

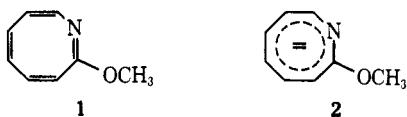
Benzo Annulation Effects on Azocine Reactivity. The Chemical and Polarographic Reduction of Several Mono-, Di-, and Tribenzomethoxyazocines¹

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Abstract: The polarographic reduction, cyclic voltammetry (CV), and alkali metal reduction of two benzomethoxyazocines together with a dibenzo derivative and the lone possible tribenzo homolog have been examined. As expected, the individual capability of each system to accept electrons varies with the extent and position of aromatic annulation. In addition, the method of reduction is seen to be of importance. Extensive comparisons of chemical behavior are made not only between the heterocycles in question, but also with structurally related cyclooctatetraenes.

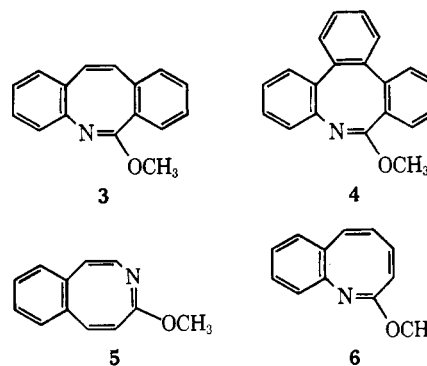
The nonplanar conformations and the decidedly polyolefinic character³ of 2-methoxyazocine (**1**) and several methyl derivatives have been established. Nevertheless, the azocines undergo ready two-electron reduction to form *directly* the related aromatic 10π -electron dianions such as **2**.⁴ Extensive electrochemical



studies have established that the second electron is added at the same potential as the first,⁵ in marked contrast to the behavior of cyclooctatetraene and several of its simple congeners which undergo distinct one-electron reductions.^{5a,6} Thus, the 2-methoxyazocines constitute the first $4n\pi$ -electron molecules which are capable of multielectron addition at the discharge potential. The unique position held by the azocines is presumably the result of a favorable balance between electron repulsion, bond strain, and delocalization energy during the ring flattening process; this combination of effects appears to be significantly less than optimal in the cyclooctatetraene examples.

In order to examine in greater detail the requirements for the attainment of planar, or at least nearly planar, structures for the azocinyl dianions, the reduction of four benzo-fused methoxyazocines (**3–6**) has been studied. This investigation was prompted by our observations that the combined effects of bond strain and benzenoid aromaticity apparently preclude

formation of planar delocalized dianions in the case of two benzo-fused derivatives of cyclooctatetraene under electrochemical conditions.⁷ Both benzocyclooctatetraene and *sym*-dibenzocyclooctatetraene undergo *single* one-electron reduction to the respective anion radicals; no further reduction to the dianions is observed.⁷ The implication here is that energetically demanding electron repulsion and bond strain considerations which must develop in the attainment of a planar conformation are not offset by possible electron delocalization in the flattened eight-membered ring dianions. Significantly, applied potentials 0.8–1.0 V (*ca.* 20 kcal/mol) greater than the $E_{1/2}$ of the first polarographic wave were insufficient to force introduction of a second electron.⁷



At issue, therefore, was a more in depth evaluation of the precise role played by the nitrogen atom in facilitating reduction directly to the corresponding dianions. In **1** and its derivatives, addition of the first electron is believed to be associated with considerable ring flattening, with the result that the radical anion is reduced more readily than the parent azocine.⁵ *A priori*, the varying types and degrees of benzo fusion in **3–6** were expected to have at least a twofold unfavorable effect: (a) minimization of π -electron delocalization (relative to **2**) in the corresponding dianions because of the obvious preoccupation of a number of the 10π electrons with benzenoid aromaticity; and (b) destabilization of the planar anion arrangement due to a

(1) Unsaturated Heterocyclic Systems. LXXXV. For the previous paper in this series, see L. A. Paquette and R. J. Haluska, *J. Amer. Chem. Soc.*, **94**, 534 (1972).

(2) National Cancer Institute Postdoctoral Fellow (No. 6 FO2 CA 45259), 1971–1972.

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(4) (a) L. A. Paquette, J. F. Hansen, and T. Kakihana, *ibid.*, **93**, 168 (1971); (b) L. A. Paquette, T. Kakihana, and J. F. Hansen, *Tetrahedron Lett.*, 529 (1970).

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(6) (a) R. D. Allendoerfer and P. H. Rieger, *J. Amer. Chem. Soc.*, **87**, 2236 (1965); (b) T. J. Katz, W. H. Reinmuth, and D. E. Smith, *ibid.*, **84**, 802 (1962); (c) D. L. Thielen and L. B. Anderson, *ibid.*, **94**, 2521 (1972).

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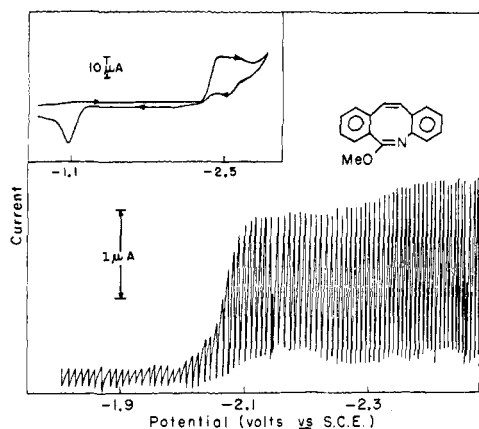
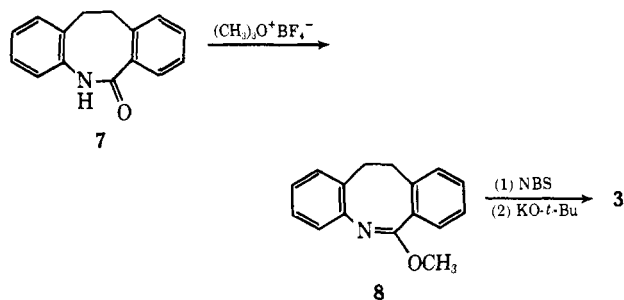


Figure 1. Polarogram of 1.71×10^{-4} M DMBA in THF containing 0.2 M TBAP. Inset shows cyclic voltammetry of same solution at growing Hg drop; scan rate 2.0 V/sec.

lessened capability for bond angle distortion in the central ring and, particularly in **4**, to the presence of nonbonded interactions between proximal benzene hydrogens.⁸⁻¹⁰

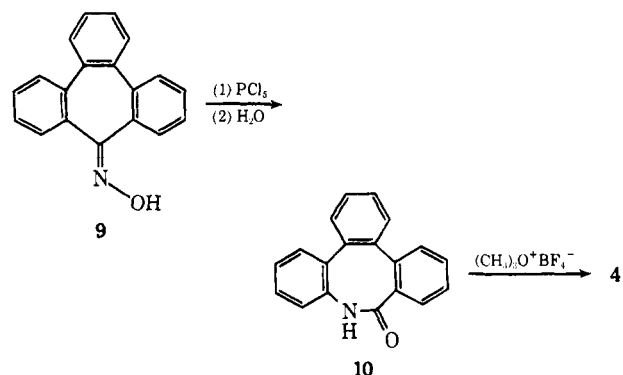
Results

Synthesis. Experiments directed toward the synthesis of **3** began with 6-keto-5,6,11,12-tetrahydrodibenz[*b,f*]azocine (**7**). When treated with trimethyloxonium fluoroborate, **7** was converted to imide **8** in 92.6%



yield. Allylic bromination of **8**, followed by direct dehydrohalogenation with potassium *tert*-butoxide, afforded **3** in 64% overall yield.

