have demonstrated that approximately 20% of *O*-benzhydryl benzophenone oxime formed from *N*-benzhydryl-α,α-diphenylnitrone under conditions of the present stereochemical study is produced via a caged process. This information was obtained from crossover experiments using mixtures of deuterated and undeuterated nitrone.[13] The maximum error in k_3 and k_4 which could result from a highly stereospecific caged process can be estimated. In the limiting case, the caged (or less likely concerted) process could be considered as competing with those in Scheme I and yielding the *O*-benzhydryl oxime with 100% geometric retention. If data used in calculating k_3 and k_4 are corrected for the contribution of this process to rates and stereochemistry of product formation, the revised k_3 and k_4 values are larger by a factor of approximately 2.

(23) K. U. Ingold and S. Brownstein, *J. Am. Chem. Soc.*, **97**, 1817 (1975).

(24) W. H. Wolodarsky and J. K. S. Wan, *Spectrosc. Lett.*, **6**, 429 (1973). See also B. L. Booth, D. J. Edge, R. N. Haszeldine, and R. G. G. Holmes, *J. Chem. Soc., Perkin Trans. 2*, 7 (1977), for a similar observation.

(25) J. W. Bird and D. G. M. Diaper, *Can. J. Chem.*, **47**, 145 (1969).

(26) The resulting hydroxynitroso derivatives previously postulated by Hawthorne and Strahm[27] as intermediates from the silver ion assisted hydrolyses of α-chloronitroso compounds then rapidly decompose to the carbonyl and nitrous oxide.

(27) M. F. Hawthorne and R. D. Strahm, *J. Am. Chem. Soc.*, **79**, 2515 (1957).

(28) The reported[24] isomerization of 7a by trace amounts of ethanol could involve reversible addition of ethanol to the carbon–nitrogen bond.

(29) A previous report[30] indicated that the half-life for the levorotatory sodium salt of cyclohexanone-4-carboxylic acid (oxime primarily un-ionized) was 54 times shorter than that for the same salt in 0.1 N NaOH (oxime largely in the form of its anion). This is one indication that oxime anions may be configurationally more stable than their parent oximes, since the above racemization almost certainly proceeds via isomerization about the carbon–nitrogen double bond. Other qualitative observations bearing on the geometrical stability of oxime anions have been noted.[31]

(30) W. H. Mills and A. M. Bain, *J. Chem. Soc.*, **97**, 1866 (1910).

(31) See, for example, J. Meisenheimer, *Justus Liebigs Ann. Chem.*, **446**, 205 (1926); I. Barnish and C. Hauser, *J. Org. Chem.*, **33**, 1372 (1968); F. L. Scott and R. MacConaill, *Tetrahedron Lett.*, 2993 (1970); H. Rydon, N. Smith, and D. Williams, *J. Chem. Soc.*, 1900 (1957); E. Buehler, *J. Org. Chem.*, **32**, 261 (1967); R. Montgomery and G. Dougherty, *ibid.*, **17**, 823 (1952); S. Ginsburg and I. Wilson, *J. Am. Chem. Soc.*, **79**, 48 (1957); J. Fraser, G. Hedwing, M. Morgan, and H. Powell, *Aust. J. Chem.*, **23**, 1847 (1970); Y. Chow and C. Colon, *J. Org. Chem.*, **33**, 2598 (1968), and references cited therein.

(32) E. J. Grubbs, D. R. Parker, and W. D. Jones, *Tetrahedron Lett.*, 3279 (1973).

(33) Professor W. D. Jones, San Diego State University, private communication.

(34) Melting points are uncorrected. The NMR spectra were obtained on a Varian Model A-60 spectrometer using tetramethylsilane as internal standard. Infrared spectra were obtained on a Perkin-Elmer 621 grating spectrophotometer. Ultraviolet spectra were measured using a Cary Model 14 recording spectrophotometer. Mass spectra were determined on a Hitachi Perkin-Elmer Model RMU-6E spectrometer. Elemental analyses were performed by C. F. Geiger, Ontario, Calif., and by M. H. W. Laboratories, Garden City, Mich.

(35) See A. Hantzsch, *Chem. Ber.*, **23**, 2325 (1890); **24**, 51 (1891); L. Semper and L. Lichtenstadt, *ibid.*, **51**, 928 (1918).

(36) R. F. Rekker and J. U. Veenland, *Recl. Trav. Chim. Pays-Bas*, **76**, 739 (1959).

(37) P. A. S. Smith and J. E. Robertson, *J. Am. Chem. Soc.*, **84**, 1197 (1962).

(38) P. L. Pickard and D. J. Vaughan, *J. Am. Chem. Soc.*, **72**, 5017 (1950).

(39) O. Exner, *Chem. Listy*, **50**, 779 (1956); *Chem. Abstr.*, **50**, 15477*h* (1956).

