

in the ground state, and the ϕ_i are inherent component quantum yields.

Table I gives data for the spectra in Figure 1. Analysis of such data in terms of ϕ_i will be published later. It suffices here to consider the dependence of x_i and x_i/N ratios on $[O_2]$ at the two λ_{exc} (last two columns of Table I). The striking result is that x_1 is remarkably insensitive to $[O_2]$ as should have been expected from the insensitivity of spectral shape to $[O_2]$. Furthermore, Stern-Volmer plots of component quantum yield ratios (Table I) show that the effective component lifetime depends on λ_{exc} : for $\lambda_{exc} = 316$ nm, $k_q\tau = 450$ and 516 M⁻¹, and for $\lambda_{exc} = 355$ nm, $k_q\tau = 186$ and 217 M⁻¹ for 2-NPE₁ and 2-NPE₂, respectively. Clearly, the notion that one of the spectral components is short-lived (2-5 ns)^{1,2,16} while the other is long-lived (19-27 ns)^{1,2} is incorrect. *Each spectral component is long- and short-lived, the lifetime mix depending on λ_{exc} .* Assuming $k_q = 3.0 \times 10^{10}$ M⁻¹ s⁻¹ for O₂ quenching,¹⁷ effective lifetimes are $\tau_1 = 15$ and 6.2 ns and $\tau_2 = 17$ and 7.2 ns for 316- and 355-nm excitation, respectively. The conclusion that each spectral component has prompt and delayed contributions invalidates Birks' elegant attempt to resolve fluorescence and absorption spectra on the basis of an analysis of diexponential decay parameters.^{1b,2b} An explanation of the results can be based on the theoretical prediction that for 2-NPE₂ the first absorption band includes a "forbidden" transition which lies somewhat below the "normal" first transition.¹⁸ Direct excitation into the "normal" states may give rise to the short-lived emissions, while excitation into the "forbidden" states may give rise to the delayed emissions. The involvement of forbidden states also become apparent when one compares effective and theoretical radiative rate constants.⁶

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Electrochemically Induced Pericyclic Reactions. A Radical Anionic Cyclization

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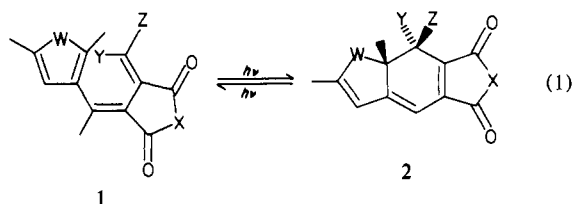
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Recently we have discovered a high-yield triene-like electrocyclic cyclization which is initiated by a reversible single-electron reduction. Its occurrence provides a direct experimental test of stereochemical preference in doublet pericyclic reactions¹ and represents, to our knowledge, the first example of a six-atom electrocyclic cyclization mediated by reversible electron exchange.

The photochemistry and electrochemistry of compounds **1** were studied. All compounds showed strong absorption bands in the long-wavelength ultraviolet region as well as quasi-reversible cyclic voltammetric waves at about -2 V. Previous study²⁻⁴ had established that **1a-c** react by conrotatory³ six-electron cyclization

upon photoexcitation, producing the highly colored cyclic compounds **2a-c**, respectively, eq 1. The intense red-to-orange



1

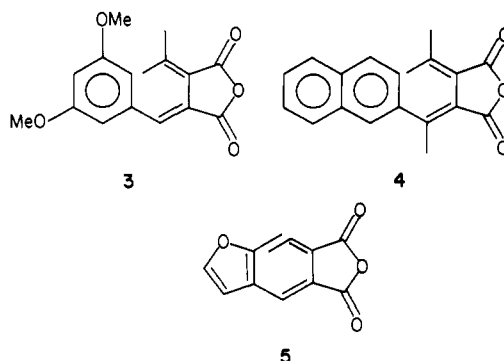
2

- a, W = X = O; Y = Z = CH₃
 b, W = X = O; Y = H; Z = CH₃
 c, W = X = O; Y, Z = adamantylidene
 d, W = S; X = O; Y = Z = CH₃
 e, W = S; X = NPh; Y = Z = CH₃
 f, W = S; X = *p*-NO₂C₆H₄N; Y = Z = CH₃
 g, W = S; X = NCH₂CO₂H; Y = Z = CH₃
 h, W = S; X = NBz; Y = Z = CH₃

coloration of **2** arises from its extended conjugation compared to the open form of the highly nonplanar π system of **1**.