6-Methoxytribenz[*b,d,f*]azocine (**4**) was prepared by Beckmann rearrangement of tribenzotropone oxime (**9**) and O-methylation of the lactam thus obtained (**10**)



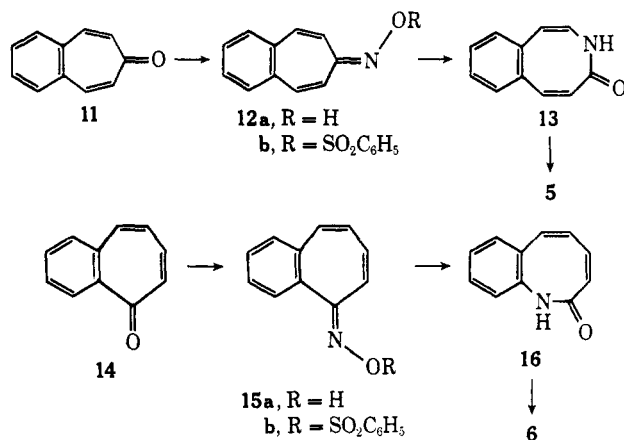
(8) K. Mislow and H. D. Perlmuter, *J. Amer. Chem. Soc.*, **84**, 3591 (1962).

(9) T. J. Katz, M. Yoshida, and L. C. Siew, *ibid.*, **87**, 4516 (1965).

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with Meerwein's reagent. The overall yield from **9** was 58%.

Benzotropones **11** and **14** seemed also to be the logical starting points for the synthesis of **5** and **6**, respectively. Ring expansion to the unsaturated eight-membered ring lactams **13** and **16** was facilitated by preliminary conversion of oximes **12a** and **15a** to their respective benzenesulfonate esters. Solvolysis of **12b** and **15b** in aqueous acetone or dioxane led to **13** and **16**, O-methylation of which led readily to the desired benzomethoxyazocines.



Polarographic Reduction. The polarography of **3** (DBMA) in aprotic tetrahydrofuran solvent (Figure 1) reveals a single nonnernstian wave with a half-wave potential of -2.08 V *vs.* sce. The diffusion current constant, $I = i_d/(C^0 m^{2/3} t^{1/6})$, was measured to be $5.2 \times 10^2 \mu\text{A mM}^{-1} \text{g}^{-2/3} \text{s}^{1/2}$, which clearly indicates transfer of more than one electron. Comparison with the I value measured for cyclooctatetraene⁵ indicates an overall two-electron process. A second fractional electron wave is observed 0.3 V negative of the wave for reduction of **3**. The source of this second wave is as yet uncertain, but several possibilities have been tested (see below).

Cyclic voltammetry of **3**, shown in the inset of Figure 1, indicates that the dianion product is reoxidized -1.2 V positive of the reduction of the neutral heterocycle. This behavior is consistent with previously reported electrochemical behavior of various simple 2-methoxyazocines,⁹ but the difference between half-peak potentials is 0.3 V greater than any value observed heretofore. The pertinent electrochemical results are summarized in Table I.

The compound 6-methoxy-11,12-dihydrodibenz[*b,f*]azocine, H₂DBMA (**8**), serves as an important link in understanding the electrochemistry of the benzo-fused methoxyazocines. Firstly, the possibility existed that **8** is the source of the spurious wave in the reduction of DBMA. Secondly, because the degree of conjugation between the benzene rings in **8** resembles that of some highly hindered stilbene derivatives,¹¹ a valuable point of reference is available. And most importantly, if the various factors alluded to earlier were to preclude the attainment of planarity to the reduction products of **3-6**, then their electrochemistry might well be expected to resemble that of **8** which must necessarily lack additional aromaticity in its negative ions.

(11) R. Dietz and M. E. Peover, *Discuss. Faraday Soc.*, **45**, 154 (1968).

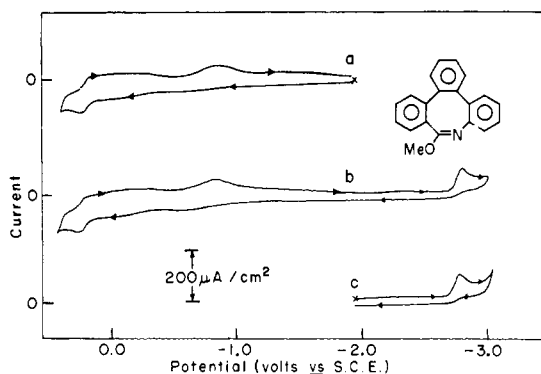


Figure 2. Cyclic voltammetry of $3.35 \times 10^{-5} M$ TBMA (3) at a stationary Pt-bead electrode in dry THF solvent. Background 0.2 M TBAHFP, scan rate, 400 mV/sec; \times indicates initial potential; a, positive going single sweep; b, steady state (free run); c, negative going single sweep.

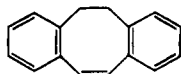
Table I. Electrochemical Data for the Benzo-Fused Methoxyazocines

Polyene	$E_{1/2}$	$I \times 10^{2b}$	Log plot, slope	Apparent n value
Polarography				
DBMA (3)	-2.08	5.2	0.057	2
Postwave	-2.32			<1
H ₂ DBMA (8)	-2.87	3.0	0.050	1
TBMA (4)				
THF	-2.81	6.2	0.049	2
AN		5.5		2
4-BMA (5)	-2.13	3.8-6.0	0.09	1-2
2-BMA (6)	-2.11	2.8-4.4	0.06	1-2
Postwave	-2.31	1.2	0.06	<1
DMMA ^a	-2.28	5.2	0.099	2
Polyene	$E_{p/2,c}$	$E_{p/2,a}$	$E^{0'}$	
Cyclic Voltammetry				
DBMA (3)	-2.42	-1.19	-1.80	
Postwave	-2.3	-2.3	-2.3	
TBMA (4)				
THF	-2.73	None		
AN	-2.5	-2.5	-2.5	
4-BMA (5)	-2.14	-2.1		
2-BMA (6)	-2.14	-1.25	-1.70	
Postwave	-2.3	-2.3	-2.3	
DMMA ^a	-2.43	-1.59	-2.01	

^a DMMA is 3,8-dimethyl-2-methoxyazocine (from ref 4) shown for comparative purposes. ^b Diffusion current constant, $\mu A mM^{-1} g^{-2/3} sec^{1/2}$.

