Electron-Transfer Reactions and Associated Conformational Changes. Extended Redox Series for Some Bianthrones, Lucigenin, and Dixanthylene

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Abstract: The severely hindered compounds bianthrone (**1**, and three derivatives, **2–4**), 10,10′-dimethyl-9,9′-biacridylidene (**5**), dixanthylene (**6**), and bifluorenylidene (**7**) have been characterized in terms of structural changes associated with their electrochemical oxidation and reduction. At low temperatures and/or rapid scan rates it was possible to detect an extended redox series for each compound in which each member of the series has a twisted structure resembling the thermochromic and photochromic B isomer of bianthrone and dixanthylene. The species have been designated B^{2+}, $B^{+}\cdot$, B, $B^{-}\cdot$ and B^{2-}. Formal potentials of the four B redox couples have been determined as well as irreversible peak potentials for oxidation and reduction of the prevalent neutral forms of these molecules, the doubly folded A form. For 1,1′-dimethylbianthrone it proved to be possible to determine the formal potential for the $A/A^{-}\cdot$ couple. The difference in the potentials for oxidation (or reduction) of A and B forms provides information about the change in free energy for the $A^{+}\cdot \rightarrow B^{+}\cdot$ (or $A^{-}\cdot \rightarrow B^{-}\cdot$) structural changes in the ion radicals. The relative free-energy changes have been interpreted in terms of the steric and electronic factors involved in the reactions.

The thermodynamics and kinetics of electron-transfer reactions should be different for different conformations of a molecule. This statement has been confirmed in a number of recent studies which have reported two types of effects. In some cases, two different conformations are found to react at an electrode at distinctly different potentials.[1,2] During the electrochemical reaction, the more difficult to reduce (or oxidize) conformer converts to the more easily reduced (or oxidized) conformer. These are examples of structural change preceding electron transfer.

In the second type, reaction of a principal (or sole) conformation at an electrode surface produces a short-lived intermediate which undergoes a significant conformational change.[3] Here structural change follows electron transfer. Numerous examples of geometrical isomerization induced by electron transfer have also been reported,[4] especially in the organometallic field.[5]

As might be expected, some systems show both effects: structural change preceding electron transfer under some conditions and following electron transfer under others.[3f]

Scheme I

$$\begin{tikzcd}
A^{2+} \arrow[r, leftrightharpoons, "e", "E^{\circ}_{2A+}"'] \arrow[d, shift left, "k^{++}_{AB}"] & A^{+}\cdot \arrow[r, leftrightharpoons, "e", "E^{\circ}_{1A+}"'] \arrow[d, shift left, "k^{+}_{AB}"] & A \arrow[r, leftrightharpoons, "e", "E^{\circ}_{1A-}"'] \arrow[d, shift left, "k_{AB}"] & A^{-}\cdot \arrow[r, leftrightharpoons, "e", "E^{\circ}_{2A-}"'] \arrow[d, shift left, "k^{-}_{AB}"] & A^{2-} \arrow[d, shift left, "k^{=}_{AB}"] \\
B^{2+} \arrow[r, leftrightharpoons, "e", "E^{\circ}_{2B+}"'] \arrow[u, shift left, "k^{++}_{BA}"] & B^{+}\cdot \arrow[r, leftrightharpoons, "e", "E^{\circ}_{1B+}"'] \arrow[u, shift left, "k^{+}_{BA}"] & B \arrow[r, leftrightharpoons, "e", "E^{\circ}_{1B-}"'] \arrow[u, shift left, "k_{BA}"] & B^{-}\cdot \arrow[r, leftrightharpoons, "e", "E^{\circ}_{2B-}"'] \arrow[u, shift left, "k^{-}_{BA}"] & B^{2-} \arrow[u, shift left, "k^{=}_{BA}"]
\end{tikzcd}$$

$$K^{n}_{AB} = k^{n}_{AB} / k^{n}_{BA} \qquad n = 2, 1, 0, -1, -2$$

Some of the most interesting examples of the structural consequences of electron-transfer reactions have been discovered[3] with a series of molecules which may be regarded as highly hindered ethylenes, **1–6**. The salient features of the behavior of these species will be illustrated by a specific discussion of the behavior of bianthrone (**1**).

At room temperature, **1** exists as the yellow A form (Figure 1) in which the severe steric interactions between hydrogens at positions 1 and 8′ (and 1′ and 8) are relieved by folding each anthrone system away from the other without twisting the 9,9′ double bond. When a solution of **1** is heated, a significant fraction is converted to the green B form. The most widely accepted structure of the B form (Figure 1) reduces the steric crowding by twisting about the 9,9′ bond and flattening the two anthrone systems.

The electrochemical behavior of **1** induces structural changes similar to the A → B thermochromic conversion described above.[3a,f] The anion–radical of **1** has reduced double-bond character in the 9,9′ bond which lowers the energy required to twist that bond. Thus, it is not surprising that the radical–anion adopts a B-type structure, $B^{-}\cdot$, with considerable twisting about the 9,9′ bond.[3a,f] The dianion undoubtedly exists in a B structure, B^{2-}.