An Electrochemical Investigation of the Effects of Antiaromaticity and Determination of the Increased Antiaromatic Destabilization of Cyclobutenedione upon Reduction

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Abstract: Electrochemical studies were carried out on a series of cyclic 1,2-diones under nonaqueous conditions. From the reduction potentials and Hückel molecular orbital calculations, the increase in antiaromatic destabilization of cyclobutenedione upon reduction is estimated to be at least 14 kcal/mol. The EPR spectrum of the radical anion of naphtho[*b*]cyclobutadienoquinone is presented. Also, INDO calculations were carried out on several of the diones and the results are consistent with the experimental observations.

Recently there has been considerable interest in small ring compounds possessing four electrons in a π system.[1c,2] Cyclobutadiene is the most studied member of this group of molecules.[1c] There is evidence that the cyclic array of four electrons in a Hückel basis set significantly destabilizes the molecule, and this destabilization is termed antiaromaticity.[1c,2] Owing to the instability of antiaromatic compounds, quantitative estimation of antiaromatic destabilization is difficult and few experimental estimates have been published.[1c] Breslow and co-workers[3] have oxidized hydroquinone anions electrochemically and reported the antiaromatic destabilization of cyclobutadiene to be 15-20 kcal/mol. Recently, Breslow and Sondheimer reported the reduction of some cyclobutenediones.[3]

In this paper we would like to present our attempt to measure the increase in antiaromatic destabilization of cyclobutenedione from the reduction potential of cyclic 1,2-diones (Figure 1). From classical resonance arguments, semidione (II) has increased double bond character between the carbonyl

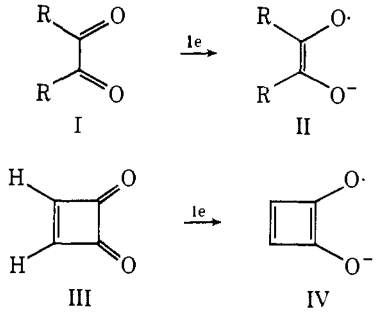


Table I. Polarographic Data for 1,2-Diones[a,e]

Compd	$-E_{1/2}$ (1)[h]	$E_{3/4} - E_{1/4}$[h]	i_d	I_d	$-E_{1/2}$ (2)	$E_{3/4} - E_{1/4}$	i_d	$-E_{1/2}$ (3)	$E_{3/4} - E_{1/4}$	i_d	$-E_{1/2}$ (4)	i_d	$-E_{1/2}$ (5)	i_d
V	0.95	56	1.10	0.79	1.63	65	0.60	2.15	Overlap with 4	0.22	2.4	0.15		
VII	1.74	71	1.57	1.33	>2.75									
VII (in THF)[f]	1.78	73	2.40		2.90									
VIII	1.08	58	3.64	1.42	1.92	115	2.63							
VIII (in AN)[g]	1.19	56	6.9	4.1	*c*		5.9[c]							
IX	0.76	62	4.1	2.2	1.64	58	3.3							
X	0.82	56	3.2	2.1	1.60		0.83	1.78		1.55	2.17	0.85	2.48	1.05
XI	1.25	37	3.00	1.80	1.93	68	3.2							

[a] The solvent was dimethylformamide (DMF) with 0.1 M tetraethylammonium perchlorate (TEAP) as supporting electrolyte; the temperature was 24 ± 1 °C. [b] The small height of this wave made accurate determination of $E_{3/4} - E_{1/4}$ difficult. [c] The current begins rising at −1.85 in a series of three indistinct waves reaching a maximum current of 5.9 μA at −2.5 V. [d] Poorly formed wave. [e] $E_{1/2}$ values are ±10 mV. [f] Tetrahydrofuran (THF) with 0.2 *m* tetrabutylammonium perchlorate as supporting electrolyte. [g] Acetonitrile (AN) with 0.1 *m* TEAP as supporting electrolyte. [h] Units of mV. [i] Units of μA.

Table II. Cyclic Voltammetry of 1,2-Diones[a]

Compd	$-E_{pc}(1)$	$E_{pc} - E_{pa}$, mV	i_{pc}/i_{pa}	$-E_{pc}(2)$	$E_{pc} - E_{pa}$	i_{pc}/i_{pa}	ν, V/s
V	1.01		00				0.1
	1.04	52	0.42				0.5
	1.04	50	0.22				1
	1.06	95	1.04				60
VII	1.82		0				0.05
	1.86		0				0.5
	1.88		0				50
VIII	1.24	65	0.90	1.95	63	0.89	0.3
	1.13	64	0.92	1.98		0	0.2
IX	0.80	65	1.02	1.67	67	0.87	0.05
X	0.86	62	0.93				0.05
	0.87	62	0.94	1.69	90	1	0.30
XI	1.31		0				0.1
	1.30	60	0.93				5.0

[a] In DMF, 0.1 M TEAP, 24 ± 1 °C. [b] In acetonitrile, 0.1 M TEAP.