The electrochemical data relating to H₂DBMA are summarized in Table I. This imino ether undergoes a nearly nernstian one-electron reduction, and the half-wave potential (-2.87 V) effectively precludes that this substance is the source of the second wave observed in the reduction of DBMA ($E_{1/2}$ ca. -2.3 V).

Comparison of $E_{1/2}$ for 8 with those reported for the hindered stilbene derivatives¹¹ indicates that H₂DBMA is significantly more difficult to reduce than the hydrocarbon analogs whose $E_{1/2}$ values range from -2.0 to -2.5 V. This suggests that immobilization of the benzene rings by the ethano bridge strongly inhibits electron delocalization through the unsaturated segments of the molecule. This conclusion is supported further by lack of appearance of a reduction wave for 17, a likely product



17

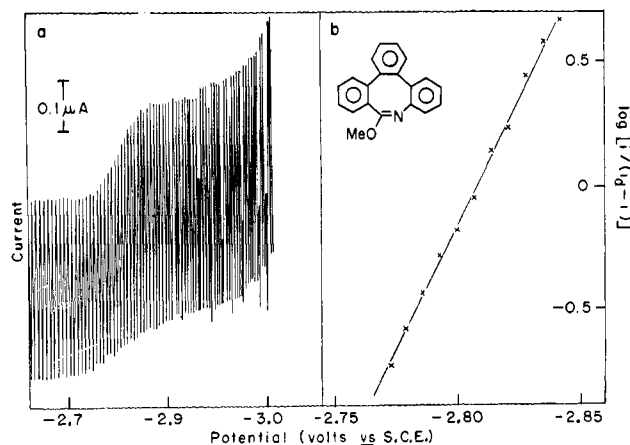


Figure 3. (a) Polarogram of $3.35 \times 10^{-5} M$ TBMA in THF, 0.2 M in TBAHFP; (b) log plot of same data.

of polarographic reduction of dibenzcyclooctatetraene in the presence of proton donors.⁷ These observations render all the more remarkable the fact that the DBMA dianion shows evidence of a very high degree of aromatic stabilization in spite of the obvious costs in bond angle strain. Also worthy of note is the fact that the discharge potential of H₂DBMA (8) is very close to that observed for TBMA (4), but significantly different from those of 5 and 6.

The electrochemical reduction of TBMA is characterized by a single wave at -2.81 V which shows evidence of a second or higher order chemical reaction following electron transfer (see below). In the anodic region, there appears a wave, $E_{1/2}$ ca. +0.3 V, corresponding to one-electron oxidation of the neutral azocine. The cyclic voltammograms shown in Figure 2 qualitatively depict these two electrode processes. A typical polarogram of TBMA is illustrated in Figure 3. The diffusion current constant has a value of 5×10^2 which is indicative of an overall two-electron transfer process.¹² The unusual characteristic of the TBMA reduction is that the half-wave potential shows a clear dependence on concentration and drop time (Table II). This be-

Table II. Half-Wave Potential Dependence of TBMA (5) on Concentration and Drop Time, t_1

C^0a	$\ln C^0t_1$	$E_{1/2}b$
1.76	1.55	-2.844
1.76	1.84	-2.839
1.76	2.16	-2.823
3.35	2.47	-2.809
11.7	3.47	-2.799

^a Concentration in $mM \times 10^3$. ^b V vs. sce.

havior is diagnostic of second- or higher-order chemical reaction following electron transfer.¹³ Firm chemical evidence is presently lacking, but two possible reactions are (a) radical anion-radical anion coupling, and (b) radical anion-parent coupling, followed in either case by additional reduction processes. Others¹⁴ have observed similar spontaneous reactions of radical anion

(12) J. Heyrovsky and J. Kuta, "Polarography," Academic Press, New York, N. Y., 1966, p 98.

(13) Reference 12, p 397.

(14) R. Dietz and M. E. Peover, *Disc. Faraday Soc.*, **45**, 160 (1968).

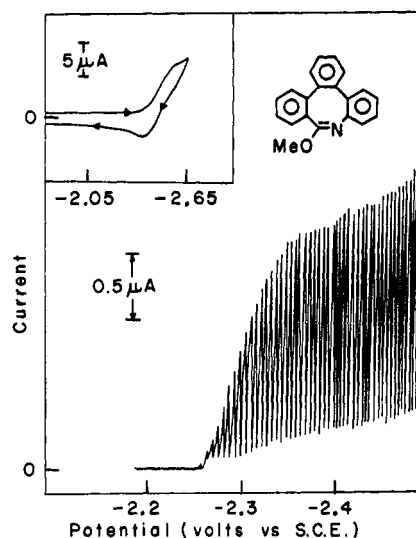


Figure 4. Polarography of $5 \times 10^{-4} M$ TBMA in AN solvent, background electrolyte $0.2 M$ TBAP. Inset shows CV at the dropping mercury electrode, scan rate $20 V/sec$.

products. In any case, the product of this chemical process is not reoxidizable anywhere in the region from $+1.0$ to $-2.8 V$. No additional wave is observed in the anodic scan of the cyclic voltammogram in THF.

This following chemical reaction appears to be somewhat slower in acetonitrile (AN) solvent. Figure 4 shows the polarogram of TBMA in acetonitrile together with the cyclic voltammogram at a growing mercury drop. A small wave is observed on the anodic scan with a peak potential comparable to that of the reduction process. Presumption that this reoxidizable material is the radical anion product of TBMA reduction is consistent with the known reversible behavior of organic parent-anion radical couples in aprotic solvents and the slightly smaller diffusion current constant in AN (which also has a lower viscosity than THF). Further progress in understanding this electrode reaction must await fast reaction studies on the metastable TBMA reduction product.

Significantly, therefore, TBMA does not undergo two-electron reduction directly to a stable dianion which has characterized the electrochemistry of all other methoxyazocines examined to date. As discussed in the subsequent section, the inability of TBMA to develop planarity in passing to its dianion is also revealed in its erratic behavior on chemical reduction.

Monobenzo derivatives **5** and **6** are also reduced at the DME. A single nonernstian cathodic wave is observed for each with $E_{1/2}$ ca. $-2.1 V$ vs. sce. The overall number of electrons transferred, estimated from the polarographic diffusion current constant, I , varies between one and two electrons. In contrast to DBMA and the methyl-substituted azocines, I values for BMA's showed a distinct increase with increase of depolarizer concentration. This suggests that initial electron transfer to these substances may be followed by a second-order chemical reaction and additional electron transfer. A possible reaction scheme is discussed below.