Electrochemical,[3a,f] spectroelectrochemical,[3a] and pulse radiolysis[3b] studies of the reduction of **1** have been interpreted by the right half of Scheme I. The reduction proceeds by an ECE reaction. A is first reduced to the A-like anion–radical, $A^{-}\cdot$, which rapidly twists to $B^{-}\cdot$ which in turn is rapidly reduced to B^{2-} because the potential required to reduce A is more negative than the formal potential of the $B^{-}\cdot/B^{2-}$ couple. All of the parameters of this reaction scheme have been evaluated and the structural changes accompanying oxidation of B^{2-} have also been studied.[3a,b,f]

Lucigenin (the dication, B^{2+}, of 10,10′-dimethyl-9,9′-biacridylidene) has been shown[3e] to fit the left half of Scheme I. The reduction of B^{2+} proceeds in stepwise fashion to $B^{+}\cdot$, then

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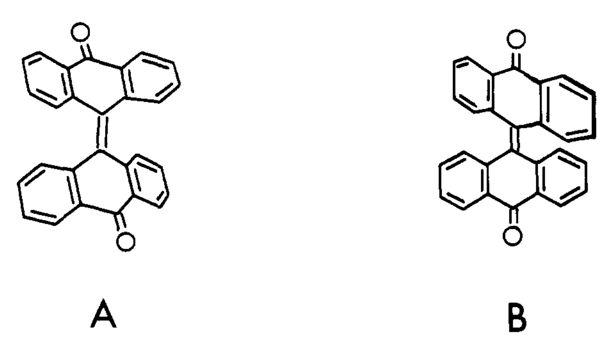
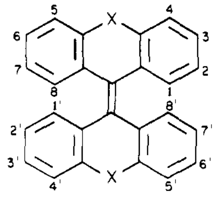


Figure 1. A and B forms of bianthrone (**1**).

to short-lived B which converts to the prevalent structure at room temperature, A.

The objective of the present research was to determine if bianthrone and related compounds underwent the redox reactions and structural changes incorporated in both sides of Scheme I. Studies of **1**–**6** show clearly that the extended redox series, B^{2+}, B$^{+\cdot}$, B, B$^{-\cdot}$, and B^{2-}, exists for each compound. The observed formal potentials give important new information about the energetics of electron transfers and structural changes occurring with **1**–**6**.



1, X = CO, bianthrone
2, X = CO, 3,3′-dimethylbianthrone
3, X = CO, 1,1′-dimethylbianthrone
4, X = CO, 3,3′-dimethoxybianthrone
5, X = NCH_3, 10,10′-dimethyl-9,9′-biacridylidene
6, X = O, dixanthylene

Experimental Section

Bianthrone (**1**), 3,3′-dimethylbianthrone (**2**), and 1,1′-dimethylbianthrone (**3**) were obtained from Aldrich Chemical Co., Milwaukee, WI, and were used as received except for **1** which was recrystallized twice from mesitylene, mp 321 °C dec (lit.[6] 315–20 °C dec). The preparation of 3,3′-dimethoxybianthrone (**4**) has been described.[3b] Lucigenin (dication of **5**) was obtained as the nitrate salt (Aldrich) and was recrystallized from ethanol/methanol. Dixanthylene (**6**) was prepared by the method of Ault, Kopet, and Serianz.[7] The preparation of 9,9′-bifluorenylidene has been described.[8] The specific workup used in our preparation consisted of extraction of the product mixture with hot $CHCl_3$, concentration of the extract, and induction of crystallization by addition of ether. Recrystallization from propionitrile produced dark orange needles, mp 188–9 °C.

Alumina (Woelm activity grade Super 1, Type W200, neutral) was activated in a tube furnace (500 °C) under nitrogen for 15 h. Dimethylformamide (Burdick and Jackson, Muskegon, MI) was passed through a column of activated alumina immediately before use. Butyronitrile (Eastman Kodak, Rochester, NY) was vacuum distilled (25 mmHg) through a 45-cm Vigreux column from $KMnO_4$ (12 g/L) and Na_2CO_3 (8 g/L) with retention of the middle half. Benzonitrile (Aldrich) was vacuum distilled at full mechanical pump vacuum using the 45-cm Vigreux column and the middle half was retained. Both butyronitrile and benzonitrile were passed through a column of activated alumina immediately before use. Tetra-*n*-butylammonium perchlorate (Eastman) was recrystallized three times from ethyl acetate or ethyl acetate/pentane and vacuum dried (100 °C) for 15 h. Preparation of tetraethylammonium perchlorate has been described.[9] All solutions were purged with nitrogen.

Electrochemical instrumentation comprised a Princeton Applied Research (EG and G Princeton Applied Research, Princeton, NJ) PAR Model 173 potentiostat, PAR 179 digital coulometer or PAR 176 current-to-voltage converter, and a PAR 175 programmer. Data was recorded with an X–Y recorder (Houston 2000 or Hewlett-Packard 7004) or oscilloscope (Tektronix D11 storage or Nicolet Explorer IIIA digital). Positive feedback compensation of solution resistance was employed.[10]

