color was observed. The color of the dianion was dark red prior to masking by the blue hue of the solvated electrons. The solution was allowed to reflux for 45 min. Methanol (5 ml) was added and the ammonia was allowed to evaporate. Water (20 ml) was added and the mixture was extracted with ether (3 × 40 ml). The combined organic layers were washed with water (2 × 50 ml) and saturated brine (50 ml), dried, and evaporated. There was obtained 170 mg (82.5%) of oily **21**. Purification of this material by preparative scale vpc at 150° (5 ft column packed with 5% SF-96 on Chromosorb G) gave **21** as a low melting white solid; $\lambda_{max}^{C_2H_5OH}$ 260 nm (ϵ 5200); $\delta_{TMS}^{CDCl_3}$ 7.19 (br s, 4, aryl), 6.68 (d, $|J|$ = 9.0 Hz, 1, vinyl), 5.73 (d, $|J|$ = 9.0 Hz, 1, vinyl), 3.43 (s, 3, -OCH_3), and 2.87 (m, 4, methylenes).

Anal. Cacld for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 76.94; H, 7.04; N, 7.45.

1,2,5,6-Tetrahydro-4-methoxy-3-benzazocine (23). To a suspension of 200 mg (1.45 mmol) of trimethyloxonium fluoroborate in 25 ml of dry methylene chloride was added 129 mg (0.74 mmol) of 1-aza-5,6-benzcyclooctanone (**22**).[29] The suspension was allowed to stir at 0° for 5 hr and the resulting solution was rendered alkaline by the addition of sodium bicarbonate solution. The layers were separated and the aqueous phase was extracted with ether. The combined organic layers were dried and evaporated to give **23** as an oil; $\delta_{TMS}^{CDCl_3}$ 7.07 (s, 4, aryl), 3.80 (t, $|J|$ = 6.5 Hz, 2, -$CH_2N<$), 2.53-3.30 (m, 4, methylenes), and 3.34 (s, 3, methoxyl).

Conversion of **23** to its perchlorate salt afforded white crystals, mp 137-138°.

Anal. Calcd for $C_{12}H_{16}ClNO_5$: C, 49.75; H, 5.57; N, 4.83. Found: C, 49.67; H, 5.61; N, 4.75.

Chemical Reduction of 6. A 207 mg (1.12 mmol) sample of **6** was reduced in a manner paralleling that described for **5**. Potassium was gradually added until the dark red-orange color of the anion was displaced by the permanent dark blue of solvated electrons. Processing furnished 160 mg (77.4%) of **25** as an oil. Similar purification of this material by preparative vpc gave **25** as a crystalline white solid, mp 55-56°; $\lambda_{max}^{C_2H_5OH}$ 240 (ϵ 3800), 273 sh (1600), and 278 sh nm (1300); $\delta_{TMS}^{CDCl_3}$ 6.74-7.38 (m, 4, aryl), 5.26-6.20 (m, 4, vinyl), 3.31 (s, 3, -OCH_3), 3.20 (d, $|J|$ = 5.5 Hz, 2), and 2.68 (d, $|J|$ = 5.5 Hz, 2). Double resonance studies at 100 MHz have confirmed the structural assignment.

Anal. Calcd for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 77.03; H, 7.08; N, 7.68.

Acknowledgment. This work was supported by grants from the National Institutes of Health (GM-14853) and Eli Lilly and Co. (L. A. P.) and in part by a grant from the Petroleum Research Fund (L. B. A.).

---

(29) N. S. Hjelte and T. Agback, *Acta Chem. Scand.*, **18**, 191 (1964).

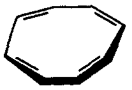
Electrochemical Investigation of Benzo- and *sym*-Dibenzocyclooctatetraenes