2-BMA (**6**) also exhibits a small postwave at $-2.3 V$ in a manner very similar to the behavior shown by **3**. Cyclic voltammetry shows this postwave to be nearly

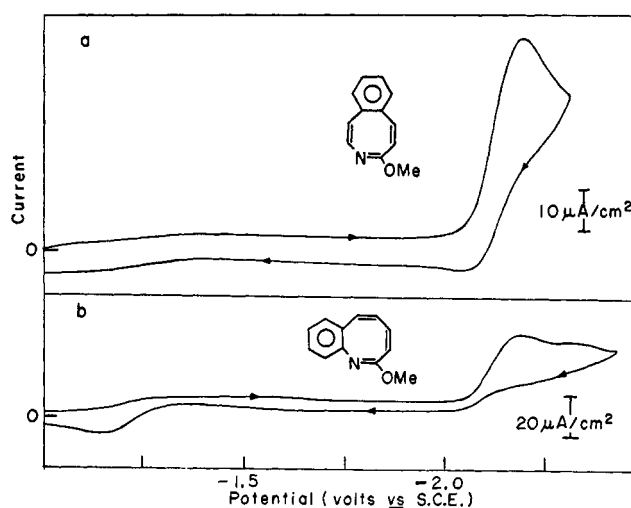


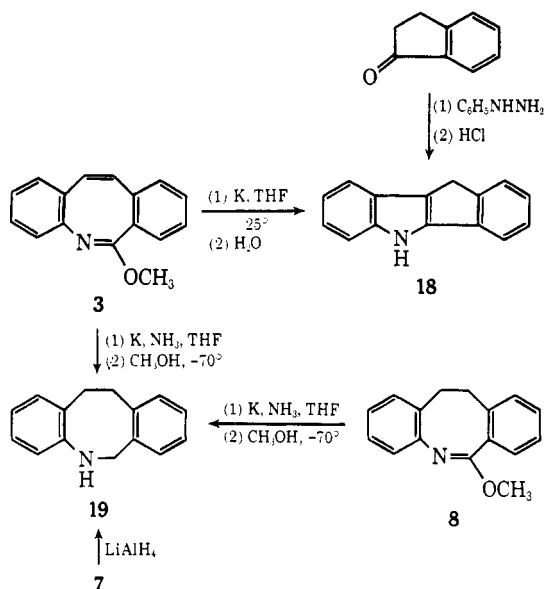
Figure 5. Cyclic voltammetry of monobenzo-fused azocines in THF, $0.2 M$ TBAHFP: (a) $1.6 \times 10^{-4} M$ 4-BMA, scan rate $40 mV/sec$; (b) $1.9 \times 10^{-4} M$ 2-BMA, scan rate $50 mV/sec$.

ernstian and its height to be directly proportional to the initial concentration of heterocycle added. 4-BMA (**5**) shows no postwave. Cyclic voltammetry of 2-BMA at a stationary Pt-bead electrode (Figure 5) clearly shows that the product of initial electron transfer to **6** is not reoxidizable at the reduction potential; rather, reoxidation occurs some $0.9 V$ positive as observed previously in the electrochemistry of other azocines.⁵ This is interpreted to mean that **6** reduces to its highly stable and aromatic dianion which can be reoxidized only by application of a considerable anodic overpotential. The concentration dependence of I is tentatively construed as an indication that this reduction occurs *via* an intermediate (perhaps the radical anion) which is subject to further rapid reduction (or disproportionation) to the dianion. However, no positive evidence has been gained in the cyclic voltammetry of **6** for any electroactive intermediate.

In contrast, 4-BMA behaves quite differently. The cyclic voltammetry of this azocine (Figure 5a) resembles more closely the reduction of TBMA. A small anodic wave appears at virtually the same potential as the reduction wave, and no other anodic wave is observed at more positive potentials. Apparently, 4-BMA reduces to the radical anion which then decays rapidly to one or more electroinactive products. The different slopes of the polarographic log plots associated with **5** and **6** (Table I) point to mechanistic differences in the reduction of the two heterocycles. The slope for **5** (0.09) is suggestive of a nonernstian one-electron transfer.

Chemical Reduction. When a solution of DBMA (**3**) in anhydrous tetrahydrofuran was stirred at room temperature with excess potassium metal, a deep magenta suspension was produced. Treatment of this suspension with water afforded in 75% isolated yield a product which has been identified by independent synthesis as 5,10-dihydroindeno[1,2-*b*]indole (**18**). A small amount of second product was also noted after quenching, but its isolation has been complicated by its inherent instability. In another reaction, an excess of potassium in liquid ammonia-ether (5:1) cooled to -70° was used to reduce **3**. Under these conditions, an intense purple mixture was formed. Quenching with

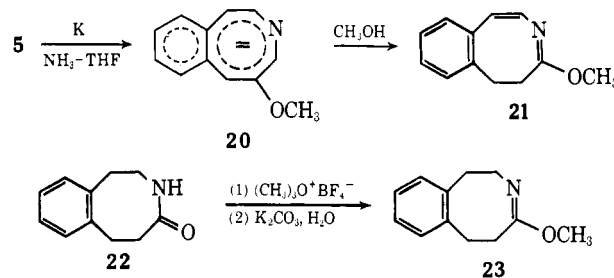
methanol at this temperature afforded amine **19** in 65% yield. The same tetrahydrodibenzazocine has been produced by similar reduction of **8** and by exposure of lactam **7** to the action of lithium aluminum hydride.



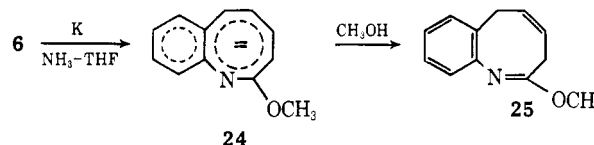
It would appear therefore that the dianion of **3** is rather reactive. In the vicinity of 25°, it is capable of transannular cyclization with attendant loss of methanol. In the -70° region, however, this pathway does not compete. Rather, overreduction is seen, a property which the simpler nonaryl fused methoxyazocinyl dianions do not share.⁴

In the presence of potassium chips in anhydrous tetrahydrofuran at 25°, solutions of TBMA (**4**) slowly became yellow, then green, and finally dark green-brown. Quenching and work-up resulted in the isolation of polymeric products. The attempted reduction of **4** with 2 equiv of potassium in liquid ammonia-tetrahydrofuran (5:1) at -40° led to the formation of a dark blue-green mixture; upon addition of methanol, the color changed initially to red-brown and then became intensely green. Upon evaporation, a dark brown color materialized and again the product was intractable. In both instances, the inability of **4** to consume all of the reducing agent (2 equiv) was in evidence.

The alkali metal reductions of monobenzomethoxyazocines **5** and **6** most closely parallel the behavior of the parent systems. Thus, when solutions of **5** in $\text{NH}_3\text{-THF}$ (5:1) were treated with potassium at -40° and subsequently quenched by addition of methanol, dihydro derivative **21** was the only substance produced (vpc analysis). The structure of **21** follows from its electronic spectrum in 95% ethanol which exhibits a lone maximum at 260 nm (ϵ 5200) and from the nmr chemical shift data (CDCl_3): a broadened aryl singlet (4 H) at δ 7.19, vinyl proton doublets ($|J| = 9.0$ Hz) at 6.68 and 5.73 (1 H each), a methoxyl singlet at 3.43, and a four-proton multiplet centered at 2.87. In particular, the presence of vinyl absorptions at δ 6.68 and 5.73 is uniquely characteristic of the $-\text{CH}=\text{CH}-\text{N}=\text{C}(\text{OCH}_3)-$ chromophore;⁴ also, as confirmed by the spectral features of **23** (cf. Experimental Section), the methylene pattern centered at δ 2.87 identifies C_5 and C_6 as the sites of protonation.