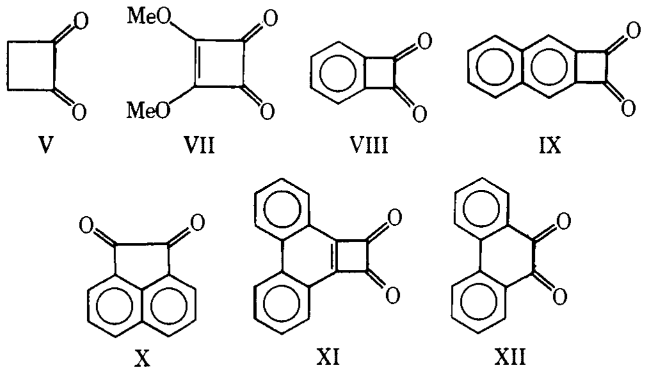
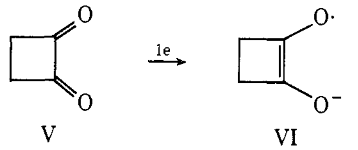


Figure 1. Compounds studied.

carbon atoms relative to the 1,2-dione (I).[4] Thus, reduction of 1,2-cyclobutenedione (III) will lead to a semidione with increased cyclobutadiene character (IV). On the other hand, reduction of 1,2-cyclobutanedione (V) would yield a semidione with no antiaromatic character (VI). The difference in energy required to add an electron to III or V should depend in part on the increased antiaromatic destabilization of IV. This approach, of course, will not provide any direct evidence on the antiaromaticity of cyclobutadiene itself. We wish to report our electrochemical studies of a series of 1,2-diones and the use of this data to make a qualitative estimate of the increased antiaromatic destabilization of cyclobutenediones upon reduction.



Results

Data for the electrochemical reduction of diones V and VII-XI are presented in Tables I and II.

Polarography of compound V is consistent with an electrochemically reversible one-electron reduction of the first wave. Cyclic voltammetry (Table II) shows the radical anion to be only moderately stable. Additionally, adsorption is indicated by the symmetrical shape of the first reduction wave (Figure 2). As the scan rate is increased, the second reduction wave disappears (Figure 2). Concurrently, the effects of adsorption (first wave) decrease until at 60 V/s, the first wave appears well behaved. This behavior suggests that a decomposition product of $V^{-}\cdot$ is the adsorbing species and is reduced at the second wave.[5] A third wave at $E_p = -2.14$ V (100 mV/s) which might be due to reduction of $V^{-}\cdot$ was not investigated. The ratio of anodic to cathodic peak currents of the first wave is consistent with the above electrode mechanism. As most of the electrochemical requirements for an electrochemically reversible reduction are met, the $E_{1/2} = -1.01$ V value for V can be assumed to be close to the true formal potential.[6,7]

The electrochemistry of dione VII is poorly behaved in that at sweep rates up to 50 V/s, no anodic current was detectable by CV. In addition, $E_{3/4} - E_{1/4}$ from polarography is significantly larger than the one-electron reversible value. At 50 V/s, E_{pc} is 60 mV more negative than at 0.05 V/s. Thus, it is clear that a combination of slow electron transfer rate coupled with follow-up chemical reactions[8] make an accurate determination of the reduction potential of VII impossible. However, a rea-