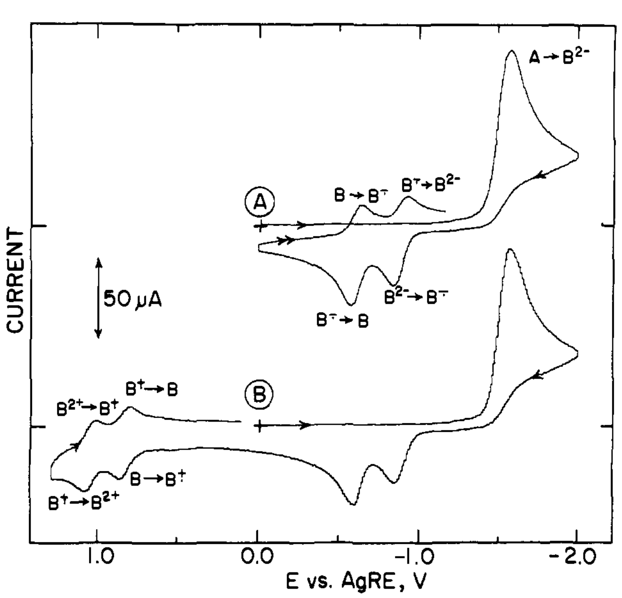


Figure 2. Cyclic voltammograms of 2.03 mM bianthrone (**1**) in 0.10 M tetra-*n*-butylammonium perchlorate/benzonitrile: 10.0 V/s, 21 °C.

The cell design has been described[11] though the present cell included an additional port for a thermocouple well and the unjacketed solution compartment was long enough (8 cm) to permit complete immersion of the solution in a cooling bath. This cell was used for experiments conducted from room temperature down to −80 °C. A dry ice/acetone bath was used and voltammograms were recorded at various temperatures during slow cooling to the bath temperature and during subsequent warmup. For lower temperatures a shorter jacketed cell[11] was used. An evacuated second jacket was provided to improve temperature stability. Cooling was provided by passing cold nitrogen through the inner jacket. The nitrogen was cooled by passage through a coil of aluminum tubing immersed in liquid nitrogen, and the steady-state temperature was adjusted by varying the nitrogen flow rate. Temperatures were measured using a Doric Model 410A digital thermometer with iron–constantan thermocouple. Accuracy was ±0.5 °C over the temperature range employed. The thermocouple temperature in the low-temperature cell was easily controlled to ±0.5 °C. When using the more convient dry ice/acetone bath, temperature changes of up to 2 °C occurred during the time required to obtain a voltammogram.

The working electrode was a 2-mm diameter disk (platinum unless specified otherwise) sealed into soft glass tubing. Preparation and polishing have been described.[12] The reference electrode (AgRE) used in all experiments was a silver wire immersed in 0.10 M $(n\text{-Bu})_4NClO_4$/0.010 M $AgNO_3$ in butyronitrile.[13] The reference electrode was at room temperature in all experiments, and its potential was +0.355 V vs. aqueous SCE. Many of the compounds studied are photosensitive so all compounds and their solutions were protected from light. The working electrode was repolished with each change of solution or more frequently as needed. This polishing was done by hand with 0.05-μ alumina (Buehler Ltd., Evanston, IL), triply distilled water, and polishing cloths (Fisher, Pittsburgh, PA).

In one case (the oxidation of 3,3′-dimethoxybianthrone (**4**)) it was necessary to remove traces of impurities from the test solution by placing activated alumina directly in the cell, a procedure introduced by Hammerich and Parker.[14]

Results

Evidence for the extended redox series of B-type species is found in the voltammograms of bianthrone (**1**) shown in Figure 2. The

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Table I. Formal Potentials and Voltammetric Peak Potentials[a]

compound	redox couple $A^{+}\cdot/A$	$B^{2+}/B^{+}\cdot$	$B^{+}\cdot/B$	$B/B^{-}\cdot$	$B^{-}\cdot/B^{2-}$	$A/A^{-}\cdot$
bianthrone (1)	+1.53[b]	+1.06	+0.85	−0.61	−0.88	−1.55[b]
3,3′-dimethyl-(2)	+1.44[b]	+0.97	+0.77	−0.68	−0.94	−1.57[b]
1,1′-dimethyl-(3)	+1.6[b]	+1.09	+0.87	−0.74	−0.93	−1.67,[b] −1.68[c,d]
3,3′-dimethoxy-(4)	+1.23[b]	+0.61	+0.56	−0.71	−0.93	−1.54[b]
10,10′-dimethyl-9,9′-biacridylidene (5)[e]	+0.16[b]	−0.73	−0.75	−2.05	−2.32	−2.60[b]
dixanthylene (6)[c,f]	+1.05[b]	+0.01	−0.10	−1.72	−2.2	−2.50[b]
9,9′-bifluorenylidene (7)[c]			+1.04[g]	−1.38	−1.85	

[a] Determined in benzonitrile containing 0.10 M tetra-*n*-butylammonium perchlorate at 21 °C; scan rate, 1.00 V/s. All values are formal potentials unless otherwise indicated; silver reference electrode (AgRE) used (see Experimental Section). Formal potentials are taken to be midway between oxidation and reduction peaks. Analysis of overlapping peaks was carried out with the aid of relevant theoretical results.[31] [b] Peak potential. [c] Butyronitrile solvent. [d] −56 °C. [e] Dimethylformamide/0.10 M tetraethylammonium perchlorate, −41 °C, 0.5 V/s. [f] −94 °C. [g] −50 °C.

