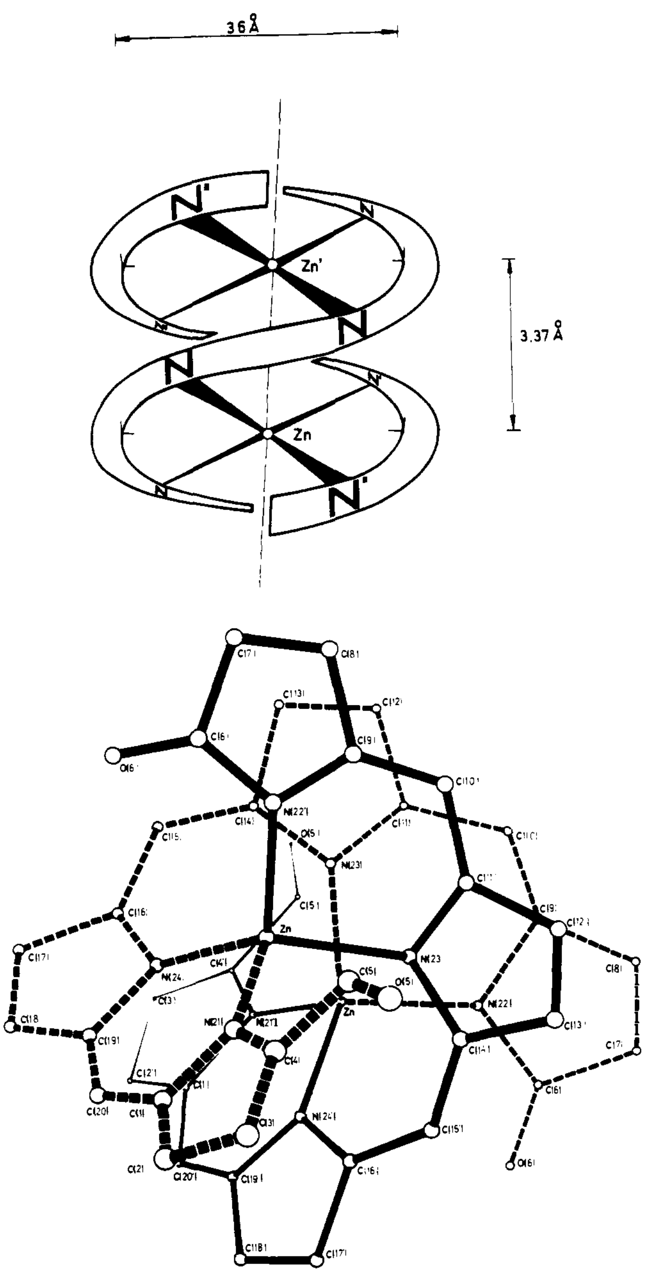

Figure 2. (Top) A schematic drawing of **2**. (Bottom) A perspective drawing of **2**. The ethyl groups have been omitted for clarity.

The height of the chromophore helix, as defined by the distance of N(21) and N(22) parallel to the Zn-Zn axis, is 5.2 Å. No anion is found in the dimer **2**, which strongly suggests that the effect of acid addition in solution is not the expected protonation of the chromophore but simply the removal of the water molecule from the hydrate **1**.

The importance of these findings on a correlation between electronic spectra and conformation of a bilatriene chromophore lies in its possible relation to the structural phytochrome problem. Phytochrome is presumably a biliprotein which controls many light responses of higher plants.[6] Its far-red form produces a broad peak at 710 nm, which is reversibly converted into a more intense peak at 660 nm (red form) by light.[6] It has been speculated that these spectral shifts may be related to cis-trans isomerizations of a bilatriene chromophore around the methine bridge atoms.[7] Calculated intensities[7] and energies[2] of bilatriene chromophores in different conformations support this hyothesis. The above results suggest that simple stretching of the molecule perpendicular to its molecular plane also produces such spectroscopic shifts without cis-trans isomerizations.

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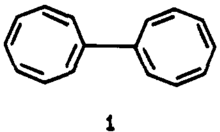
The Bicyclooctatetraenyl Tetraanion. A Quadruply Charged 20 π-Electron Biphenyl Analogue

Sir:

The ready generation of cyclooctatetraenyl dianions by alkali metal reduction of cyclooctatetraene precursors[1] constitutes convincing experimental support for the Hückel concept that a closed shell of $(4n + 2)$ π electrons (here $n = 2$) can result in a high degree of resonance stabilization. Such high affinity for 2ϵ uptake is especially remarkable when it is recognized that compressional strain energy of approximately 14 kcal/mol[2] and repulsive electron-electron interaction perhaps as high as 90 kcal/mol[3] need be overcome in arriving at such stable, planar species. These untoward energetic elements are revealed by the tendency of the apparently aromatic COT^{2-} to enter into concentration dependent disproportionation equilibria with neutral COT to generate COT$\cdot^-$.[4]

These properties intrinsic to COT^{2-} might be construed as a signal that attempts to generate more highly charged congeners of these dianions would meet with difficulty. Indeed, Stevenson and Concepci6n have found it possible to generate the dianion of **1** (K, THF, −110° to +60°) but were unable to obtain evidence for its further reduction.[5] We now report the successful synthesis of **2**, believed to be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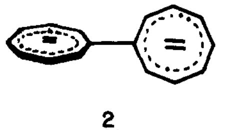
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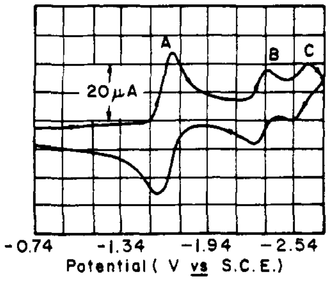