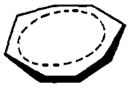
Larry B. Anderson* and Leo A. Paquette

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received August 11, 1971*

Abstract: Polarographic reduction of benzocyclooctatetraene (**4**) and *sym*-dibenzocyclooctatetraene (**5**) has been found to lead only to the respective radical anions in *anhydrous* tetrahydrofuran containing 0.1 *M* tetra-*n*-butylammonium perchlorate (TBAP). The *single* one-electron wave in each instance exhibits nernstian characteristics. The overall reversibility of these reductions was confirmed by cyclic voltammetry. The introduction of small quantities of water into the cell eventuates in rapid protonation and further reduction of the radical anions; spurious polarographic waves are then encountered due to the reduction of mono- or dihydro derivatives. When lithium ions are added to these solutions, there does *not* appear to be further reduction of the hydrocarbon radical anions. Donation of an electron to the π systems of **4** and **5** is believed to result in placement of that electron into an antibonding orbital of the puckered ring. For reasons which are discussed, the Hückel delocalization energy of the planar anion radical is insufficient to overcome the energy needed to flatten the molecule and planarity is not attained. It is remarkable that even the additional 0.8 to 1.0 eV available to the radical anions does not cause dianion formation. These results are utilized to rectify several misinterpretations which have been perpetuated in the literature over the years.

Electron diffraction[1,2] and X-ray crystallographic studies[3] have unequivocally established that cyclooctatetraene (COT) and its simple mono- and disubstituted derivatives exist in the D_{2d} tub conformation having alternate single and double bonds. Such molecules are recognized to be capable of two dynamic processes, namely, ring inversion and bond shift. Anet and coworkers[4] have suggested that the transition states for these two processes could be represented by structures **1** and **2**, respectively. Whereas planar ring **1** has unequal bond lengths and unequal resonance integrals (β) between contiguous carbon–carbon p orbitals, **2** possesses equal bond lengths and equal resonance integrals between all adjacent carbon atoms of the ring. Several reports[5] have dealt with theoretical estimates of the difference in energy between these two structures; these range from 0.02 to 1.8 kcal/mol in favor of **1**. Recent nmr studies[6] of cyclooctatetraenyldimethylcarbinol and 2-methylcyclooctatetraenylmethyl *l*-*O*-methylmandelate, have revealed the difference in bar-


1


2

---

(1) O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, **27**, 1311 (1957).

(2) M. Tratteberg, *Acta Chem. Scand.*, **20**, 1724 (1966).

(3) D. P. Shoemaker, H. Kindler, W. G. Sly, and R. C. Srivastava, *J. Amer. Chem. Soc.*, **87**, 482 (1965); D. P. Wright, K. Seff, and D. P. Shoemaker, *Acta Crystallogr., Sect. A*, **16**, 58 (1963).

(4) (a) F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *J. Amer. Chem. Soc.*, **86**, 3576 (1964); (b) F. A. L. Anet, *ibid.*, **84**, 671 (1962); (c) see also T. J. Katz, M. Yoshida, and L. C. Siew, *ibid.*, **87**, 4516 (1965).

(5) L. C. Snyder, *J. Phys. Chem.*, **66**, 2299 (1962); C. A. Coulson and W. T. Dixon, *Tetrahedron*, **17**, 215 (1962); N. L. Allinger, M. A. Miller, L. W. Chow, R. A. Ford, and J. C. Graham, *J. Amer. Chem. Soc.*, **87**, 3430 (1965).

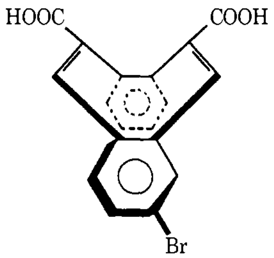
(6) L. A. Bock, Ph.D. Thesis, UCLA, 1969.

riers to bond shift and ring inversion to be approximately 2.5 kcal/mol. Since this value presumably reflects directly the difference in energy between **1** and **2**, some experimental support for the hypothesis that **1** is more stable than **2** is presently available.

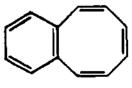
In view of the reported[4] small barrier to ring inversion in cyclic polyenes such as cyclooctatetraenyldimethylcarbinol ($\Delta H^{\ddagger} = 15.4$ kcal/mol; $\Delta S^{\ddagger} = -6.3$ eu), the failure realized in attempted resolutions of monosubstituted cyclooctatetraenes[7] is not unexpected.

Chemical and electrochemical reduction studies[8,9] also indicate that the COT ring system can undergo flattening on reduction.

