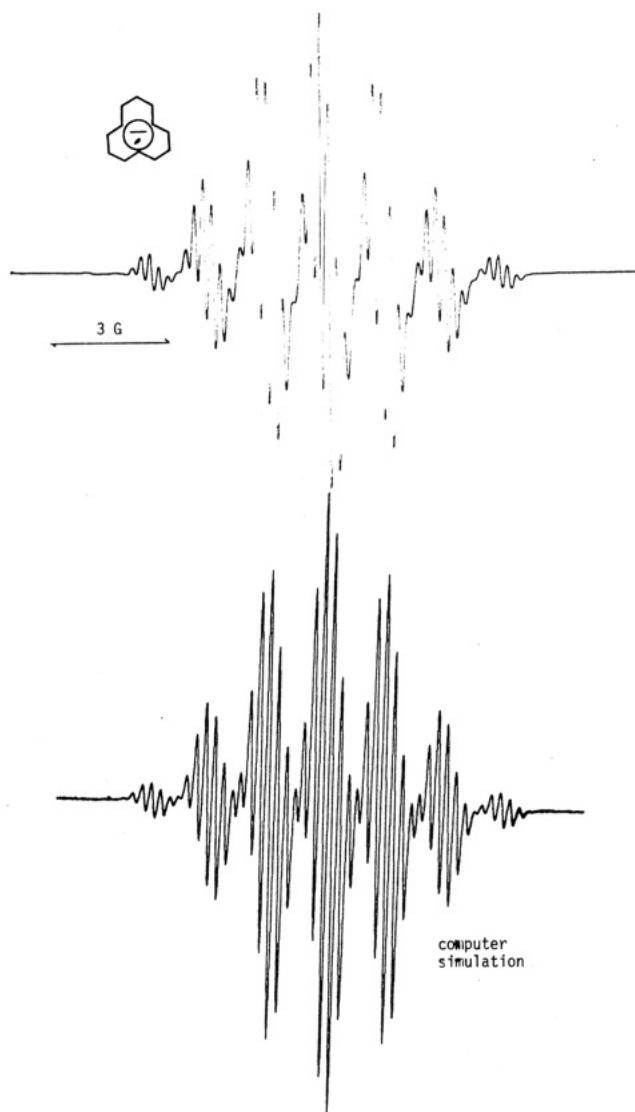
The unstable [12]annulene can be reduced either polarographically or via alkali metal in THF (tetrahydrofuran) to give the [12]annulene dianion (eq 1).<sup>4</sup> This dianion is very stable, and its <sup>1</sup>H NMR signal remains unaltered at temperatures between -90 and +30 °C (NMR signals at 6.98, 6.23, and -4.6 ppm).

(1) (a) Strauss, H. L.; Katz, T. J.; Fraenkel, G. K. *J. Am. Chem. Soc.* 1963, 85, 2360. (b) Katz, T. J.; Fraenkel, G. K. *Ibid.* 1960, 82, 3785. (c) Stevenson, G. R.; Concepcion, J. G. *J. Phys. Chem.* 1972, 76, 2176.

(2) (a) Oth, J. F. M.; Baumann, H.; Gilles, J. M.; Schröder, G. *J. Am. Chem. Soc.* 1972, 94, 3498. (b) Concepcion, J. G.; Vincow, G. *J. Phys. Chem.* 1975, 79, 2037.

(3) Oth, J. F. M.; Rottele, H.; Schröder, G. *Tetrahedron Lett.* 1970, 1, 61.

(4) Oth, J. F. M.; Schröder, G. *J. Chem. Soc. B* 1971, 904.



**Figure 1.** ESR spectrum (upper) of the [12]annulene anion radical recorded at -100 °C. The lower spectrum is a computer simulation generated by using the experimental coupling constants listed in Table I. This spectrum looks very similar to the small picture of the ESR spectrum in ref 4 that was recorded during the generation of the annulene dianion. No mention of the spectrum appears in this paper<sup>4</sup> or in any other to our knowledge. Continued reduction of the solution results in the disappearance of the ESR signal and simultaneous appearance of the NMR spectrum for the [12]annulene dianion. Under high-gain conditions, no further lines can be observed either at lower or higher fields.

### Experimental Section

Samples of TDT dissolved in THF were sealed under vacuum in a 4-mm quartz EPR tube. A potassium mirror was deposited at the top of the tube out of contact with the solution. The frozen solution was irradiated at liquid nitrogen temperature with a high-pressure mercury lamp for 40 h. After each hour of irradiation the solution was allowed to thaw at -100 °C in an acetone slush bath. The sample was then replaced in liquid nitrogen and the irradiation continued. At the end of the irradiation period, the quartz tube was inverted, allowing the [12]annulene solution to come into contact with the potassium mirror at -100 °C. Low-temperature EPR experiments were then carried out on the potassium-reduced solutions with a Varian E-4 EPR spectrometer.