fact that the A form is reduced to B^{2-} which is oxidized first to $B^{-}\cdot$ then to B on the positive-going scan (Figure 2A) has been firmly established in earlier studies.[3a,f] The B form rapidly converts to A as it diffuses near the electrode, and voltammetric detection via the reduction $B \rightarrow B^{-}\cdot \rightarrow B^{2-}$ requires scan rates greater than about 0.5 V/s.[3a] Similarly, the new redox couples associated with oxidation of B at +0.9 and +1.1 V (Figure 2B) are readily detected at scan rates exceeding about 0.5 V/s but are absent at slower scan rates. The relative peak heights for the $B \rightarrow B^{+}\cdot$ and $B^{+}\cdot \rightarrow B^{2+}$ processes increase with scan rate approaching the peak heights of the $B^{2-} \rightarrow B^{-}\cdot$ and $B^{-}\cdot \rightarrow B$ processes at 100 V/s. The $B^{2+}/B^{+}\cdot$ and $B^{+}\cdot/B$ electron-transfer reactions are reversible and rather rapid as expected for species of similar conformation. The new redox couples do not appear unless the potential interval scanned includes the A reduction peak; i.e., no peaks for any of the B couples will be observed if the potential is limited to the range of +1.3 to −1.4 V.

Similar results were obtained with 3,3′-dimethylbianthrone, 3,3′-dimethoxybianthrone, and 1,1′-dimethylbianthrone and the data are summarized in Table I. In each case the minimum scan rate needed to detect the $B \rightarrow B^{+}\cdot$ and $B^{+}\cdot \rightarrow B^{2+}$ peaks was consistent with the previously determined rate constants for the $B \rightarrow A$ conversion.[3c]

The above results show that the manifold of species having a B-type conformation may be entered by initial reduction of A to B^{2-}. It ought also to be possible to enter this set of species via initial oxidation of A to B^{2+}. This expectation was realized for bianthrone and the 3,3′-dimethyl and 1,1′-dimethyl derivatives, but in each case other products in addition to B^{2+} were detected by voltammetry after oxidation of A on the initial positive-going scan. These other products may arise through reactions of the initially formed $A^{+}\cdot$.

The stabilizing influence of the methoxy groups in 3,3′-dimethoxybianthrone (4) makes it possible to oxidize A to B^{2+} without producing other species which can be detected by voltammetry. Results of a series of experiments are presented in Figure 3. In Figures 3A and 3B the system of B-type species was entered by initial reduction of A. The reversibility of all four redox couples involving B-type species is evident, and the formal potential of each couple can be evaluated (Table I). Small reduction peaks for B can be seen in the initial negative-going scan in Figure 3A because the equilibrium concentration of B is significant for 3,3′-dimethoxybianthrone[3c] whereas it is too small to be detected with the other bianthrones. In Figure 3C, an initial oxidation of A occurs and B^{2+} is detected on the return sweep. The potential range was extended to −2.0 V to show that no additional electroactive species were generated.

When a population of B-type species was generated by either initial reduction or oxidation of A and subsequent scans were limited to the +1.0 to −1.3 V range, peaks for the four reversible couples involving the B-type species were observed and these peaks decreased in magnitude as the species diffused away from the electrode surface and B was converted to A.

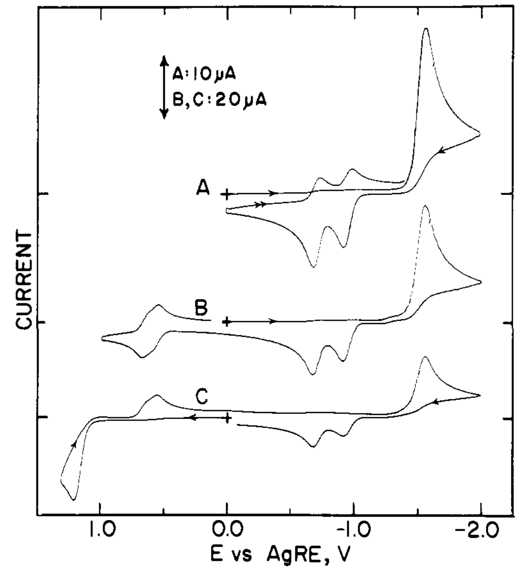


Figure 3. Cyclic voltammograms of 3,3′-dimethoxybianthrone (**4**), in 0.10 M tetra-*n*-butylammonium perchlorate/benzonitrile, 21 °C: (A) 1.74 mM **4**, 1.00 V/s; (B) 2.44 mM **4**, 1.00 V/s; (C) 1.74 mM **4**, 0.50 V/s.

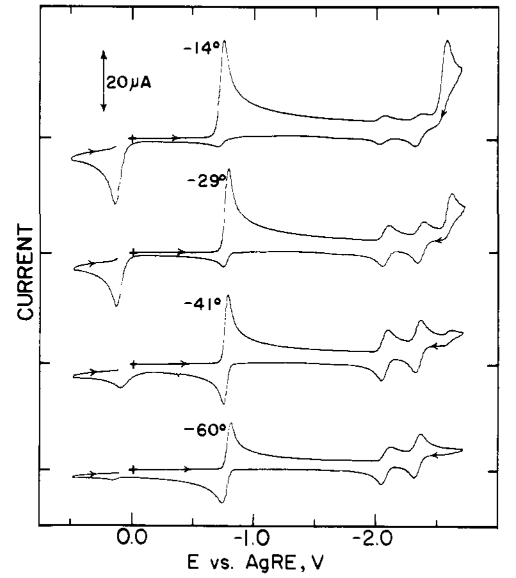


Figure 4. Effect of temperature on electrochemical behavior of 2.19 mM lucigenin (B^{2+} of **5**) in 0.10 M tetraethylammonium perchlorate/DMF, 0.50 V/s.