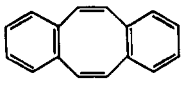
In striking contrast to the behavior of simple COT derivatives, the *sym*-dibenzocyclooctatetraene **3** has been successfully resolved.[10,11] The liberated acid was stable to inversion in solution at room temperature for at least 8 weeks without loss of optical activity. At higher temperatures (120–140°), racemization occurs, and the barrier to ring inversion in **3** has been estimated to be 27 kcal/mol.[10] The effect of the two fused benzene rings in **3** in reducing the capability of the eight-membered ring for conformational inversion is clearly apparent. However, the demonstrated potential barrier could originate from several possible sources and to gain some insight into this question we have now examined the electrochemical reduction of benzocyclooctatetraene (BCOT, **4**) and *sym*-dibenzocyclooctatetraene (DBCOT, **5**). The present paper describes the remarkable electrochemical behavior of BCOT and DBCOT.



3



4



5

Results

Polarography in THF Solvent. In the aprotic solvent tetrahydrofuran (THF) containing 0.2 *M* TBAP background electrolyte, DBCOT (**5**) is reduced in a single nernstian step to the radical anion. A *single* polarographic wave is observed with a half-wave potential of −2.29 V *vs.* sce, as shown in Figure 1. A plot of log $[i/(i_d - i)]$ *vs.* E is a straight line with a reciprocal slope of 56 mV, indicating nernstian behavior with an n value of 1.0. No evidence of further reduction of the radical anion is observed, and the polarogram maintains a steady limiting current until discharge of solvent at *ca.* −3.1 V.

Analysis of the polarographic wave height demonstrates convincingly that the reduction process involves only one electron per molecule (see Table I). The diffusion current constant indicates a diffusion coefficient of *ca.* 1.6×10^{-5} cm^2 sec^{-1}, which is a typical value expected for a conjugated polyene in THF.[9b]

Table I. Polarographic Diffusion Current Constants and Half-Wave Potentials[a]

Polyene	Concn, m*M*	$E_{1/2}$ V *vs.* sce	I[b]	n_{app}[c]
COT	0.534	−2.11	307	1
		−2.27	275	1
DBCOT (**5**)	0.615	−2.29	370	1
BCOT (**4**)	0.380	−2.13	346	1

[a] In THF solvent, 0.1 *M* in TBAP. [b] Diffusion current constant, μA mM^{-1} gm$^{-2/3}$ sec$^{1/2}$. [c] Taken as nearest integral number, $n = I(n_{\text{COT}}/I_{\text{COT}})$.

The polarographic behavior of BCOT (**4**) (Figure 2) closely parallels that of DBCOT. A single one-electron wave is observed at −2.13 V and no further reduction of the radical anion occurs before discharge of solvent. However, a small wave, involving less than one electron per molecule of **4**, appears at *ca.* −2.8 V in this instance. This wave was found to be due to reduction of the product arising from protonation of the radical anion by reactive proton donors (probably the tetrabutylammonium ion of a background electrolyte[12a]) present in the system. Such a mechanism involving electron transfer, chemical reaction, electron transfer (ECE) processes is not unexpected and was verified by addition of small increments of the active proton donor, water, to both **4** and **5** (see below). In the case of **4**, the wave in question was seen to increase proportionally in height as the concentration level of water increased.

The overall reversibility of the one-electron reduction of BCOT was verified by cyclic voltammetry (CV) (Figure 2 inset). The CV behavior shows no evidence for merger of two separate waves due to nonnernstian electron transfer. While peak (and half-peak) potentials of CV in Figure 2 will be shifted to positive potentials by the coupled protonation reaction,[12b] this shift should only amount to a few millivolts. Addition of 50 μM water to the solutions of BCOT (see Table II) resulted in a 10-mV shift of the polarographic half-wave potential while increasing the height of both waves by approximately 50%. The stoichiometry of this enhancement indicates that the addition of small amounts of water has a catalytic effect on anion protonation in this system, and also allows an estimate of the half-wave potential for BCOT in the absence of coupled chemical reactions to be near −2.14 V.

Effects of the Addition of Water. When water is introduced into the dry THF solutions of the cyclooctatetraenes of interest, one additional wave appears in

---

(7) A. C. Cope and M. R. Kinter, *J. Amer. Chem. Soc.*, **73**, 3424 (1951); A. C. Cope, M. Burg, and S. W. Fenton, *ibid.*, **74**, 173 (1952); A. C. Cope and D. F. Rugen, *ibid.*, **75**, 3215 (1953); A. C. Cope and J. E. Meili, *ibid.*, **89**, 1883 (1967).