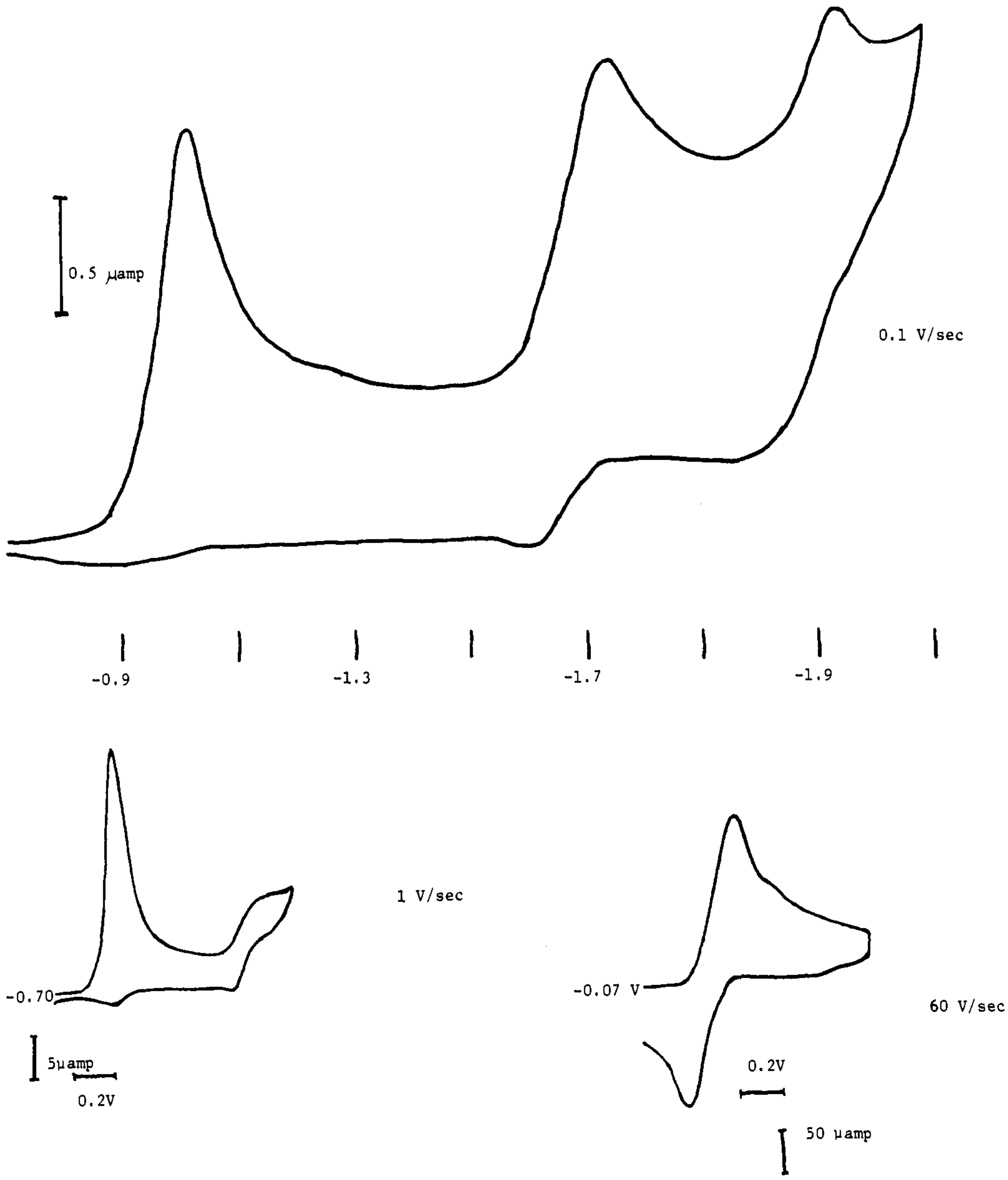


Figure 2. Reduction of V at 0.1, 1, and 60 V/sec.

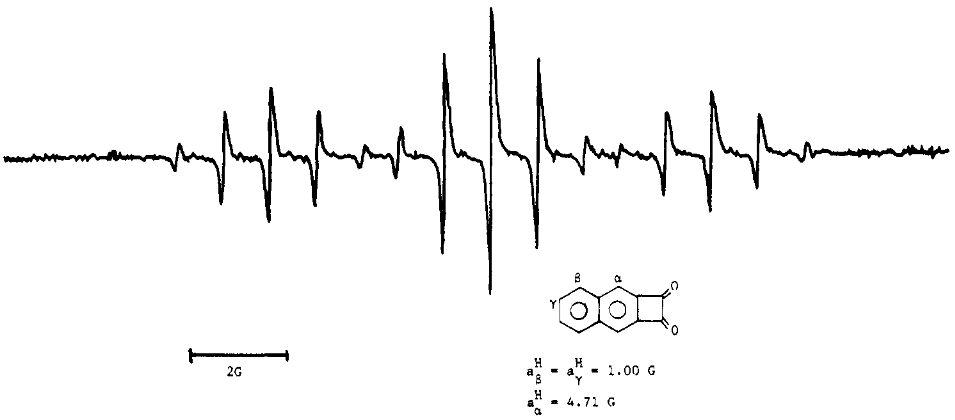
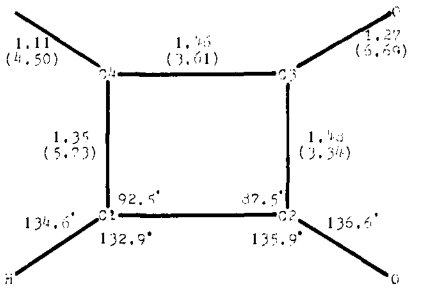


Figure 3. Electron paramagnetic resonance of IX.

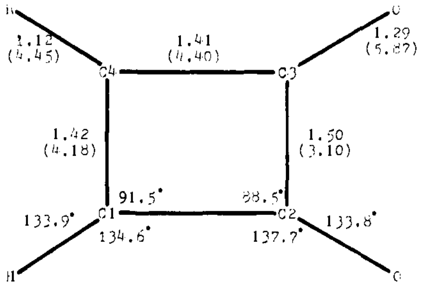
sonable guess would be that it falls in the range of −1.8 to −1.9 V.

The first reductions of compounds VIII, IX, and X are electrochemically reversible and produce a stable product. The EPR spectrum of $IX^{-}\cdot$ is shown in Figure 3.

Compound XI reduces at −1.25 V polarographically (Table I). Cyclic voltammetry indicates that the reduction product is unstable at slow (0.1 V/s) sweep rates (Table II). At 50 V/s, the ratio of anodic to cathodic currents is near unity (0.93) and $E_{pa} - E_{pc}$ is 60 mV. These data indicate that at this high sweep

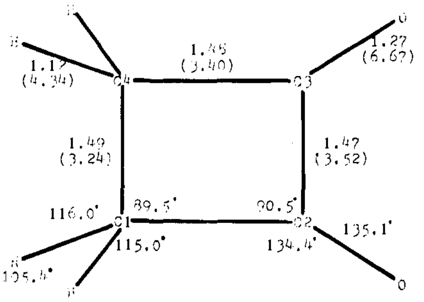


Neutral
III

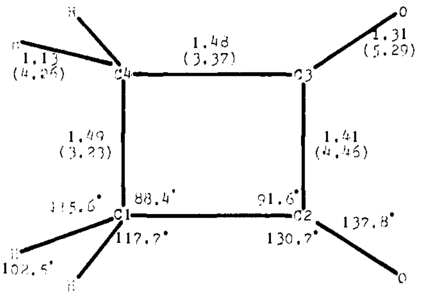


Radical Anion
III

Figure 4. INDO geometries in Å, bond angles in degrees, and bond energies in eV (in parentheses).