Lucigenin, 10,10′-dimethyl-9,9′-biacridinium ion, is a readily available example of a stable B^{2+} species. It is reduced first to $B^{+}\cdot$ then to B which converts to A at a rate about 100 times greater than that of the analogous bianthrone reaction.[3e] In order to determine if A and B in the lucigenin system could be reduced, the negative potential limit was extended to −2.75 V and the temperature was lowered in order to detect the short-lived B form.

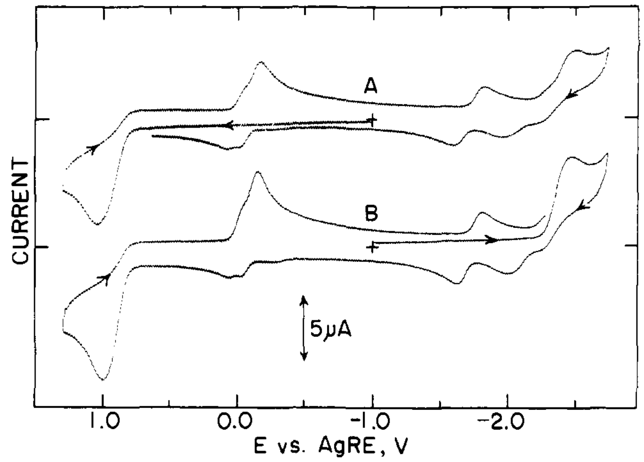


Figure 5. Cyclic voltammograms of 1.14 mM dixanthylene in 0.10 M tetra-*n*-butylammonium perchlorate/butyronitrile: 1.00 V/s, -94 °C.

Results are shown in Figure 4. Under all conditions the reductions of B^{2+} to $B^{+}\cdot$ and $B^{+}\cdot$ to B occur at almost the same potential, producing a single composite reduction peak at about -0.8 V. This overlap of the two reactions and the fact that better resolution is obtained in dichloromethane solvent have been noted previously.[3e] At -14 °C the peak for oxidation of B to B^{2+} is barely noticeable at -0.8 V but it increases as the temperature is lowered and the rate of the B → A conversion decreases. Conversely, oxidation (+0.2 V) and reduction (-2.6 V) peaks for A are observed at the higher temperatures, but these are almost completely absent at -60 °C where the rate of the B → A conversion is negligible.

Prominent peaks for the reversible $B/B^{-}\cdot$ and $B^{-}\cdot/B^{2-}$ couples are observed at -2.1 and -2.4 V and their magnitudes grow as the B oxidation peak grows and the A oxidation and reduction peaks recede. Clearly these new peaks have the characteristics expected for B-type species. Slight broadening of the reduction (-2.1 V) and oxidation (-0.8 V) peaks of B was noted at -60 °C. This observation may signal the onset of the sluggish electron-transfer kinetics.

Redox couples for B-type species from dixanthylene (**6**) were also discovered. Dixanthylene is most readily prepared as the neutral A form. The B → A transformation is extremely rapid for this compound[15,16] so extremely low temperatures were required to detect the redox properties of B (Figure 5). Entry into the B manifold could be achieved by either initial oxidation (5A) or reduction (5B) of A, and peaks arising from the species B^{2+}, $B^{+}\cdot$, B, $B^{-}\cdot$, and B^{2-} are readily apparent in each voltammogram. (Origin of the small oxidation peak at -0.3 V in Figure 5B is unknown.) As with lucigenin and 3,3′-dimethoxybianthrone the $B^{2+}/B^{+}\cdot$ and $B^{+}\cdot/B$ potentials are close to one another. The electron-transfer rate constant for the $B^{-}\cdot/B^{2-}$ couple is sufficiently small at the very low temperature used to cause the $B^{-}\cdot \rightarrow B^{2-}$ process to merge partially with the A reduction peak.

The preceding data permit evaluation of the four formal potentials of the B-type couples but so far no direct determination of formal potentials of the A-type couples have been obtained. An indirect evaluation of the formal potential of the $A/A^{-}\cdot$ couple for bianthrone (-1.14 V vs. SCE in dimethylformamide) has been reported,[3b] but the detection of an oxidation peak for $A^{-}\cdot$ (necessary for voltammetric evaluation of the formal potential of the $A/A^{-}\cdot$ couple) is not possible because of the very rapid conversion of $A^{-}\cdot$ to $B^{-}\cdot$.

The rate constant for $A^{-}\cdot \rightarrow B^{-}\cdot$ for 1,1′-dimethylbianthrone (**3**) is much smaller than for bianthrones with no substituents in the 1 and 1′ positions. The value found for **3** by pulse radiolysis[3b] in alkaline tetrahydrofuran/2-propanol/water was 1.1×10^{3} s^{-1} which is small enough to permit voltammetric detection of $A^{-}\cdot$.