(8) (a) T. J. Katz, W. H. Reinmuth, and D. E. Smith, *ibid.*, **84**, 802 (1962); (b) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *ibid.*, **85**, 2360 (1963); (c) R. D. Allendoerfer and P. H. Rieger, *ibid.*, **87**, 2336 (1965); and references cited in these papers.

(9) (a) L. A. Paquette, J. F. Hansen, T. Kakihana, and L. B. Anderson, *Tetrahedron Lett.*, 533 (1970); (b) L. B. Anderson, J. F. Hansen, T. Kakihana, and L. A. Paquette, *J. Amer. Chem. Soc.*, **93**, 161 (1971); (c) L. A. Paquette, J. F. Hansen, and T. Kakihana, *ibid.*, **93**, 168 (1971).

(10) K. Mislow and H. D. Perlmutter, *ibid.*, **84**, 3591 (1962).

(11) It is important to call attention to the fact that for cyclooctatetraene derivatives having one or more groups other than hydrogen on the ring, the ring inverted forms can be enantiomers of each other, depending on the number and position of substituents.

(12) (a) D. L. Thielen and L. B. Anderson, *J. Amer. Chem. Soc.*, **94**, 2521 (1972); (b) R. S. Nicholson and J. Shain, *Anal. Chem.*, **36**, 706 (1964).

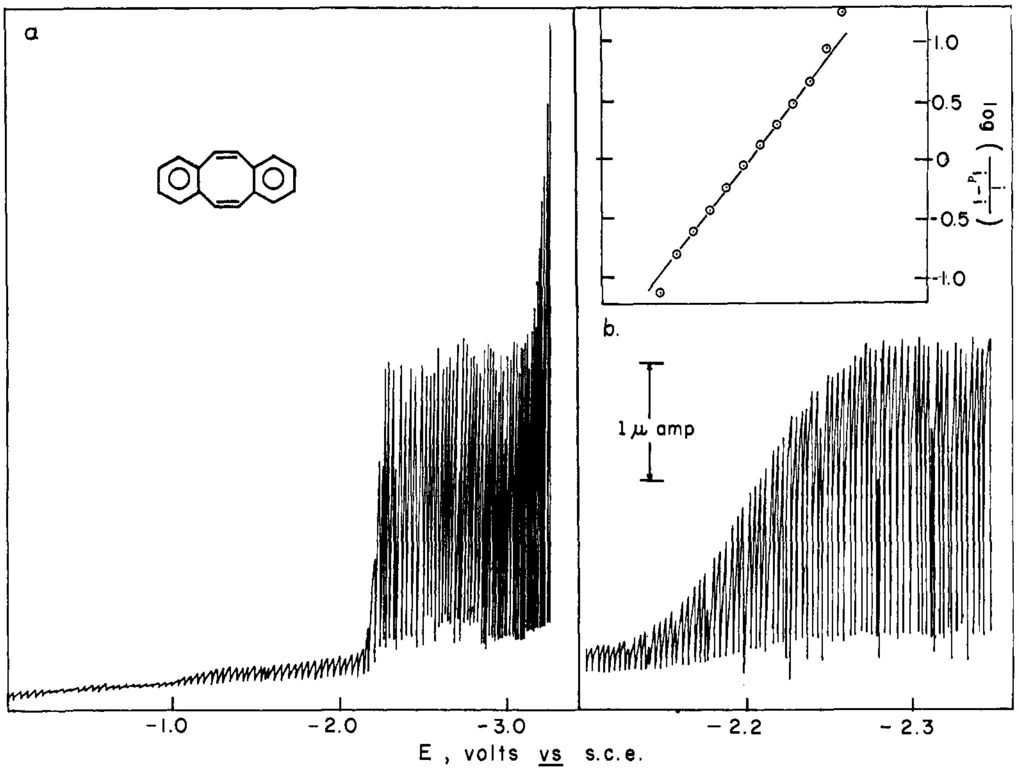


Figure 1. Polarography of 6.2 × 10^{-4} *M* DBCOT in anhydrous THF, 0.2 *M* TBAP. (a) Complete scan of negative potential region; (b) polarographic wave on expanded potential scale with inset showing log plot of the current data.