Analogous photocyclization was also observed for **1d-g**, affording **2d-g** in high chemical yield. With **1h**, however, the initial photocyclization product **2h** proved to be photolabile.

The phenyl **3** and naphthyl **4** analogues of these heterocycles



failed to cyclize upon excitation, presumably because of the energetic cost for disruption of ring aromaticity in the transition state.

Controlled potential one-electron electrochemical reduction⁵ of compounds **1a**, **1b**, **1d**, and **1h** in partially deaerated acetonitrile led to efficient formation of cyclized products.⁶ Compounds **1c**, **1e-g**, **5**, and **6** resisted electrochemical cyclization, although stable radical anion solutions were formed in deoxygenated solution.⁷ Detailed analytical electrochemical investigation of **1** gave no evidence for two-electron reduction or for the disproportionation of the initially generated monoanions to dianions. Preparative one-electron oxidation of **1** did not result in cyclization.

We propose that the observed electrocyclic cyclization occurs through the intermediacy of the radical anion as in eq 2. Radical ion electrocyclic cyclization may be facilitated by a flattening of the π system in the radical anion which allows for effective overlap of the termini of the six carbon atom system. MNDO calculations⁸ indicate, for example, that the dihedral angle between the furan ring of

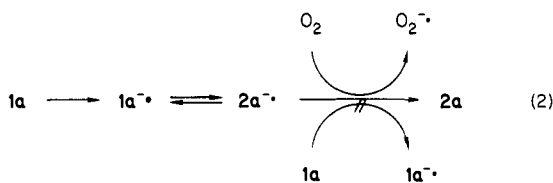
(5) Electroreductions were conducted in a divided electrochemical cell at a Pt working electrode in dry tetrahydrofuran containing 0.1 M tetrabutylammonium perchlorate. Both cyclic voltammetric measurements and preparative electrolyses were conducted on a Princeton Applied Research Electrochemical System. Preparative electrolyses were conducted at a constant potential of -2.1 V.

(6) The assignment of structures to **2a**, **2b**, and **2d** was based on the identity of the isolated electrolysis products with those obtained by photolysis of **1a**, **1b**, and **1d**. The structure assigned to **2h** was based on its spectroscopic properties and by the demonstration that it could be converted by photolysis to the product obtained by excitation of **1h**. Quasi-reversibility of the cyclic voltammetric reduction wave of **1a**, **1b**, and **1d** is consistent with at least partial cyclization to **2**.

(7) Intensely colored solutions were obtained upon preparative reduction of **1d-g**. The color faded immediately upon exposure to oxygen, with starting material being isolated as the only monomeric species. If oxygen is excluded, low cyclization yields are found.

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5 and the rest of the π system decreases dramatically upon one-electron reduction, from 82° in the neutral molecule to 25° in the radical anion. Those systems that resist electrochemical cyclization are precisely those in which electronic localization of the odd electron inhibits extended π interaction or in which steric interactions drive the $1^- \rightleftharpoons 2^-$ equilibrium toward 1^- .

A catalytically driven electrocyclization, i.e., that 2^- might reduce **1**, producing **2** and 1^- (eq 2) which could reenter eq 2 in a repetitive chain sequence, was not achieved, for coulometry indicates that a stoichiometric one-electron reduction is required for the cyclization.⁹

The identity of the electrocyclization product and that observed by photolysis of **1b**, the only molecule studied that contains a stereochemical probe, establishes that the radical anionic cyclization, like the photoinduced one, proceeds in conrotatory fashion.⁹ The like stereochemical course in the photochemical and radical anionic cyclizations is predicted by simple FMO theory, since the nodal properties of the highest lying singly occupied molecular orbital are identical in both the ground-state radical anion and in the neutral photoexcited state. The same conclusion is also reached from semiempirical (MNDO) calculations, in which the conrotatory reaction path of the radical anion **7** is significantly favored over the alternate disrotatory route. Moreover, Bauld and Cessac predicted in 1977 that for the parent C_6^- (hexatriene \rightleftharpoons cyclohexadiene) conrotation would be the preferred reaction mode, even through orbital symmetry/topology favors disrotation.^{1a}