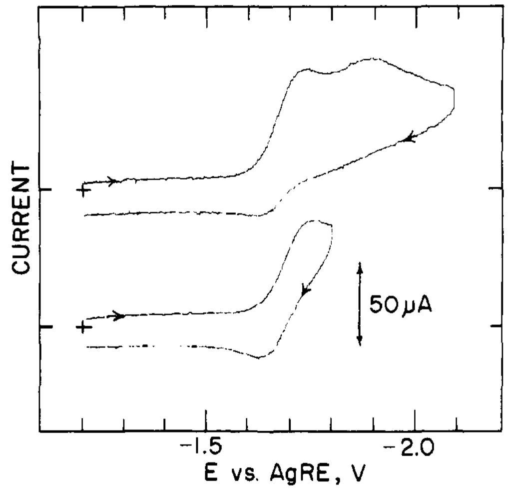


Figure 6. Cyclic voltammograms of 1.02 mM 1,1′-dimethylbianthrone (**3**) in 0.10 M tetra-*n*-butylammonium perchlorate/butyronitrile: 20.0 V/s, -56 °C, gold disk electrode.

A low-temperature cyclic voltammogram of 1,1′-dimethylbianthrone is shown in Figure 6. The behavior is consistent with the ECE reaction scheme $A \rightarrow A^{-}\cdot \rightarrow B^{-}\cdot \rightarrow B^{2-}$. The single reduction peak observed at room temperature has been split into two peaks. The first peak results from the $A \rightarrow A^{-}\cdot$ reaction and the second from further reduction of $A^{-}\cdot$ presumably to A^{2-} which rapidly twists to B^{2-}. Estimation of the rate constant for $A^{-}\cdot \rightarrow B^{-}\cdot$ based on theory for an ECE scheme[17,18] gives about 800 s^{-1}, a value which seems much too large for -56 °C. In view of the value previously determined by pulse radiolysis, 1.1×10^{3} s^{-1} at room temperature,[3b] an abnormally low activation energy would be indicated in order for 800 s^{-1} to be the true value at -56 °C. The ECE scheme is probably not operative.

It is possible that $A^{-}\cdot$ is disappearing via a competing disproportionation scheme[19] given by

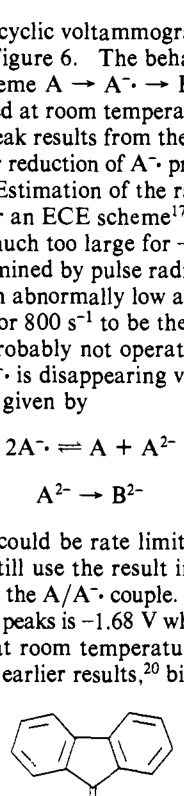
$$2A^{-}\cdot \rightleftharpoons A + A^{2-}$$

$$A^{2-} \rightarrow B^{2-}$$

where either reaction could be rate limiting.

However, we may still use the result in Figure 6 to estimate the formal potential for the $A/A^{-}\cdot$ couple. The midpoint between reduction and oxidation peaks is -1.68 V which is close to the value of the peak potential at room temperature.

In concurrence with earlier results,[20] bifluorenylidene (**7**) was



found to undergo stepwise, reversible reduction to a dianion. Oxidation was irreversible at room temperature, probably because of rapid reactions of the cations. At -50 °C the first step of oxidation of **7** was reversible although the second step was not.

Discussion

The doubly folded A conformation is well established in the solid state for bianthrone[21] and dixanthylene,[22] and 10,10′-di-

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methyl-9,9′-biacridylidene is assumed to adopt such a structure.[23] For bianthrone the structure shown for B in Figure 1 is the most widely accepted description of the thermochromic form and the B photoisomer.[24] Spectra of B generated by electrochemistry are the same as those of the thermochromic and photochromic species.[3a]

By contrast, 10,10′-dimethyl-9,9′-biacridylidene (**5**) is not thermochromic and does not form a B photoisomer.[25] The strong similarity between the electrochemical behavior of **5** and bianthrone and dixanthylene noted in this and previous work[3a,e,f] supports the conclusion[3e] that a B-type conformation is formed on reduction of B^{2+} from **5**. Thus the electrochemical reduction appears to produce a novel form of **5**, but its short lifetime makes nonelectrochemical (e.g., spectral) characterization difficult.

Bifluorenylidene (**7**) is exceptional. X-ray crystallograpy[26] reveals a twisted B-type structure rather than the doubly folded A form. Properties of solutions of **7** and derivatives have been interpreted in various ways but we concur with the conclusion[27] that **7** is also twisted in solution. The electrochemical data[20] for **7** are consistent with reduction of a B structure to $B^{-}\cdot$ and B^{2-}, and the potentials in Table I have been assigned on that basis. In any case, it is clear that the reduction and oxidation do not follow the pattern observed for the A conformations of the bianthrones, dixanthylene, and 10,10′-dimethyl-9,9′-biacridylidene. It is interesting that suggestion of a twisted form of **7** was made at a very early date on the basis of its facile electrochemical reduction.[28]

The chemical reduction of the A form of dixanthylene[29] has also been postulated to produce a twisted dianion, B^{2-}, and an extended redox series involving eight species has been established for the twisted molecule, 9,9′-bianthryl-10,10′-dicarbonitrile.[30]

The various B-type species which have been postulated in this work (B^{2+}, $B^{+}\cdot$, B, $B^{-}\cdot$, and B^{2-}) will not have identical structures but the differences are expected to be small. Very minor structural changes are associated with the electron-transfer reactions involving these species so the electrochemical reactions are fast and reversible; i.e., there is not a significant barrier associated with the electron-transfer reaction. The most probable change is an increase in the dihedral angle between the halves of the molecule (estimated to be ca. 57° in the B form of bianthrone[23]) upon going from B to the ion radicals ($B^{-}\cdot$ or $B^{+}\cdot$) and then to the doubly charged ions (B^{2-} or B^{2+}). The angle is probably close to 90° in B^{2-} and B^{2+}. Similarly, the A-type species will differ from one another through small changes in bond lengths and bond angles but each is expected to have a recognizable doubly folded conformation and consequently the electron-transfer reactions involving these species should be fast and reversible. This expectation was confirmed in the one case where voltammetric measurements were possible, the $A/A^{-}\cdot$ couple of 1,1′-dimethylbianthrone.