Neutral
V



Radical Anion
V

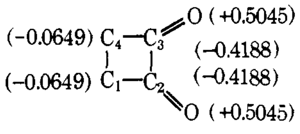
Figure 5. INDO geometries in Å, bond angles in degrees, and bond energies in eV (in parentheses).

rate, the electron transfer is electrochemically reversible. Therefore, $E_{1/2}$ derived from the data at 50 V/s should be near E^0 for compound XI.[6]

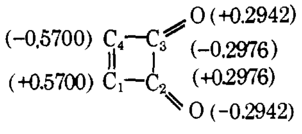
Molecular Orbital Calculations. In order to gain more quantitative insight into the effects of antiaromaticity in simple systems, INDO calculations were carried out on the neutral ground states of III and V and on the corresponding radical anions. Since our primary interest is in the *relative* changes (from III to V) in bonding and in ΔE due to the addition of an electron, the structures of all four species were optimized using the gradient method of McIver and Komornicki. C_{2v} symmetry was assumed throughout.

The calculated energy changes for the processes III → $III^{-}\cdot$ and V → $V^{-}\cdot$ are +13.4 and −14.7 kcal/mol, respectively. Thus, the relative ΔE (i.e., ΔE(III) − ΔE(V)) of 28.1 kcal/mol is consistent with the experimental results.

A qualitative picture of the effect of reduction may be obtained from the π LCAO coefficients in the LUMOs of III and V:



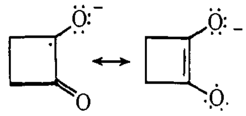
V



III

In V, the π density is concentrated in the adjacent carbonyl groups and is C═O antibonding; thus occupation of this MO should result in weaker C═O bonds and a stronger C_2C_3 bond, with little effect on the rest of the molecule. In III, on the other hand, there is a large shift of π density to the α carbons, so the effect of reduction on the carbonyl bonds should be smaller. However, the LUMO in III has b_2 symmetry (vs. a_1 in V), and this is expected to result in weaker C_2C_3 and C_1C_4 bonds and stronger C_1C_2 and C_3C_4 bonds when an electron is added.

The qualitative analysis of the preceding paragraph is supported by the INDO geometries and bond energies displayed in Figures 4 and 5. In all cases the bonds expected to be weakened in the anions are longer than the same bonds in the corresponding neutral molecules, while those bonds expected to be strengthened are shorter. The major change in bonding in V is a 1.38-eV decrease in the carbonyl bond energy. At the same time the C_2C_3 bond connecting the two carbonyl carbons is strengthened by nearly 1 eV. This is consistent with the classical resonance forms for the radical anion of V:



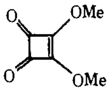
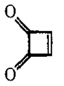
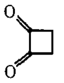
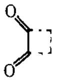
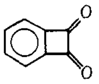
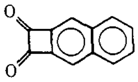
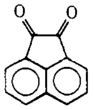
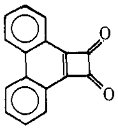
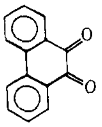
In contrast, when III is reduced to the radical anion, the weakening of the C═O bonds is only 60% of that for V, and the C_2C_3 bond is weakened slightly. Further, the strength of the C_1C_4 bond is drastically diminished, while C_1C_2 is significantly stronger in the anion. Changes in the latter two bonds are negligible when V is reduced. It appears, therefore, that III is attempting to avoid a cyclobutadiene-like structure by lengthening C_2C_3. This is consistent with the standard qualitative notions of antiaromaticity.

Hückel molecular orbital (HMO) calculations were carried out on the various structures given in Table III. The parameters used for these HMO calculations were those of Skujins and Webb[10] adjusted to account for ring strain.[11] The effects of auxillary inductive parameters (AIPs)[12] δ' and δ'' were included. The inductive effect of a methylene group was taken as $+0.2|\beta|$.[12]

The calculated energy of the lowest unoccupied molecular orbital (LUMO) is plotted vs. the experimental reduction potential in Figure 6 for the compounds of Table III. The least-squares line through the points for V, VII, X, and XII (9,10-phenanthroquinone) has a slope of −2.45 and an intercept of −0.81 similar to other such plots.[12] The correlation coefficient for this line is 0.99.