Imino ether **6** underwent similar two-electron chemical reduction to afford **25** as the lone dihydro product



(vpc analysis). This substance displays the expected magnetic nonequivalence of the two methylene groups as broadened doublets centered at *ca.* δ 3.20 and 2.68, and an extensively coupled vinyl pattern ($W_{1/2} = 45$ Hz, 2 H). The ultraviolet spectrum in 95% ethanol has a maximum at 240 nm (ϵ 3800) in addition to two shoulders at 273 (1600) and 278 nm (1300), thereby attesting to the absence of a styrene moiety. Both **21** and **25** are stable to gas chromatographic conditions and could be readily purified by this technique.

Discussion

Comparison of the above data with our earlier reduction studies of 2-methoxyazocines^{4,5} dramatizes the importance of the following factors on the observed chemical reactivities: (1) electron delocalization in the conjugate dianions is significantly affected by the extent of benzo fusion to the eight-membered ring; (2) substitution of nitrogen for a carbon moiety in such systems efficiently stabilizes the dianion relative to the radical anion at the discharge potential; (3) structural features of steric or conformational origin which inhibit attainment of planarity apparently decrease the disproportionation rate relative to the rates of alternative processes; and (4) solvation factors and the presence of alkali metal ions may exert a profound influence on the particular system under investigation.

Benzomethoxyazocines. The electrochemical reduction mechanism for **5** and **6** proceeds by the initial transfer of one electron to form the respective radical anions as revealed by diffusion current constants at low depolarizer concentrations. In addition, 4-BMA (**5**) exhibited a reoxidation peak near the reduction potential at moderately rapid scan rates. Interestingly, the near identical $E_{1/2}$ values for **5** and **6** suggest that comparable energy changes accompany the addition of an electron to the lowest lying molecular orbital of each of these azocines. However, because of the nonernstian nature of the 2-BMA electron transfer, this last conclusion must be considered tentative in this instance.

Following addition of the first electron, **5** and **6** behave quite differently albeit both undergo additional reduction at the potential of the first wave. *A priori*, there exist several reaction paths for removal of the initial radical anion product. If a planar conformation can be readily achieved by the heterocyclic ring, dispro-

portionation may result; alternatively, a second electron may be added at the same potential as the first. While dianion formation is expected to be highly exothermic for these benzo-fused species, the energy barrier to attainment of planarity may be substantial due to steric energy requirements. In this eventuality, the radical anion could enjoy a lifetime sufficiently long to undergo one of several alternative reactions, *e.g.*, protonation, skeletal rearrangement, polymerization, etc. Examples of each reaction type have been observed in the chemistry of the azocines.

The radical anion of 4-BMA at 0.16 mM appears to have a lifetime (cycle time through the wave for $i_{p,r}/i_{p,t} = 0.5$) of about 10 sec. The polarographic log plot slope of 0.09 is consistent with a nonnernstian electron transfer involving one electron in the rate-determining step. No anodic peaks are observed in the CV except the reoxidation of the anion radical at -2.1 V. This behavior closely parallels that observed for benzocyclooctatetraene,⁷ except that the diffusion current constant for 4-BMA is strongly concentration dependent. This suggests that 4-BMA undergoes further reduction after an intermediate second-order chemical reaction. Alkali metal reduction of **5** has elucidated that the dianion is stable in liquid ammonia in the presence of strongly ion-pairing potassium ions. In tetrahydrofuran containing a tetra-*n*-butylammonium salt at room temperature, the data show that the dianion is not formed or, if formed, is subject to rapid secondary reactions. In view of electrochemical evidence for dianion formation in related azocines, we are presently inclined to believe that chemical reactions other than disproportionation compete successfully for the radical anion in this instance, thereby precluding its passage to the doubly charged species.

Appearance of the fractional-electron second wave in the polarogram of 2-BMA (**6**) denotes the presence of a second reducible species. Analytical data, as well as several electrochemical checks (discussed below under DBMA), are presented as evidence that this postwave is not due to reduction of contaminating species. Although combined experimental evidence does not allow definitive characterization of this species, the similarity in half-wave potential of the postwaves for 2-BMA and DBMA can be employed to implicate structural similarity of these intermediates.¹⁵ Notwithstanding the lack of structural information on this entity, its formation and chemical behavior must be consistent with the electrochemical behavior of the wave. As the concentration of 2-BMA was increased from 5×10^{-5} to 2×10^{-4} M the ratio i_d/C^0 decreased from 1.2 to $0.9 \mu\text{A mM}^{-1}$. In addition, the ratio $i_d/h^{1/2}$ showed a slight decrease from 10.7 to $9.5 \times 10^{-3} \mu\text{A cm}^{-1/2}$ on increasing the mercury column height, h , from 220 to 478 mm. Both ratios should be constant for a diffusion-controlled polarographic wave. These effects are small but consistent with kinetic control of the limiting current in the postwave step. The data are inconsistent with reduction of adsorbed 2-BMA which, in contrast, should ex-

hibit direct dependence of i_d on h ($i_d/h^{1/2}$ would increase).

The fate of the radical anion of **6** may be most concisely, albeit tentatively, viewed as the result of competing chemical reactions to produce in part the azocinyl dianion (the anodic wave for which is observed in the cyclic voltammogram at -1.3 V) and a second product¹⁵ which is reduced and reoxidized reversibly in the region of -2.3 V.

The much greater energy of solvation of liquid ammonia and the possibility of strong dianion-alkali metal ion pairing¹⁶ allows for ready reduction of both **5** and **6** to their doubly charged aromatic counterparts in this medium at -30° . Under these conditions, side reactions, if any, are reduced to an undetectable minimum. Also, no skeletal rearrangements are seen. The sole formation of **21** from **5** reveals that protonation of dianion **20** at C₃-C₄ is overwhelmingly preferred on a kinetic basis. Clearly, C₃-C₆ protonation, the pathway most commonly followed by the parent azocines,⁴ cannot be operative in this instance. The exclusivity of this reaction mode in the case of dianion **24** (from **6**) clearly attests that the already strong kinetic preference for initial protonation of azocinyl dianions at C₆⁴ is further enhanced when this ring position is also benzylic. Additionally, ultimate protonation of the intermediate monoanion from **24** does not appear to be influenced by thermodynamic considerations.

Dibenzomethoxyazocine 3. The electrochemical behavior of DBMA parallels that of 2-BMA discussed above. Specifically, reduction of DBMA is likewise followed by competing chemical reactions, *viz.*, disproportionation and a process leading to a reducible product. The possibility of sample contamination was again considered and removed from consideration. Significantly, the magnitude of the postwave (Figure 1) was electrochemically equivalent to at least a 20% concentration level relative to **3**. Furthermore, H₂DBMA (**8**), the most likely impurity or primary protonation product, is not reduced until *ca.* -2.9 V.