By contrast, the activation barrier associated with an electron transfer reaction which bridges the two types of structures is so large that a direct reaction has not been observed. For example, in the lucigenin system,[3e] $B^{+}\cdot$ is not reduced directly to A but instead proceeds by the sequence $B^{+}\cdot \rightarrow B \rightarrow A$. Similarly for bianthrone[3a–c] and its 1,1′-dimethyl derivative, A is not reduced directly to $B^{-}\cdot$ but proceeds by $A \rightarrow A^{-}\cdot \rightarrow B^{-}\cdot$.

One of the most striking characteristics of the B forms of all the molecules studied is that they are both more easily oxidized and more easily reduced than the corresponding A forms. This result may be understood by considering the effect of twisting an isolated carbon–carbon double bond on the π and π^* orbital energies (Figure 7). Twisting facilitates oxidation by raising the π orbital energy and facilitates reduction by lowering the π^* orbital energy. The central 9,9′ double bond is not twisted in A but is significantly twisted in B. Of course, the molecules studied here do not contain an isolated double bond so there are many other orbitals of similar energy but the raising of the HOMO and lowering of the LUMO observed on going from A to B must contain a residue of the effect illustrated in Figure 7. The effect is also reflected in the large red shift in the first absorption band on going from A to B.[23]

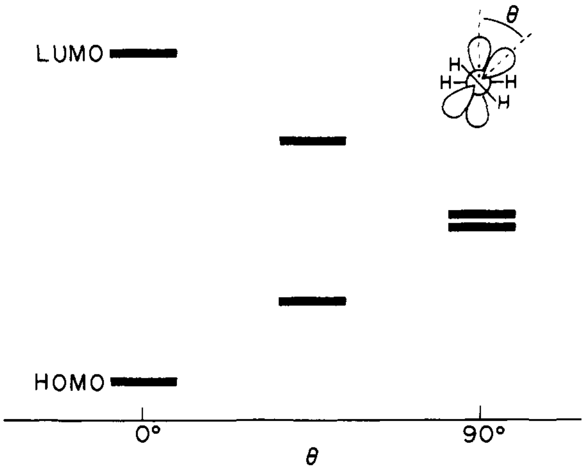

Figure 7. Qualitative variation of LUMO and HOMO energies of ethylene with twist angle, θ.

It is quite evident that the difference between the potentials for oxidation of A and B and the difference between the potentials for reduction of A and B are not identical (Table I). To interpret these differences we turn to the relationships between the equilibrium constants and standard (formal) potentials defined in Scheme I. It can be shown that

$$K_{AB}^{-} = K_{AB} \exp(F/RT(E^\circ_{1B^-} - E^\circ_{1A^-})) \tag{1}$$

$$K_{AB}^{+} = K_{AB} \exp(F/RT(E^\circ_{1A^+} - E^\circ_{1B^+})) \tag{2}$$

The formal potentials for the B couples have been evaluated and are listed in Table I. However, only one direct measurement of a formal potential of an A couple is available, that of $E^\circ_{1A^-}$ of 1,1′-dimethylbianthrone obtained at −56 °C in butyronitrile solvent. Nevertheless, this formal potential is quite close to the peak potential for reduction of A observed at room temperature in benzonitrile (Table I). This observation is not too surprising since the first step of A reduction at room temperature is the formation of $A^{-}\cdot$. In fact, when the value of k_{AB}^{-} for 1,1′-dimethylbianthrone[3b] is inserted in the relationship for the peak potential for an ECE process,[17] it is predicted that the formal potential should be only 20 mV negative of the peak potential at 1.0 V/s. The difference increases by 29 mV for each decade increase in k_{AB}^{-}, but it reaches only 75 mV for bianthrone and 3,3′-dimethylbianthrone which have the largest value[3b] of k_{AB}^{-} among the four bianthrones, 7×10^4 s^{-1}. Values of $E^\circ_{1A^-}$ for the four bianthrones were estimated from the observed peak potentials and the kinetic shifts which were calculated according to the procedure just described. Assuming that similar processes are underlying the observed reduction peak potentials of the A form of lucigenin and dixanthylene and the oxidation of the A forms of all the species studied, the formal potentials were estimated to be 0.10 V negative of the reduction peak potentials and 0.10 V positive of the oxidation peak potentials. Uncertainty is introduced because values of k_{AB}^{-} and k_{AB}^{+} are not known for these compounds. An indication of the possible magnitude of the error may be found in the fact that a range of 10^3 to 10^9 s^{-1} for the

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Table II. Relative Changes in Free Energy for Radical–Cation and –Anion Structural Changes[a]

compound	$\Delta\Delta G^\circ_{\mathrm{AB}^{+\cdot}}$, kcal/mol[b]	$\Delta\Delta G^\circ_{\mathrm{AB}^{-\cdot}}$, kcal/mol
bianthrone (1)	−18	−23
3,3′-dimethyl-(2)	−18	−22
1,1′-dimethyl-(3)	−19	−22
3,3′-dimethoxy-(4)	−18	−21
10,10′-dimethyl-9,9′-biacridylidene (5)	−23	−15
dixanthylene (6)	−29	−20

[a] Temperatures and solvents as given in Table I. $\Delta\Delta G^\circ_{\mathrm{AB}\pm} = \Delta G^\circ_{\mathrm{AB}\pm} - \Delta G^\circ_{\mathrm{AB}}$. [b] 1 kcal = 4.184 kJ.

unknown rate constants would lead to an uncertainty of only ±0.1 V in the formal potentials (±2.3 kcal/mol in $\Delta\Delta G^\circ$ values to be calculated).