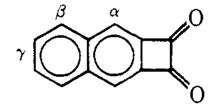
Using the parameters of Rieke, Westmoreland, and Rieke,[11] the proton hyperfine splitting constants (hfsc) for IX are calculated as shown in Table IV. The experimental hfsc were

Table III. HMO Calculations of Reduction Potentials of 1,2-Diones

Compd	M(LUMO)[a]	$E_{1/2}$ (calcd)[b]	$E_{1/2}$ (obsd)
 VII	0.4354	−1.88	−1.88
 III	0.3152	−1.58	
 V	0.0725	−0.99	−1.01
 Va	−0.0757	−0.75	
 VIII	0.1567	−1.19	−1.08
 IX	0.0681	−0.97	−0.764
 X	0.0166	−0.85	−0.828
 XI	0.2771	−1.48	−1.27
 XII	−0.0980	−0.57	−0.58[c]

[a] In terms of $|\beta|$. [b] $E_{1/2} = -2.45m - 0.81$. [c] Reference 13.

Table IV. Hyperfine Coupling Constants (a^{H}) of IX



	$a^{\mathrm{H}}_{\mathrm{calcd}}$, G[a]	$a^{\mathrm{H}}_{\mathrm{obsd}}$, G
α	4.60	4.71
β	1.87	1.00
γ	1.06	1.00

[a] $a^{\mathrm{H}} = Q\rho$ where $\rho = c^2$ and c is the coefficient of the adjacent carbon in the LUMO; Q = 27 G.

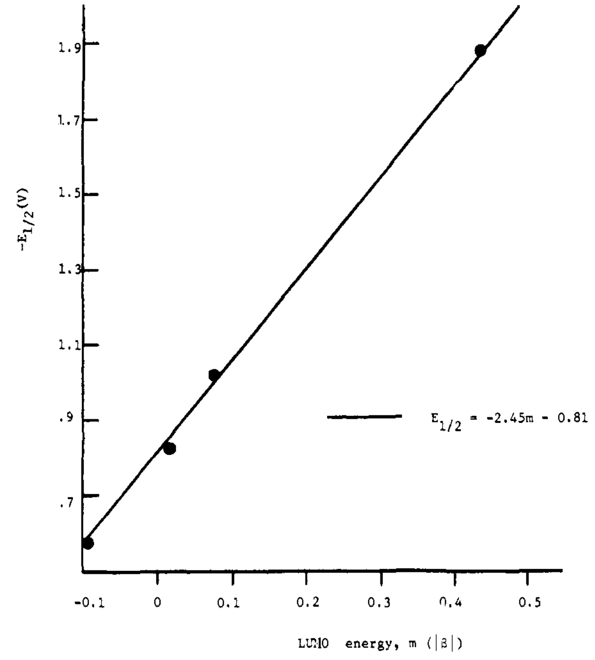
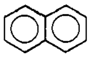
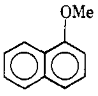
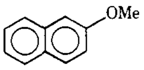
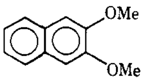


Figure 6.

Table V[a]

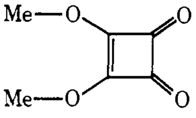
Compd	$-E_{1/2}$ (vs. SCE)
	2.52
	2.65
	2.60
	2.73

[a] C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems", Marcel Dekker, New York, N.Y., 1970, pp 251, 252.

assigned according to these calculations as shown in Table IV.

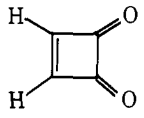
Discussion

The difference in reduction potentials of III and V should be an indication of the increased antiaromatic destabilization of IV. The reduction potential of V has been determined (−1.01 V). However, the reduction potential of III is not available owing to its instability.[13] One might attempt to use the reduction potential of VII as the next best choice even though the effect of the two methoxy groups is difficult to accurately determine. The apparent reduction potential of VII of −1.88 V would yield a net destabilization of the order of 0.87 eV or 20.8 kcal/mol. The effects of the two methoxy groups can be estimated to shift the reduction potential of III by about 0.2 or 0.3 V cathodic, using a series of methoxy-substituted naphthalene compounds as models (see Table V). This would result in an estimated reduction potential for the unknown compound III of −1.7 to −1.6 V. The antiaromatic destabilization could be then estimated to be roughly between 16 and 14 kcal/mol. A second approach would be to use HMO calculations which give excellent correlation with the experimental reduction potentials of V and VII (Table III) and their LUMO. Using the HMO calculated LUMO and eq 1, one



VII

−1.88 V



III

Est. −1.60

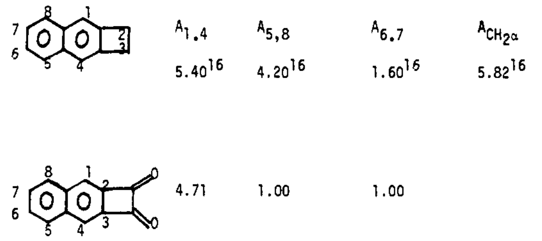


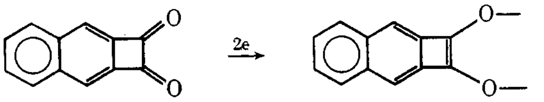
Figure 7. Hyperfine coupling constants of two substituted naphthalenes.

predicts a reduction potential of approximately −1.6 V for III which is in the range of the first estimate.