The chemically generated dibenzomethoxyazocinyl dianion exhibits an interesting reactivity dependence on temperature. When kept at -70° in liquid ammonia solution, this anion remains monocyclic. In unique fashion, however, it is subject to overreduction when excess potassium metal is present. At 25° , transannular cyclization is evidenced. A similar capability for transannular bonding has also been noted in the case of the 3,4:5,6-dibenzocyclononatetraenyl anion.¹⁷ The only discernible basis for the high propensity of this dianion for disruption of its aromatic delocalization would appear to be minimization of π -electron delocalization resulting from the rather high level of benzo fusion.

Tribenzomethoxyazocine 4. Azocine **4** is sterically incapable of attaining a planar or nearly planar conformation. As a result, it does not resemble its congeners in chemical reactivity. Translated into the experimental terms of this investigation, **4** is seen to undergo approximate one-electron reduction with subsequent polymerization, even under conditions of substantial solvation and ion pairing.

(15) The transannular cyclization product **18** was isolated from room temperature reduction of DBMA. Both 2-BMA and DBMA share the common structural feature of benzo fusion at C₇-C₈ of the azocine ring. Accordingly, analogous structural rearrangements may be operative in the two cases. Unfortunately, it has not been possible to obtain results from the reaction of 2-BMA with potassium in THF at 25° because of the very low reactivity of this azocine under these conditions.

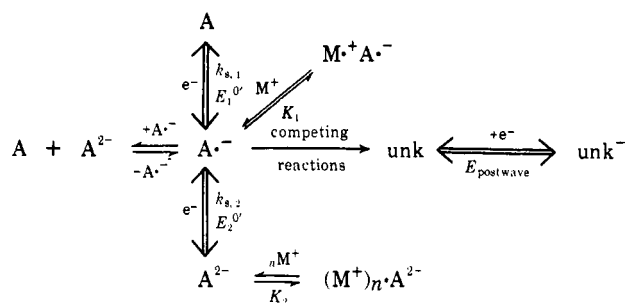
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Summary

Combination of the present results with those previously reported for the chemical and electrochemical reduction of 2-methoxyazocines provides for the pathways in Scheme 1 which summarizes the behavior of

Scheme 1



this heterocyclic system. Radical anion stability is the factor of critical importance in the electrochemical reductions. The radical anions derived from the simple 2-methoxyazocines display an instability to further reduction at the discharge potential of the neutral heterocycle with the result that a highly irreversible two-electron transfer is observed. As mentioned earlier,⁵ lack of knowledge of the anion radical concentration at the electrode surface precludes positive assignment of the individual values for either the standard potentials or the first-order heterogeneous rate constants for the first and second electron transfers, $E_{1'}^{0'}$ and $E_{2'}^{0'}$, or $k_{s,1}$ and $k_{s,2}$, respectively. Any one of the following situations could account for the observed separation between the reduction and oxidation waves: (1) $E_{2'}^{0'} > E_{1'}^{0'}$ (i.e., more positive), (2) $k_{s,1} \sim k_{s,2} \ll 10^{-3} \text{ cm sec}^{-1}$, or where (3) $E_{1'}^{0'} > E_{2'}^{0'}$ and $k_{s,1} \ll 10^{-3} \text{ cm sec}^{-1}$.^{18a} Because no separate one-electron transfers are observed in the systems to which these remarks apply, we are uncertain whether it is appropriate to refer to the electrode kinetics in terms of first-order heterogeneous rate constants, $k_{s,1}$ and $k_{s,2}$. The rate constants so calculated⁵ then may not be directly comparable to the $k_{s,1}$ of $2 \times 10^{-3} \text{ cm sec}^{-1}$ reported for cyclooctatetraene.^{18b} At this time, therefore, we prefer to view the drastic effect on electron transfer rate, of substitution of a nitrogen for a C-H moiety, simply as a result of a fundamental and incompletely understood difference in reduction mechanism between the azocine and hydrocarbon systems. Evidence is available,¹⁹ for drastic variations of values of $(E_{1'}^{0'} - E_{2'}^{0'})$ for oxidation with relatively minor structural changes in *N,N*-dimethylaminoalkenes. In fact, these alkenes provide two examples of systems wherein the radical species (a cation in this case) apparently undergoes spontaneous disproportionation to the parent and dication.

Experimental Section²⁰

6-Methoxy-11,12-dihydrodibenz[*b,f*]azocine (8). A mixture of 15.61 g (0.07 mol) of lactam 7²¹ and 15.5 g (0.15 mol) of trimethyl-

oxonium fluoroborate in 250 ml of dry methylene chloride was stirred under nitrogen at room temperature. The lactam gradually dissolved and after 2 hr the excess oxonium salt was removed by filtration and the filtrate was shaken vigorously with a solution of 15 g of potassium carbonate in 100 ml of water. The mixture was filtered and the organic layer was dried, filtered, and evaporated. The residue was extracted with 150 ml of hot petroleum ether (bp 60–110°). Concentration of this solution afforded 13.06 g of 8 as tan crystals, sublimation of which at 80° (0.1 mm) gave a white solid, mp 82–84°; $\nu_{\text{max}}^{\text{Nujol}}$ 1665 cm^{-1} ; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.6–7.2 (m, 8, aryl), 3.99 (s, 3, -OCH₃), 3.10 and 2.90 (dd, $J = 12.0$ and 5.0 Hz, 2 each, methylene groups).

Anal. Calcd for C₁₈H₁₅NO: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.20; H, 6.44; N, 5.88.

The residue from the petroleum ether extraction was identified as unreacted 7 (2.5 g). The yield of 8 based on recovered starting material is therefore 92.6%.

6-Methoxydibenz[*b,f*]azocine (3). A mixture of 13.00 g (0.055 mol) of 8, 10.68 g (0.06 mol) of *N*-bromosuccinimide, and 250 mg of benzoyl peroxide in 200 ml of carbon tetrachloride was stirred at reflux for 3 hr, cooled in ice, and filtered. The filtrate was evaporated to yield a viscous red oil which was purified by chromatography on neutral alumina. Elution with benzene and chloroform yielded 12.0 g of clear oil. This oil was dissolved in 100 ml of tetrahydrofuran to which was added 15 g of powdered potassium *tert*-butoxide. After the solution was allowed to stir for 6 hr at room temperature, the solvent was evaporated *in vacuo* and the residue was treated with 75 ml of cold water. The aqueous mixture was extracted with ether (3 × 200 ml) and the combined organic layers were washed with water, dried, filtered, and evaporated. The residue was recrystallized from petroleum ether to yield 8.3 g (64% overall) of a tan solid. A sample was sublimed and again recrystallized to give pure 3 as white prisms, mp 91–93°; $\nu_{\text{max}}^{\text{Nujol}}$ 1680 cm^{-1} ; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.8–7.25 (m, 8, aryl), 6.60 (s, 2, vinyl), and 3.90 (s, 3, -OCH₃).

Anal. Calcd for C₁₆H₁₃NO: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.33; H, 5.73; N, 5.91.

