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AN ESR STUDY OF THE BENZOCYCLOOCTATETRAENE RADICAL ANION

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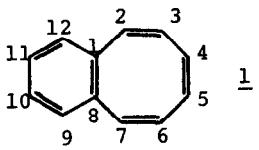
The ability of cyclooctatetraene (COT) to undergo flattening upon reduction to its monoanion or dianion derivatives has been extensively investigated using both chemical[1] and electrochemical[2] reduction techniques. Similar studies have been carried out on the benzo-substituted derivatives 1 and 2 of COT, but in these latter cases the conclusions regarding the geometries of the resulting anions have not always been in agreement. Carrington et al.[3a] in an esr study of the radical anion of sym-dibenzocyclooctatetraene (2) con-



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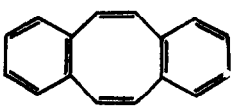

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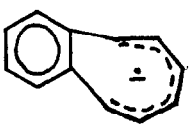

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cluded that this species has a nonplanar geometry consisting of four π-moieties which are only weakly interacting (good agreement between experimental and theoretical spin densities resulted when the latter assumption was made).

Katz et al.[3b] later showed, however, that the magnitudes of the HMO theoretical spin densities calculated for the radical anion of 2 are not sensitive to the type of geometry assumed (e.g. a planar geometry with strongly interacting π-moieties or a highly nonplanar geometry with weakly interacting π-moieties); hence the experimental spin densities can also be considered consistent with a planar geometry for this radical anion. On the basis of additional spec-

troscopic and polarographic evidence, Katz et al.[3b] concluded that the interaction between the π-moieties in the anions of 2 is strong, implying a planar or nearly planar geometry for these species. Anderson and Paquette[3c] have found that both 1 and 2 show only a single one-electron polarographic wave in anhydrous media corresponding to reduction to the radical anion stage; they concluded primarily on the basis of the irreducibility of either of the radical anions of 1 or 2 to their respective dianions under anhydrous conditions that both of these radical anions are probably nonplanar.

Anderson and Paquette[3c] suggest a hypothetical structure 3 for the radical anion of benzocyclooctatetraene (1, BCOT) in which the benzo group is considerably out-of-plane with respect to the remaining "hexatriene" portion of the molecule and the odd electron resides primarily on the approximately planar hexatriene moiety. In the present communication, we wish to report the results of an esr investigation of the BCOT radical anion, providing additional data concerning the geometry of this species.

The BCOT radical anion was generated for esr study by the in situ electrolytic reduction[4] in a flat cell of an $\sim 3 \times 10^{-3}$M solution of BCOT in anhydrous DMSO containing 0.1M Bu_4NClO_4 as supporting electrolyte; the applied potential was gradually increased until a strong esr signal was detected and required a setting of $\sim$ -2.5V. The hyperfine esr spectrum is shown in Figure 1; analysis of the esr spectrum afforded the following sets of hfsc: 3.68(2H), 3.11(2H), 1.89(4H), and 0.44G(2H). The experimental spectrum could be simulated satisfactorily using the above hfsc and assuming a Lorentzian linewidth of 0.20G. The experimental spin densities (assumed positive) shown in Chart 1 were calculated using the McConnell equation[5] with Q^H_{CH} = -23G. The assignment of the experimental spin densities to the specific positions as shown in Chart 1 has been based upon the results of HMO and McLachlan[6] calculations (vide infra), and thus should be regarded as being somewhat tentative; in particular, the assignments indicated for the smaller spin densities could conceivably be reversed from the true ones.

HMO and McLachlan calculations were carried out on the BCOT radical anion

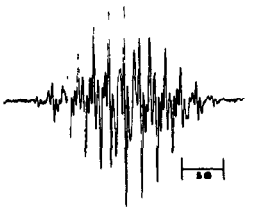

Figure 1. ESR spectrum of the BCOT Radical Anion

Chart 1

β'		Position				
		2,7	3,6	4,5	9,12	10,11
1.0	H	.152	.088	.121	.034	.046
	McL	.183	.072	.123	.016	.042
.75	H	.183	.075	.131	.022	.037
	McL	.236	.034	.128	.005	.036
.50	H	.217	.064	.145	.011	.025
	McL	.294	-.001	.138	.000	.025
.25	H	.253	.056	.164	.003	.009
	McL	.351	-.030	.154	-.001	.009
0.0	H	.272	.054	.175	.000	.000
	McL	.380	-.043	.163	.000	.000
	Exp	.160	.082	.135	.019	.082

Positions numbered as shown in Structure 1. H = Huckel spin density, McL = McLachlan spin density, Exp = experimental spin density calculated using McConnell equation.

for a planar geometry and then for geometries of the type represented by 3 in which the relative amount of interaction between the benzo and hexatriene moieties is varied. This was done within the HMO framework by assuming that the π-electrons occupy Huckel molecular orbitals and that the resonance integrals between p orbitals on atoms 1 and 2 and atoms 7 and 8 are equal to β', while all other resonance integrals between adjacent atomic orbitals are equal to the normal β. The value of β' was then varied between 0 (nonplanar case, no interaction between the benzo and hexatriene moieties) and β (planar case). The Huckel and McLachlan spin densities calculated in this manner for differing values of β' are given in Chart 1.

In contrast to the radical anion of 2, the magnitudes of the HMO and McLachlan theoretical spin densities for the BCOT radical anion are sensitive to the value of β' used and hence to the relative degree of planarity of the radical anion. The magnitude of the spin density at positions 2 and 7 is particularly sensitive to the value of β'. If the BCOT radical anion has the structure 3 with the benzo and hexatriene moieties noninteracting (β' = 0), one would expect the odd electron to occupy the lowest antibonding mo of the hexatriene moiety and result in a large spin density appearing at positions 2 and 7. Using the calculated Huckel spin density of .272 and the McConnell equation with Q^{H}_{CH} = -23G, one would expect the esr spectrum to exhibit a large hfsc having a magnitude of ∿ 6.2G. Since the largest experimental hfsc (3.68G) is much smaller in

magnitude than 6.2G, the esr spectral data rules out a structure of type 3 for the BCOT radical anion in which the benzo and hexatriene moieties are noninteracting or weakly interacting ($\beta' = 0$ or .25).

In fact, of all cases shown in Chart 1, the experimental spin densities are in best agreement with the theoretical ones for the case of the planar or nearly planar BCOT radical anion ($\beta' = 1.$ or .75). In these cases the Huckel spin densities do not differ significantly from the McLachlan spin densities and they are both in good agreement with the experimental spin densities. In addition to comparing the theoretical spin densities directly with the experimental ones, one can also compare the ratios of the theoretical spin densities at the various positions (relative, for instance, to the spin densities at positions 2 and 7 which are largest) to the corresponding ratios of the experimental spin densities. When this is done, it is likewise found that best agreement between theoretical and experimental ratios of spin densities occurs when a planar or nearly planar geometry is assumed ($\beta' = 1.$ or .75). Thus the esr spectral evidence as interpreted above indicates that the BCOT radical anion is best viewed as having a planar or nearly planar structure with strongly interacting π-moieties.

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