Table II. Polarographic Characteristics of COT, **4**, and **5** in the Presence and Absence of Water

Polyene concn, m*M*	H_2O concn, *M*	$E_{1/2}$[a] for waves 1	2	i_d[b] for waves 1	2
DBCOT (**5**)					
0.62		−2.29		1.99	
0.60	1.0	−2.24	−2.56	2.28	1.97
BCOT (**4**)					
0.38		−2.13	−2.95	1.09	0.35
0.38	0.5 × 10^{-4}	−2.12	−2.95	1.54	0.54
0.38	8.5 × 10^{-2}	−2.09	−2.87	1.5	1.2
COT					
		−1.97		0.49	
0.145		−2.15[c,d]	−2.67	0.26	0.34
		−1.97		0.57	
0.145	36.4 × 10^{-4}		−2.66		0.62
		−2.14[c]		0.26	

[a] Volts *vs.* sce. [b] Current in microamps. [c] Two one-electron waves; current quoted is for the sum of the two waves. [d] Background electrolyte 0.2 *M* TBAHFP.

each instance. A fourth wave is observed for COT (due to 1,3,6-cyclooctatriene) at very high (>0.1 *M*) water concentrations, but this wave is negligible in solutions containing millimolar water. Table II summarizes the polarographic characteristics of these new waves. In the COT example, the third wave has previously been identified as the reduction of the protonation product, 1,3,5-cyclooctatriene (**6**).[8d] By analogy, the additional wave observed with **5** is assigned to reduction of derived protonated anion radicals.

Effect of Addition to Alkali Metal Ions. Alkali metal ions are known to form ion pairs with hydrocarbon anions and dianions. Estimates have been advanced[13] that dianion–alkali metal ion pairs are two orders of magnitude stronger than analogous monoanion pairs. Addition of lithium chloride to THF solutions containing BCOT and 0.2 *M* TBAHFP affects the half-wave potential of the BCOT wave only slightly. Two new waves appear (see Table III) at −0.34 and −2.44 V *vs.* sce, and these may be attributed to anodic dissolution

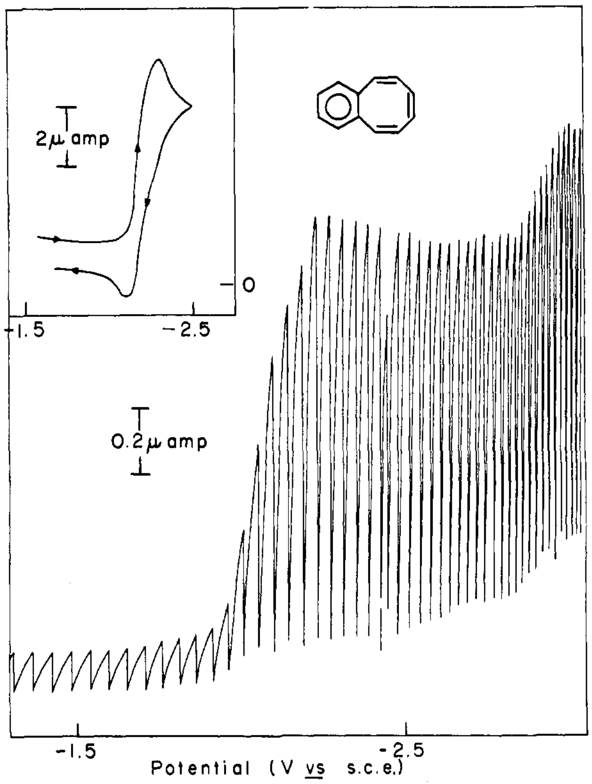


Figure 2. Polarography of 3.4 × 10^{-4} *M* BCOT in THF, 0.2 *M* TBAP. Inset shows cyclic voltammetry of 3 × 10^{-4} *M* BCOT; scan rate, 50 mV/sec.

---

(13) C. N. R. Rao, V. Kalyanaraman, and M. V. George, *Appl. Spectrosc. Rev.*, 3, 164 (1970).