Taking the 14 kcal/mol as a lower limit, we can attribute this to the increased antiaromaticity (AA) of IV. In the absence of AA effects, one would expect that in going from V to III the reduction potential would become more anodic owing to the increased conjugation of the additional double bond in III. It is difficult to try to relate this number to the AA of cyclobutadiene itself, which has been calculated to vary from 18 to 33 kcal/mol, as IV represents a substituted cyclobutadiene with a negative charge.[14,15] The INDO calculations, it might be added, are consistent with both of the preceding methods of determining the AA of $III^{-}\cdot$.

The reduction potentials of VIII and IX give insight into the effects of antiaromaticity. VIII reduces only 0.07 V cathodic to V and IX reduces anodic to X. The ease of reduction of these compounds indicates a lack of significant antiaromatic character in their LUMO. Apparently, these molecules avoid antiaromaticity by adjusting their electronic distribution to minimize cyclobutadiene character.

The above ideas are supported by the experimental spin distributions in these molecules as well as the hyperfine coupling constants predicted by INDO for $III^{-}\cdot$ and $V^{-}\cdot$. For example, compound IX reduces very readily and has apparent high spin density next to and in the O=CC=O portion of the molecule. Figure 7 shows the hfsc's of $IX^{-}\cdot$ and naphtho[*b*]cyclobutene radical anion.[16,17] It is well established that the 2,3-bond length in naphthalene is relatively long and there is reduced double bond character. Accordingly, one way of viewing IX would be that of a substituted benzene derivative shown below which upon reduction generates little cyclobutadiene character.



In contrast, XI apparently develops considerable cyclobutadiene character and this is reflected in the very cathodic reduction potential and great instability of the radical anion.

Thus, it would seem that some large molecules can readily avoid cyclobutadiene character by changes in electron distribution. Accordingly, attempts to use large molecules to measure antiaromatic effects are likely to give answers which are too small.

Conclusion

The increased antiaromatic destabilization of cyclobutenedione upon reduction to the radical anion was estimated to be 14 kcal/mol or more by an electrochemical method. The results also indicate that electron configurations of large molecules can be perturbed to avoid antiaromaticity. INDO calculations were consistent with these observations.

Experimental Section

General. Melting points were taken with a Thomas-Hoover oil bath melting point apparatus and were corrected. Infrared spectra were obtained with a Perkin-Elmer 257 spectrometer. A Hewlett-Packard Model S750-B gas chromatograph was used. NMR spectra were recorded on a JEOL C-6OHL spectrometer. EPR spectra were determined on a JEOL JESME instrument. Temperatures were determined with a copper-constantan thermocouple. Computer simulation of theoretical EPR spectra was done using a Fortran IV program for mixtures employing Lorentzian line shapes written by R. G. Griffin.[18] The program used for the Hückel MO calculations was written by Munch and Rieke[19] and modified by T. H. Ridgeway for simplified input. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, Tenn. UV spectra were taken on the Unicam SP 800B spectrophotometer. Most of the electrochemical studies were performed on the UNC Electrochemistry unit designed and built by Fox.[20] A Data Technology Model 351 digital voltmeter was used to accurately determine initial potential settings. The sampled dc, pulse, and differential pulse polarograms were performed using a PAR 174.

Data were recorded on a Hewlett-Packard Model 7004 B X-Y recorder, a Tektronic type R564B oscilloscope with two type 2A63 modules, and a Tektronix C-12 polaroid camera unit or a Houston Omnigraphic X-Y recorder. All salts were dried in vacuo at 100 °C before use.

Compounds. Cyclobutane-1,2-dione (V) was synthesized by the methods of Conia and Denis[21] and Heine,[22] mp 61–62 °C (lit. 56,[21] 67–68 °C[22]).

1,2-Dimethoxycyclobutenedione (VII) was synthesized by the method of Cohen and Cohen,[23] mp 52–53 °C (lit.[23] 56 °C).

Benzocyclobutadienoquinone (VIII) was prepared by the method of Cava and Napier,[24] mp 130–131.5 °C (lit.[24] 132–135°C).

Naphtho[*b*]cyclobutene-1,2-dione (IX) was prepared by the method of McOmie and Perry,[25] mp 250–255 °C.

Acenaphthenequinone (X) was purchased from the Aldrich Chemical Co. and was recrystallized before use.

Electrochemistry. Compound XI was made by N. P. Hacker (Ph.D. Thesis, University of Bristol, England, 1977), mp 285–286 °C.

Acentonitrile was prepared by rapidly distilling CH_3CN (Fisher commercial) from $KMnO_4/Na_2CO_3$ and storing it over dry (24 h at 200 °C in vacuo) 4A molecular sieves (MCB).

Dimethylformamide was prepared by allowing spectrograde DMF (MCB) to stand over dried 4A molecular sieves overnight followed by vacuum distillation (1 mmHg) with ice water circulated through the condenser. The DMF was stored under N_2 at room temperature.

Tetrahydrofuran (MCB) was distilled from lithium aluminum hydride immediately prior to use.

Tetraethylammonium perchlorate (TEAP) was prepared by dissolving tetraethylammonium bromide in boiling water and adding perchloric acid. The TEAP was filtered and recrystallized twice from distilled water and dried at 60 °C in vacuo. It was again dried immediately before each use.