Beckmann Rearrangement of Tribenzotropone Oxime (9). Tribenzotropone, synthesized by the method of Tochtermann,²² was converted to its oxime in the manner outlined by Stiles.²³ A mixture of 1.36 g (5.0 mmol) of 9 and 5.0 g of phosphorus pentachloride in 50 ml of dry ether was stirred for 12 hr at room temperature. The ether was evaporated and the residue was treated with 50 ml of water and heated on a steam bath for 12 hr. Lactam 10 was recovered as a grey powder by filtration of the cooled solution. The yield of crude lactam was 1.31 g (96%), mp 259–264°. Recrystallization from methylene chloride–hexane followed by sublimation (150° (0.1 mm)) gave white crystals, mp 267–269°; $\nu_{\text{max}}^{\text{Nujol}}$ 3120 and 1660 cm^{-1} ; $\delta_{\text{TMS}}^{\text{DMSO-}d_6}$ 9.76 (br, s, 1, >NH) and 6.90–7.60 (m, 12, aryl).

Anal. Calcd for C₁₉H₁₃NO: C, 84.11; H, 4.83; N, 5.16. Found: C, 83.70; H, 4.63; N, 4.93.

6-Methoxytribenz[*b,d,f*]azocine (4). A mixture of 680 mg (2.5 mmol) of 10 and 1.0 g of trimethyloxonium fluoroborate in 20 ml of methylene chloride was stirred overnight under nitrogen at room temperature. The mixture was filtered and the filtrate was treated with an excess of concentrated aqueous potassium carbonate solution at 0°. The methylene chloride layer was decanted and the residual paste was extracted with an additional 25 ml of the same solvent. The combined organic layers were washed with water, dried, and evaporated. The residue was extracted with benzene and 110 mg (16%) of unreacted 10 was recovered by filtration. The benzene filtrate was concentrated to 5 ml and 25 ml of pentane was added. Upon cooling, 420 mg (60%) of white needles, mp 149–152°, was obtained. Sublimation and recrystallization from benzene–pentane gave pure 4 as white crystals, mp 150–152°; $\nu_{\text{max}}^{\text{Nujol}}$ 1670 cm^{-1} ; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.80–7.60 (m, 12, aryl) and 3.82 (s, 3, -OCH₃).

Anal. Calcd for C₂₀H₁₅NO: C, 84.18; H, 5.30; N, 4.91. Found: C, 83.91; H, 5.36; N, 4.78.

4,5-Benzotropone Oxime (12a). To a solution of 680 mg (9.8 mmol) of hydroxylamine hydrochloride in a hot mixture of 15 ml of absolute ethanol and 10 ml of pyridine was added 500 mg (3.12 mmol) of 4,5-benzotropone²⁴ in 10 ml of pyridine and the resulting solution was refluxed for 3 hr. The solution was cooled, the solvent removed under reduced pressure, and the residue recrystallized

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from methanol–water to give 418 mg (60%) of **12a** as yellow crystals, mp 173–175°; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7–7.5 (m, 6) and 6.50 (d, $|J|$ = 12 Hz, 2); m/e 171.

Anal. Calcd for $\text{C}_{11}\text{H}_9\text{NO}$: C, 77.15; H, 5.30; N, 8.21. Found: C, 76.90; H, 5.31; N, 8.18.

4,5-Benzotropone Oxime Benzenesulfonate (12b). A solution of 390 mg (2.28 mmol) of **12a** in 25 ml of pyridine cooled to 0° was treated dropwise with 460 mg (2.60 mmol) of benzenesulfonyl chloride. After the solution was allowed to stir for 30 min at 0° and 60 min at room temperature, it was diluted with ether and filtered. After evaporation of the solvent *in vacuo*, the residue was extracted with a small amount of warm methylene chloride and large amounts of hexane. Purification of this material by elution through silica gel and recrystallization from ethyl acetate–hexane afforded light yellow crystals, mp 138–139°.

Anal. Calcd for $\text{C}_{17}\text{H}_{13}\text{NO}_3\text{S}$: C, 65.67; H, 4.22; N, 4.50. Found: C, 65.45; H, 4.35; N, 4.42.

3-Benzazocin-4(3H)-one (13). A solution of 280 mg of **12b** in 50 ml dioxane–water (1:1) was refluxed for 24 hr with intermittent addition of sodium bicarbonate (total 120 mg) to maintain neutrality. The solvents were removed *in vacuo* and the residue was thoroughly extracted with ether. The combined organic layers were washed with water and 5% sodium bicarbonate solution, and dried. Chromatography on silica gel (elution with benzene–ether, 9:1) furnished 52 mg (50%) of **13** as a white solid, mp 201.5–203°, from methylene chloride–hexane; $\nu_{\text{max}}^{\text{CHCl}_3}$ 1660 and 1655 cm^{-1} ; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.25 (s, 4), and 6.8–7.1 (s, br, >NH), 6.87 (d, $|J|$ = 12.5 Hz, 1), 6.48 (d, $|J|$ = 9.0 Hz, 1), 6.20 (d, $|J|$ = 9.0 Hz, 1), 6.11 (d, $|J|$ = 2.5 Hz, 1).

Anal. Calcd for $\text{C}_{11}\text{H}_9\text{NO}$: C, 77.17; H, 5.30; N, 8.18. Found: C, 76.97; H, 5.34; N, 8.14.

4-Methoxy-3-benzazocine (5). To a suspension of 2.38 g (16.0 mmol) of trimethylxonium fluoroborate in 25 ml of dry methylene chloride was added 12.5 g (14.6 mmol) of **13** and the suspension was stirred at room temperature for 10 hr. The suspension was poured onto a solution of 2.69 g (32.0 mmol) of sodium bicarbonate in 150 ml of water and shaken thoroughly. The organic phase was separated, washed with water, and dried. The imino ether was separated from unreacted lactam by chromatography on silica gel. Pure **5** was obtained as white crystals, mp 76.5–77°, from ether–pentane in the cold; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.14 (m, 4), 6.82 (d, $|J|$ = 11 Hz, 1), 6.67 (d, $|J|$ = 9 Hz, 1), 6.02 (d, $|J|$ = 11 Hz, 1), 5.87 (d, $|J|$ = 9 Hz, 1), and 3.62 (s, 3).

Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{NO}$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.93; H, 6.04; N, 7.46.

1-Benzazocin-2(1H)-one (16). From 12.6 g (0.079 mol) of 2,3-benzotropone (**14**),²⁵ 17.1 g (0.246 mol) of hydroxylamine hydrochloride, 130 ml of absolute ethanol, and 130 ml of pyridine, there was obtained after processing as above 8.0 g (59%) of **15a** as yellow flakes, mp 102–103.5° (lit.²⁶ mp 105.5–106.5°), which were employed without further purification.

The benzenesulfonate of **15a** (**15b**), mp 115–117° (lit.²⁶ mp 116–117°), was solvolyzed in aqueous acetone (reflux 40 hr) to give **16** as white needles, mp 169–170°, from methylene chloride–hexane (lit.²⁶ mp 170.5–171.5°).