Table III. Polarography of BCOT in the Presence of Lithium Chloride

Depolarizer concn, m*M*	$E_{1/2}$[a] for waves 1	2	3	i_d[b] for waves 1	2	3
BCOT, 0.31		−2.09			1.35	
BCOT, 0.31 LiCl, 6	−0.34	−2.09	−2.44	−5.4	1.2	6.0

[a] In volts *vs.* sce. [b] Current in microamps.

of mercury to form Hg_2Cl_2 and reduction of Li^+ ion, respectively. No additional hydrocarbon reduction waves were observed and there was no enhancement of the limiting current of the BCOT wave subsequent to addition of LiCl. The overall height of the two cathodic waves was stoichiometric with reduction of the hydrocarbon to the radical anion and of lithium ion to the amalgam.

Discussion

Reduction Mechanism. The electrochemical behavior of benzo-fused cyclooctatetraenes **4** and **5** differs in a fundamental way from that reported previously.[4c] BCOT and DBCOT reduce only as far as the radical anion stage in the range of potentials accessible to the polarographic technique in water-free THF solvent.

The benzo-fused derivatives **4** and **5** give rise to a single one-electron process in aprotic solvent, *e.g.*, eq 1.

$$\mathrm{BCOT} + e^- \overset{E^{\circ} \sim -2.2\,\mathrm{V}}{\rightleftharpoons} \mathrm{BCOT}\cdot^- \tag{1}$$

Upon addition of water (as a source of protons), the height of the hydrocarbon reduction wave is enhanced, and a second wave appears at potentials anticipated for reduction of the diprotonated product, most likely by the sequences in eq 2 and 3. A similar situation obtains in the corresponding reduction and protonation of DBCOT. The apparently catalytic nature of these protonation reactions when water is the donor is less well understood and thus not included in the simplified scheme above. It is possible that the hydroxide ion produced in reaction 2 rapidly removes a proton from solvent or background electrolyte thereby regenerating water for reaction with the anionic organic species. In any case, it is obvious that extreme care must be employed in removing water completely from organic solvents such as tetrahydrofuran (where water activity is reportedly higher at a given concentration than in, say, DMF)[14] if valid results are to be obtained.

$$\begin{gathered}\mathrm{BCOT}\cdot^- + H_2O \longrightarrow \mathrm{HBCOT}\cdot + OH^- \\ \mathrm{HBCOT}\cdot + e^- \overset{E^{\circ} > -2.2\,\mathrm{V}}{\rightleftharpoons} \mathrm{HBCOT}^- \end{gathered}\tag{2}$$

$$\begin{gathered}\mathrm{HBCOT}^- + H_2O \longrightarrow \mathrm{H_2BCOT} + OH^- \\ \mathrm{H_2BCOT} + e^- \overset{E^{\circ} \sim -3.0\,\mathrm{V}}{\rightleftharpoons} \mathrm{H_2BCOT}\cdot^- \end{gathered}\tag{3}$$

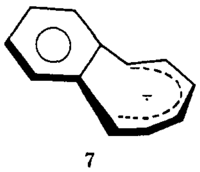
The effects observed upon addition of lithium ion are entirely consistent with radical anion production and ion-pair formation of this species with the alkali metal cation. No evidence has been gained for enhancement of the reduction wave by further reduction of the ion-paired hydrocarbon radical anion.

Anion Conformation. The electrochemical activity of BCOT and DBCOT is limited to a single one-electron reduction wave in the accessible region of potential (−0.5 to −3.1 V *vs.* sce). As indicated by studies of optical activities,[10] the radical anions of **4** and **5** must experience considerable opposition to attainment of a planar conformation. Earlier correlations between the calculated and observed epr proton hyperfine coupling constants for the DBCOT radical anion[15] have led to the conclusion that there is relatively weak conjugation across the bonds connecting the four unsaturated fragments. This is consistent with the present demonstration of the irreducibility of either of the benzo-fused radical anion species and supports the proposal that these radical anions are nonplanar.

The presence of one or more fused benzene rings will certainly minimize (but to an ill-defined extent) π-electron delocalization in the planar conformation. Also, the added structural rigidity introduced by the aromatic rings will ensure increased opposition to the enforcement of the cyclic eight-membered carbon framework into a flattened arrangement. The combination of minimization of delocalization and opposition to bond angle distortion quite probably adds to coulombic repulsion causing **4** and **5** to be unable to aromatize. It seems rather unlikely that the barrier to ring flattening is significantly steric in origin. Although nonbonded interaction of carboxyl groups and benzene hydrogens in **3** is likely contributing to the destabilization of the planar configuration, repulsions between adjacent hydrogens in **4** and **5** should be no greater than in COT.