Water analyses were done using the method of Hogan et al.[26] Analyses were done using a 6-ft column of Porpak Q, 8–100 mesh (Waters Associates). Injection volumes were 50 mL.

Water content of solution in the cell was determined by withdrawal of a 50-μL sample directly from the cell and injecting in the GC. The water content was determined by comparison of the area of the peak to that of a known concentration of methanol.[26] Water concentration in the cell was found to be 5–10 mm and determinations were considered accurate to $\simeq 1$ mm.

Bethlehem Instrument Grade mercury was used in the precision hanging mercury drop electrode (Metrohm); triple distilled mercury was used for polarography.

The platinum bead electrode was cleaned with aqua regia before each use. The DME used in this study was characterized by $m^{2/3}t^{1/6} = 1.40$ and $m = 1.04$ mg/s at 40 cmHg; at 50 cmHg, $m^{2/3}t^{1/6} = 1.57$ and $m = 1.28$ mg/s; at 60 cmHg, $m^{2/3}t^{1/6} = 1.64$ and $m = 1.41$ mg/s. The electrochemical cell has been described previously.[28]

Nitrogen was passed through a dry ice/acetone trap, Drierite, dried molecular sieves, and a saturator containing the proper dry solvent. This nitrogen was used to degas the electrochemical solutions. Once degassing was complete, the N_2 steam was diverted over the solution surface.

The cell for in situ electrochemical generation of radical species has been described elsewhere.[27]

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$$h_O = -0.96\ \alpha_{\dot{O}} = \alpha_C - 0.96|\beta|;\ k_{C=O} = 1.0$$

$$h_{\ddot{O}} = -2.28\ \alpha_{\ddot{O}} = \alpha_C - 2.28|\beta|;\ k_{C-O-CH_3} = 0.8$$

$$\delta' = 0.1\ \alpha' C_{(C=O)} = \alpha_C - 0.096|\beta_C|$$

$$\delta = 0.05\ \alpha C_{(C-O-CH_3)} = \alpha_C + 0.0435$$

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Electrogenerated Chemiluminescence of Naphthalene Derivatives. Steric Effects on Exciplex Emissions

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Abstract: Electrogenerated chemiluminescence (ecl), electrode potentials, and fluorescence of 14 substituted naphthalenes are reported. Fluorescence maxima of these compounds were rather poorly correlated with electrode potentials. Six of fourteen naphthalenes gave ecl corresponding to their fluorescence emissions. An ecl spectrum having both monomer and excimer bands was observed from 4,5,6,7-tetrahydrodinaphtho[2,1-*g*:1′2′-*i*][1,2]dioxecine, which is a dimeric form of naphthalene. Exciplex emissions were observed from mixed donor-acceptor systems containing naphthalene derivatives and triphenyl amines and the energy of the exciplex was linearly correlated with electrode potentials with smaller slopes than previously reported. This phenomenon was attributed to the entropy effect on the formation of exciplexes between bulky donor and acceptor molecules.

Electrogenerated chemiluminescence (ecl) is a unique technique of exciting ground state molecules to excited ones by an electron transfer reaction from the anion radical to the radical cation (both electrogenerated at the electrode surface),[1-8] i.e.,

$$A^- + D^+ \rightarrow A^* + D \text{ or } A + D^* \qquad (1)$$

The multiplicity of excited states thus produced depends on the energetics of the electron transfer reaction 1. Recently it was reported by several investigators that various excited states, i.e., singlet excited molecules, triplet excited molecules, and/or the excited complex (exciplex) between two molecules A and D,[9-15] can be formed as a result of reaction 1. An exciplex intermediacy in the electron transfer reaction 1 was demonstrated by carrying out a series of experiments using various hydrocarbons as acceptor molecules for the donor molecule, tri-*p*-tolylamine (TPTA).[14] Thus, Park and Bard[14] showed from their experimental observations that, in the homogeneous electron transfer reactions of geometrically smaller molecules, exciplexes are intermediate species before decomposition to the individual excited molecule, A* or D*, while a long-range outer-sphere fast-electron transfer, a model theoretically suggested by Marcus,[16] is more probable in sterically hindered bulky molecules. Absence of exciplex emission in the case of rubrene or 9,10-diphenylanthracene (DPA) is an example of the latter cases. Tachikawa and Faulkner,[15] more recently, observed an exciplex from systems containing 1,4-dicyanobenzene (DCNB) and aromatic hydrocarbons in polar solutions and reported the quantum yield for the exciplex.

Contrary to the theory postulating no intermediacy in the homogeneous electron transfer reaction,[16,17] it now appears to be established that, at least in electron transfer reactions between smaller molecules, an encounter complex, or an exciplex, is formed as an intermediate species as follows:

$$A^-\cdot + D^+\cdot \rightleftarrows \underset{\text{(exciplex)}}{(A^-D^+)^*} \rightleftarrows A^* + D \text{ or } A + D^* \qquad (2)$$

Depending on the equilibrium situation, reaction 2 may proceed to the right or left hand side. Thus an exciplex can be produced either by quenching of excited molecules or from the recombination reaction of radical ions as shown above. When the potential surface of this exciplex is crossed with those of