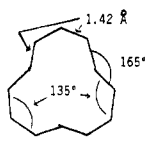
### Results and Discussion

The EPR pattern from the reduction of [12]annulene with potassium metal results from two sets of three equivalent protons with coupling constants of 1.53 and 1.30

Table I. ESR Coupling Constants, INDO-Calculated  $p_z$  Spin Densities, and Resulting Coupling Constants for the Planar [12]Annulene Anion Radical

position	$A_H$ , G (exptl)	$\rho_{p_z}$ (INDO)	$A_H$ (INDO), G ( $Q = -24.5$ G)	$A_H$ (INDO), G ( $Q = -5.3$ G)
1, 5, 9	1.53	0.288	-7.1	-1.53
2, 4, 6, 8, 10, 12	0.225	-0.120	2.94	0.064
2, 7, 11	1.30	0.285	-7.0	-1.51

<sup>a</sup> The bond distances and angles used for this calculation are shown in structure II. The C-H bond distances are 1.08 Å.



II

G and one set of six equivalent protons with a hyperfine splitting of 0.225 G (Figure 1). This spectrum is invariant from -40 to -120 °C, but the sample decomposes irreversibly at warmer temperatures. The spectrum is consistent with the anion radical having the same structure as does the dianion (groups of six, three, and three protons) if the internal protons have one of the larger coupling constants. The surprising fact is that the total spectral line width is only 9.8 G. This is very small compared to those for the anion radicals of [8]annulene (25.7 G) and [16]annulene (38.5 G).<sup>1,2</sup>

This very small  $Q$  value can only mean that the [12]-annulene anion radical is severely distorted from planarity. Distortion from planarity lowers the  $Q$  value due to the fact that in addition to the usual  $\sigma$ - $\pi$  transmission of spin density there is a contribution of the opposite sign to the spin density due to the direct overlap of the hydrogen atoms involved and the  $p$  orbitals centered on the carbon atoms in which the unpaired electron is distributed. A similar effect, but of smaller magnitude, was observed in the case of the methano[10]annulene anion radical.<sup>5</sup> This mechanism is thoroughly discussed by Reddoch and co-workers.<sup>6</sup>

Comparison of the EPR coupling constants predicted by an INDO open-shell calculation to the experimental values shows very good agreement if a small  $Q$  value is utilized in the McConnell relationship ( $A_H = Q\rho$ ; Table I). However, if the INDO-calculated  $p_z$  spin densities are multiplied by -24.5 G (the  $Q$  value predicted in the INDO calculation), all of the calculated  $A_H$ 's are more than 400% too large, and the total spectral width is predicted to be 60 G. The same INDO calculation was carried out on the nonplanar system. The molecule was twisted so that one of the internal protons protruded 0.05 Å above the plane of the ring, one protruded 0.05 Å below the plane of the ring, and the third remained in the plane of the ring. This resulted in a reduction of the predicted spectral line width by 4.4 G. Although the magnitude of this reduction is not nearly large enough, the prediction of a smaller spectral line width with a decrease in the planarity of the ring system supports our conclusion that the [12]annulene anion radical is severely distorted from planarity. The distortion from planarity was intentionally made much smaller in the INDO calculation than that probable in the real anion radical to permit observation of the trend

without requiring major structural changes.

To be sure that the effects described above are structural and not an artifact of ion association, we repeated the experiments with 5% HMPA added to the THF solvent. The addition of hexamethylphosphoramide (HMPA) did not result in EPR spectral changes. The anion radical (I) does not exhibit bond alternation but does have a delocalized 13-electron  $\pi$ -bond system.



I

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**Registry No.** [12]Annulene anion radical, 86257-88-7.

### Stereoselective Preparation of *trans*-2,3-Dideuterioprop-2-en-1-ol

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*cis*-2,3-Dideuterioallyl alcohol (*cis*-2,3-dideuterioprop-2-en-1-ol) may be prepared readily through the methyl propiolate-anthracene Diels-Alder adduct, and the same chemistry will provide *cis*-3-deuterioallyl alcohol.<sup>1,2</sup> *trans*-2,3-Dideuterioallyl alcohol and *trans*-3-deuterioallyl alcohol, however, have not been so accessible. Reduction of methyl propiolate with chromous chloride<sup>3</sup> in deuterium oxide affords a plausible precursor to *trans*-2,3-dideuterioallyl alcohol, methyl *trans*-2,3-dideuterioacrylate, with high stereoselectivity but in extremely low yield.<sup>1,4</sup>

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(6) Reddoch, A. H.; Dodson, C. L.; Paskovich, D. H. *J. Chem. Phys.* 1970, 52, 2318.

(7) The ring proton coupling constants for methano[10]annulene are 2.70 and 0.10 G compared to those of 4.53 and 1.73 G expected for a  $Q$  value of 25 G.<sup>5</sup> The loss of spin density (decrease in  $Q$ ) for this system is comparable to that observed for the [12]annulene anion radical.

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