A secondary indication that the one-electron addition product of the benzo-fused derivatives is substantially nonplanar is that the reductions appear to be nernstian. The extremely small value of the heterogeneous electron transfer rate constant for COT has been rationalized[8c,16] in terms of the activation free energy for achieving a transition state for the electron transfer that is substantially different from the tub conformation of COT. If such an analysis has validity, then the substantially nernstian behavior of the benzo-fused congeners indicates that no extensive conformational change accompanies electron transfer in these hydrocarbons. This interpretation is also consistent with the contrasting conclusions reached on spectroscopic grounds for the conformation of the radical anions of DBCOT[15] and COT.[17]

Assuming that the observed irreducibility of the BCOT and DBCOT radical anions implies puckered configurations for both, their reversible half-wave potentials (−2.14 and −2.29 V, respectively) indicate a greater degree of conjugation between the unsaturated centers in BCOT. A hypothetical structure such as **7** would allow substantially reduced bond angle strain at carbons 1 and 2 compared to a planar eight-membered ring, and would still permit conjugation among the three double bonds consequently isolated from the aromatic



7

---

[14] C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Non-Aqueous Systems," Marcel Dekker, New York, N. Y., 1970, p 31 ff.

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

[16] B. J. Huebert and D. E. Smith, *J. Electroanal. Chem.*, **31**, 333 (1971).

[17] P. I. Kimmel and H. L. Strauss, *J. Phys. Chem.*, **72**, 2813 (1968).

benzo group. Such a seemingly favorable configuration is not energetically favorable for DBCOT. This is consistent with the relative ease of reduction of the two compounds.

Chemical evidence indicates that the equilibrium products of alkali metal reduction of BCOT[18] and DBCOT[19] are the respective aromatic dianions. It is thus notable that no further reduction of the radical anions is observable under electrochemical conditions. Any estimate of the expected potential required for addition of a second electron to such benzo-fused cyclooctatetraenes must consider factors such as electron repulsion, electron delocalization in both radical anion and dianion (aromaticity), strain induced by enforcing planarity or near-planarity upon the anion, solvation and complexation of these intermediates, nonnernstian electron transfer, and the like. Each of these factors except the onset of aromatic character will act to make the second wave more negative. Theoretical studies[20] have estimated that the enthalpy of formation of the COT dianion from the radical anion may be as high at 80 kcal/mol. Because the benzo-fused congeners are expected to be similar to COT in most of the respects mentioned above, their obviously increased structural rigidity should be manifest in an even greater enthalpy of formation of the dianion.

Of particular importance, comparison of chemical and electrochemical results must allow for ion pairing with alkali metal ions which greatly stabilizes the dianion products. Such ion pairs may well also undergo disproportionation at significantly different rates from those of uncomplexed radical anions. Assuming that the DBCOT radical anion is nonplanar, an estimate of *ca.* -3.1 V *vs.* sce can be ventured for the $E_{1/2}$ of dianion formation on the basis of previously published figures: electron repulsion, *ca.* -0.4 V; aromaticity gained (same as COT), *ca.* $+0.8$ V;[8c] strain introduced (activation energy for ring inversion), *ca.* -1.2 V. This potential is at the limit of observation in THF solvent. Furthermore, when the large anticipated difference in conformation between radical anion and dianion is considered, the effects of slow electron transfer may well cause the reduction to be still more negative. Thus, it is not impossible that, under equilibrium conditions and in the presence of alkali metal ions, a stable aromatic dianion could exist even though it cannot be produced polarographically.

Because the chemical and electrochemical behavior of COT and its congeners is pivotal to our understanding of aromaticity in alternant hydrocarbons, it is important to place the results of the present work in the perspective of the known behavior of COT and to point out again several misinterpretations of this behavior which continue to be perpetuated in the literature.