The facilitation of cyclization observed here upon radical ion generation is reminiscent of the dramatic acceleration of pericyclic reactivity induced by hole catalysis, e.g., in Bauld's cation radical Diels-Alder reactions.¹⁰ Our case represents a parallel approach to reducing activation enthalpies by reversible electroreduction. Several other cases are known in which electroreduction of π systems induces pericyclic reactivity.¹¹ In these instances, however, the rearranged products were either solely studied spectroscopically or, if isolated, were obtained at a reduced oxidation level. Furthermore, mechanistic detail is often lacking. The reactions in eq 1 are unique as triene cyclizations induced by reversible electroreduction.

It is interesting to note that the radical cations of **1** failed to cyclize in parallel fashion,¹² an observation that can be explained reasonably by the opposing demands of the helical canting of **1** (a geometry favoring a conrotatory approach) and orbital topo-

logical requirements (favoring disrotation). A current thrust of our research effort is involved with establishing predictive norms for understanding the proclivity for rearrangement of radical ions.

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How Short Is a Bond of Order Zero? A Close Cs...Cs Contact in the $[Cs_2(18\text{-crown-6})]^{2+}$ Cation

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The reaction of aluminum alkyls with alkali metal salts has produced several interesting chemical results. Two comparatively recent developments have concerned (1) the use of crown ethers to solubilize the salts¹ and (2) the observation of the surprisingly high thermal stability of high-oxygen content anions.² We have previously reported the synthesis and structure of $K_2[Al_4Me_{12}SO_4]$,² and in a subsequent effort to find stoichiometries other than 4:1 for the sulfate ion, we have carried out the reaction of $AlMe_3$ with Cs_2SO_4 in the presence of 18-crown-6.³ The major product (and the only one isolated) is a colorless crystalline compound of formulation $[Cs_2 \cdot 18\text{-crown-6}][Al_3Me_9SO_4]$. To our great surprise the X-ray structural analysis⁴ has shown that the cation exhibits a Cs...Cs contact only slightly longer than the sum of ionic radii.

The compound crystallizes in infinite (sulfate/aluminum)cesium(18-crown-6)cesium(sulfate/aluminum) chains as shown in Figure 1. Each cesium can be considered to be nine-coordinate, each interacting with the six crown oxygens, two sulfate oxygens, and the other cesium. Cs(2) is coordinated to an "aluminum oxygen" at Cs-O = 3.08 Å and the unique sulfate oxygen at Cs-O = 3.24 Å, while Cs(1) is found at 3.16 and 3.20 Å from the remaining sulfate oxygens in an adjacent asymmetric unit. The crown ether oxygen atoms interact in a weaker fashion, especially with Cs(1), the distances ranging from 3.33 to 3.59 Å (av = 3.48 Å) and 3.13 to 3.48 Å (av = 3.29 Å) for Cs(2).

The Cs...Cs distance is to our knowledge the closest contact (corrected for ionic radii) found to date between alkali metal ions. Indeed, the metal ion separation in the zero bond order Cs_2^{2+} ion is close to what one would predict for a full bond between cesium ions. The distance in cesium metal is 5.38 Å,⁵ and the lengths

(9) While coulometry results make a cyclization mechanism involving a radical anion likely, they do not strictly exclude the possible intervention of a reversibly formed dianionic intermediate. A conrotatory mechanism is required by our data only if geometrical isomerization of the starting material (either as a neutral or a reduced species) is much slower than the electrocyclic reaction.

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(4) Single crystals of the title compound were obtained by the slow cooling of a toluene solution. Space group $P2_1/n$; cell constants $a = 13.552$ (2) Å, $b = 16.731$ (4) Å, $c = 17.029$ (4) Å, $\beta = 94.79$ (2) $^\circ$ with four formula units per unit cell, and $D_c = 1.46$ g cm $^{-3}$. Least-squares refinement based on 2311 observed reflections led to a final $R = \sum(|F_o| - |F_c|) / \sum |F_o| = 0.064$. The details of data collection and refinement are as given by Holton et al.: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45. An empirical absorption correction was done according to Churchill and Hollander: Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 1957. Anisotropic thermal parameters were used for all atoms except those of the crown ether. Hydrogen atoms were not located.