2-Methoxy-1-benzazocine (6). To a suspension of 420 mg of trimethylxonium fluoroborate in 15 ml of methylene chloride at room temperature was added 440 mg of **16**. After being allowed to stir at room temperature for 8 hr, the resulting solution was shaken with a solution of 390 mg of sodium bicarbonate in 25 ml of water. The organic phase was separated, washed with water, and dried. After solvent removal, the residual oil was purified by preparative scale vpc on a 6 ft \times 0.25 in. column packed with 10% SF-96 on Chromosorb G at 150°. Benzazocine **6** was a somewhat viscous yellow oil; $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 243 sh (ϵ 7200) and 280 nm (1300); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.90 (m, 4), 6.50 (m, 1), 6.05 (m, 3), and 3.71 (s, 3).

Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{NO}$: C, 77.81; H, 5.99; N, 7.56. Found: C, 78.12; H, 6.11; N, 7.49.

Electrochemical Measurements. Chemicals. The tetrahydrofuran was prepared by predrying over calcium hydride and storing *in vacuo* over sodium–potassium alloy. The supporting electrolyte, tetra-*n*-butylammonium perchlorate (TBAP, Southwestern Analytical, Austin, Tex.), was dried by heating *in vacuo* at 90°. Tetra-*n*-butylammonium hexafluorophosphate was synthesized from ammonium hexafluorophosphate and TBAI and recrystallized once from ethanol. It also was dried *in vacuo* prior to use.

Apparatus. The electrochemical instrumentation, cells, and procedures for achieving measurements under rigorously aprotic conditions have been previously described.²⁷ All measurements were made at ambient laboratory temperature, $23 \pm 1^\circ$. Potentials were measured against a silver wire|0.1 M Ag^+ (THF) reference electrode, but are reported herein *vs.* the aqueous saturated calomel electrode and are not corrected for *iR* drop. The Ag/Ag^+ (0.1 M) reference electrode was measured to be +0.49 V *vs.* sce. From previous work,⁶ the *iR* drop is estimated to be between 1 and 5 mV for the concentrations employed herein; the effect on the potentials is considered to be negligible.

Chemical Reduction of 3. A. In Tetrahydrofuran Solution at Room Temperature. A solution of 118 mg (0.5 mmol) in **3** in 5 ml of anhydrous tetrahydrofuran was stirred under nitrogen with an excess of freshly cut potassium metal. After 60 hr at room temperature, the residual metal was removed and the red mixture was treated with 2 ml of water and extracted with 50 ml of ether. Drying and evaporation of the organic phase gave a residue, recrystallization of which from methylene chloride–carbon tetrachloride yielded 78 mg (75%) of 5,10-dihydroindeno[1,2-*b*]indole (**18**), mp 253–256° dec (lit.²⁸ mp 258°). The product was identical with a sample of **18** prepared by the literature method. Very small quantities of a second product, mp 97–99° (from petroleum ether), could also be isolated; however, insufficient quantities of this material precluded its complete characterization.

B. Dianion Generation in Liquid Ammonia with Low Temperature Quenching. To a stirred solution of **3** (118 mg, 0.5 mmol) in 30 ml of liquid ammonia–ether (5:1) cooled to -70° was added an excess of freshly cut potassium metal. A deep maroon color was produced. The mixture was then subjected to dropwise addition of methanol (1 ml), during which time the solution became yellow. The ammonia was allowed to evaporate and the residue was taken up into ether (50 ml). The extract was washed with water (3×10 ml), dried, and evaporated to give a yellow oil. Recrystallization from benzene–petroleum ether resulted in removal of 51 mg of an unidentified yellowish solid, mp 100–105°. The mother liquor from this procedure afforded 68 mg (65%) of slightly impure **19**, mp 128–131°, identical with the material prepared below.

C. Dianion Generation in Liquid Ammonia with Quenching at Room Temperature. **3** (1 g, 4.5 mmol) in 100 ml of liquid ammonia–tetrahydrofuran (9:1) was treated at -70° with 2 g-atom equivalents of freshly cut potassium metal. After 1 hr, the ammonia was evaporated under nitrogen and the residue was treated with 20 ml of water at room temperature. After the customary work-up, there was isolated 205 mg (22%) of **18** and 760 mg of recovered starting material.

5,6,11,12-Tetrahydrodibenz[*b,f*]azocine (19). A. Reduction of 7. A mixture of 446 mg (2.0 mmol) of **7** and 240 mg of lithium aluminum hydride in 50 ml of anhydrous tetrahydrofuran was stirred at reflux for 5 days. The excess hydride was decomposed by the addition of water and the mixture was extracted with chloroform (2×50 ml). The organic phase was washed with water (25 ml), dried, and evaporated. The residue was extracted with benzene (5 ml), and the extract was applied to a 1×25 cm column of silica gel. Elution with 75 ml of benzene yielded 155 mg (37%) of **19** as white needles, mp 132–133°, from benzene–petroleum ether; $\nu_{\text{max}}^{\text{Nujol}}$ 3250 cm^{-1} ; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.10 (s, 4), 6.42–6.97 (m, 4), 4.34 (s, 2), 3.41 (br, s, 1), and 3.25 (t, $|J|$ = 3.0 Hz, 4).

Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{N}$: C, 86.08; H, 7.22. Found: C, 86.10; H, 7.24.

B. Reduction of 8. A solution of 320 mg (1.35 mmol) of **8** in 50 ml of liquid ammonia–tetrahydrofuran (4:1) at -70° was treated with small freshly cut pieces of potassium metal until the blue color persisted. The cold solution was treated with 5 ml of methanol and the resulting yellow solution was allowed to evaporate and warm to room temperature. The residue was extracted with 75 ml of ether, and the extract was washed with water (3×25 ml), dried, and evaporated. The yellowish wax so obtained was sublimed at 100° (0.5 mm) to afford 185 mg (62%) of **19**. Recrystallization of this material as above gave white needles, mp 132–133°.

Chemical Reduction of 5. A solution of 206 mg (1.11 mmol) of **5** in 3 ml of anhydrous tetrahydrofuran was added in one portion to 27 ml of liquid ammonia which had been freshly distilled from sodium. With stirring at the refluxing ammonia temperature, small slivers of potassium metal were added until a persistent dark blue

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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; $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 260 nm (ϵ 5200); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 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, -OCH₃), and 2.87 (m, 4, methylenes).

Anal. Calcd for C₁₂H₁₃NO: 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; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.07 (s, 4, aryl), 3.80 (t, $|J|$ = 6.5 Hz, 2, -CH₂N<), 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 C₁₂H₁₆ClNO₅: 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°; $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 240 (ϵ 3800), 273 sh (1600), and 278 sh nm (1300); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.74–7.38 (m, 4, aryl), 5.26–6.20 (m, 4, vinyl), 3.31 (s, 3, -OCH₃), 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 C₁₂H₁₃NO: C, 76.97; H, 7.00; N, 7.48. Found: C, 77.03; H, 7.08; N, 7.68.

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Electrochemical Investigation of Benzo- and sym-Dibenzocyclooctatetraenes

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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 studies³ 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 coworkers⁴ 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 reports⁵ 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 studies⁶ of cyclooctatetraenyldimethylcarbinol and 2-methylcyclooctatetraenylmethyl *l*-O-methylmandelate, have revealed the difference in bar-

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