(1) *Reactions between hydrocarbon radical anions and proton donors may be extremely rapid, and the chemistry observed in solvents containing even very small protic impurities is not a reliable indication of the chemistry of such reactive intermediates under truly aprotic conditions.* Earlier use of electrochemical solvents containing water (*e.g.*, 96% dioxane) led to incorrect conclusions about the endothermic nature of the COT$\cdot^-$ disproportionation[8a] as well as about the reducibility of the DBCOT radical anion.[4c] Results uncovered during the present study indicate that the presence of water at concentration levels as low as 0.1 ppm in THF will lead to observation of spurious waves due to reduction of protonation products. In addition, other "inert" components of the electrochemical system such as solvent and background electrolyte may act as chemical reactants, particularly in the presence of small quantities of substances such as water that can act as catalytic agents in protonation reactions.

(2) *Disproportionation of the radical anions of COT and each of its hydrocarbon congeners is an endothermic process.* This is not only a conclusion of this work, but has been stated explicitly elsewhere.[8c,15,16] Nevertheless, the erroneous conclusions reached by early workers[8a,b,4c] continue to appear as fact in the recent literature.[20] In fact, evidence is accumulating[12,21] that free dianion species are seldom if ever produced in electrochemical reductions.

Experimental Section

Benzocyclooctatetraene, prepared from the silver(I)-catalyzed benzyne addition to benzene as described in the literature,[22] was purified by recrystallization from aqueous methanol, mp 49–50°. *sym*-Dibenzocyclooctatetraene, synthesized by silver(I)-promoted rearrangement of dibenzotricyclooctadiene,[23] was employed as received from Professor Pettit; colorless crystals, mp 109°.

Electrochemical Measurements. Electrochemical instrumentation used in this work was standard and has been described elsewhere,[9b,24] together with the cells and specific techniques employed for purification of solvents and background electrolytes, and analysis of water concentrations. In addition, an electrochemical instrument constructed in this laboratory,[25] was employed for several of the polarographic and cyclic voltammetric experiments.

Stationary electrode cyclic voltammetry was carried out at a Pt-bead microelectrode ($A = 0.051$ cm^2). The dropping mercury electrode capillary had a mercury flow rate of 0.63 mg/sec at h_{corr} of 400 mm, and the diffusion current constants, I, quoted were computed using this value and the drop time of the capillary measured at a potential near the top of the polarographic wave for each wave reported.

The salt, tetrabutylammonium hexafluorophosphate (TBAHFP), was precipitated from an ethanolic solution of $(n\text{-Bu})_4NI$ by addition of a stoichiometric excess of an aqueous solution of NH_4PF_6. The TBAHFP was then filtered and washed with a dilute aqueous solution of NH_4PF_6 until the effluent did not color on addition of a few drops of $AgNO_3$. The salt was then recrystallized once from ethanol and dried at 110° overnight. Thereafter its storage and use in the vacuum line electrochemical cell were identical with the methods described previously.[24]

All potentials are reported *vs.* the aqueous saturated calomel electrode. Correction was made for uncompensated resistance between the reference luggin capillary and the working electrode in both the polarography and the cyclic voltammetry. This uncompensated resistance was estimated by shift of half-wave potentials of reversibly reduced compounds to be 13 kΩ in the polarographic and 8 kΩ in the cyclic voltammetric experiments. Figures 1 and 2 depict original data and *have not* been corrected for iR drop.

Acknowledgments. This work was supported in part by a grant from the Petroleum Research Fund (L. B. A.) and by grants from the National Institutes of Health (GM-14853) and Eli Lilly and Company (L. A. P.). The authors also wish to express their gratitude to Dr. John R. Malpass and Professor R. Pettit for gifts of hydrocarbons **4** and **5**, respectively.

---

(18) L. A. Paquette and M. J. Broadhurst, unpublished results.

(19) L. B. Anderson and L. A. Paquette, unpublished results.

(20) M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Amer. Chem. Soc.*, **91**, 7521 (1969).

(21) K. W. Bowers, R. W. Giese, J. Grimshaw, H. O. House, N. H. Kolodny, K. Krenberger, and D. K. Roe, *ibid.*, **92**, 2783 (1970).

(22) L. Friedman and D. F. Lindow, *ibid.*, **90**, 2329 (1968).

(23) W. Merk and R. Pettit, *ibid.*, **89**, 4788 (1967).

(24) J. L. Mills, P. Nelson, S. G. Shore, and L. B. Anderson, *Anal. Chem.*, **43**, 157 (1971).

(25) M. L. Rose, Ph.D. Dissertation, Ohio State University, 1970.