The formal potentials so obtained were placed in eq 1 and 2 and $K_{\mathrm{AB}}{}^{-}/K_{\mathrm{AB}}$ and $K_{\mathrm{AB}}{}^{+}/K_{\mathrm{AB}}$ were calculated. From these equilibrium constants, the change in free energy associated with the conformational change in the radical ions relative to the free-energy change for the analogous reaction of the neutral compounds was calculated.

$$\Delta\Delta G^\circ_{\mathrm{AB}^-} = \Delta G^\circ_{\mathrm{AB}^-} - \Delta G^\circ_{\mathrm{AB}} \quad (3)$$

$$\Delta\Delta G^\circ_{\mathrm{AB}^+} = \Delta G^\circ_{\mathrm{AB}^+} - \Delta G^\circ_{\mathrm{AB}} \quad (4)$$

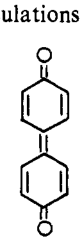
The results are summarized in Table II. (In those cases where $\Delta G^\circ_{\mathrm{AB}}$ is known,[3c] absolute values of $\Delta G^\circ_{\mathrm{AB}^-}$ and $\Delta G^\circ_{\mathrm{AB}^+}$ could be calculated if desired).

All the $\Delta\Delta G^\circ$ values are large and negative reflecting the fact that the radical ions of all the compounds show a strong preference for the B form whereas the A form is the more stable structure in the neutral molecules.

Two principal factors influence the equilibrium between the two forms: considerable steric hindrance is relieved on going from A to B forms but this is counterbalanced in the neutral molecule by the formal 9,9′ double bond which tends to force the molecule into the doubly folded A form in which the double bond is not twisted.[21,22] In the ion radicals the 9,9′ bond order is lowered so that the steric factor will be dominant, causing the B forms to be energetically favored (large, negative $\Delta\Delta G^\circ$).

If one assumes that the relief of steric strain on going from A to B form of bianthrone is approximately the same in the anion and cation, the difference between $\Delta\Delta G^\circ_{\mathrm{AB}^+}$ (−18 kcal/mol) and $\Delta\Delta G^\circ_{\mathrm{AB}^-}$ (−23 kcal/mol) must be attributed to significantly larger 9,9′ π bond order in the cation compared to the anion. This view was supported by approximate MO calculations[32] on idealized, planar cation and anion radicals of **8** for which the calculated 9,9′ π bond order was 0.68 for $\mathbf{8}^{+\cdot}$ and 0.58 for $\mathbf{8}^{-\cdot}$.

Similar calculations for $\mathbf{9}^{+\cdot}$ (0.60) and $\mathbf{9}^{-\cdot}$ (0.54) showed a



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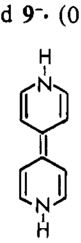

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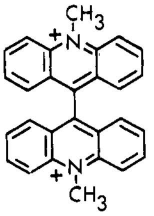
smaller difference but the same order, whereas the experimental values of $\Delta\Delta G^\circ_{\mathrm{AB}^+}$ (−23 kcal/mol) and $\Delta\Delta G^\circ_{\mathrm{AB}^-}$ (−15 kcal/mol) for the 10,10′-dimethyl-9,9′-biacridylidene (**5**) system show that the cation tends to twist more readily than the anion. Here the energy changes appear to be strongly affected by a change in geometry at the nitrogen atoms on going from cation to anion radicals. The cationic forms (cf. **10**) will tend to be planar at nitrogen which enforces a degree of planarity to each tricyclic half of the molecule. This tends to destabilize the folded A form. On the other hand, the geometry at nitrogen will be pyramidal in the neutral and anionic forms and the lower C–N–C bond angle will favor (cf. Figure 1) folding in the A form which reduces strain and lowers the magnitude of $\Delta\Delta G^\circ_{\mathrm{AB}^-}$. No such change in geometry is expected at the carbonyl carbon in the bianthrones so the bond-order factor can remain dominant. The relative values of $\Delta\Delta G^\circ_{\mathrm{AB}^+}$ and $\Delta\Delta G^\circ_{\mathrm{AB}^-}$ in dixanthylene (**6**) follow the same pattern as **5**. Like N–CH_3, the O bridge in the cationic forms of **6** will impose some planarity in the xanthylene fragment which will destabilize the A form more in the cation than in the anion–radical.



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Registry No. 1, 434-85-5; **2**, 3438-08-2; **3**, 24541-19-3; **4**, 79943-80-9; **5**, 23663-77-6; **6**, 517-45-3; **7**, 746-47-4; lucigenine, 2315-97-1.

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[32] Pople INDO calculations by Program BONDO; Professor F A. Weinhold, University of Wisconsin—Madison.