Figure 1. Single sweep voltammogram of **1** (1.47×10^{-3} M solution) in HMPA solvent, $v = 20$ V/sec.

the most highly charged analogue of biphenyl, and also describe the intriguing polarographic behavior of **1**.[6]

Electrochemical measurements on **1** were conducted under vacuum line conditions employing anhydrous HMPA solutions containing tetra-*n*-butylammonium perchlorate as supporting electrolyte with strict exclusion of moisture and atmospheric oxygen. Three nicely separated reduction waves were observed having half-wave potentials ($E_{1/2}$) of -1.657, -2.324, and -2.566 V vs. SCE.[7] Their respective peak current constants (i_p) were calculated to be 0.855, 0.417, and 0.360, the middle value being nearly the same as that determined for the first (1ϵ) reduction wave of COT (0.42) in this solvent system.[8] According to the Nicholson–Shain approximation[9] which begets the proportionality relationship, $i_p \propto (\alpha n)^{1/2} n$, a concerted two-electron transfer will necessarily exhibit a diffusion current constant greater than twice the magnitude of a 1ϵ transfer. The i_p value of 0.42 for $n = 1$, for instance, corresponds to an i_p of 1.2 for synchronous 2ϵ discharge. Since the first reduction wave for **1** is characterized by the significantly lower i_p value of 0.855, the diminution in peak height could be the result of non-Nernstian 2ϵ uptake by one ring (dianion formation) with resultant peak broadening. Alternatively, nonsimultaneous introduction of two electrons (2×0.42) at nearly the same potential associated with individual reduction of the two cyclooctatetraene rings (bis radical anion formation) could be operative.

Cyclic voltammetric studies (Figure 1) revealed the reversibility of wave A and provided revealing information on the pair of subsequent 1ϵ transfer steps. At slow scan speeds (20–400 mV/sec), wave B associated with radical trianion formation proved to be equally reversible, but the tetraanionic species generated at very negative potential was seen to be rapidly consumed by further chemical reaction. At much faster scan speeds (oscilloscope measurements at 20–40 V/sec), the reversibility of the fourth electron addition was dramatically improved (see Figure 1). In actuality, the entire electrochemical cycle $\mathbf{1} \rightarrow \mathbf{2} \rightarrow \mathbf{1}$ proved to be almost totally reversible ($i_{\text{anodic}}/i_{\text{cathodic}}$ for wave A = 0.92) under these conditions. Interestingly, the contour of the B/C portion of the cyclic voltammogram mirrors the polarographic behavior of COT under analogous conditions but with pronounced shifting to more negative potentials.

Since counterion and solvation effects are known to markedly effect the stabilities of anions by ion pairing and hydrogen bonding mechanisms,[1,4,10] the reduction of **1** with potassium in liquid ammonia was also examined. Upon treatment of **1** with 5 g-atom equiv of K in ND_3 at -55 to $-78°$, there was generated a species whose ^1H NMR spectrum (recorded at various temperatures between $-55°$ and $0°$; Me_3N as internal standard) displays two multiplets at δ 6.2–6.6 (4 H) and 5.4–5.82 (10 H). When comparison is made with the spectrum of **1** (mult at δ 5.65–6.08 in $CDCl_3$), the attendant changes are seen to be consistent with the development of diatropic character[11] and formation of **2**. The upfield portion of the spectrum in particular compares very favorably with those chemical shifts customarily exhibited by cyclooctatetraene dianions (δ 5.3–5.8).[1] The four deshielded protons presumably occupy the ortho and ortho′ positions, since in the twisted form of the tetraanion these hydrogens fall well into the deshielding cone generated by the magnetic anisotropy of the opposite ring.

While the ^{13}C NMR spectrum of **1** is characterized by five signals at 141.4, 131.9, 131.6, 131.1, and 128.4 ppm (in $CDCl_3$), that of the reduction product shows maintenance of symmetry and considerable upfield shifting of all resonances (121.7, 97.3, 88.3, 87.6, and 86.9 ppm in ND_3 at $-55°$). Since solvent changes of this type generally affect ^{13}C chemical shifts to the extent of only 1–2 ppm,[12] the rather large shifts encountered in this work (20–43 ppm) cannot be attributed to such minor alterations. Rather, these findings parallel closely the ^{13}C chemical shift difference previously determined for COT and COT^{2-} (46.6 ppm in THF)[13] and are uniquely consistent with development of local 10π electron density in each ring. Although the two quaternary carbons are influenced by ring current circulation in the adjoining ring, the remaining carbons show the magnitude of change in ^{13}C shift anticipated for distribution of doubly negative charge over eight carbon atoms.[13,14] There is no evidence that the two charged rings in **2** are mutually interactive; in fact, the combined data support the premise that the two dianionic entities adopt a perpendicular or near perpendicular geometric relationship. No complications from paramagnetic effects were encountered during our spectral measurements.

Solutions of tetrapotassio **2** in ND_3 have proven to be stable at 0 °C for extended periods. Quenching with CH_3OD resulted in formation of $C_{16}H_{14}D_4$ (*m/e* 214.1663, calcd 214.1659), probably a mixture of tetradeuterio hydrocarbons. Comparable reduction of **1** in NH_3, followed by addition of methanol and NH_4Cl, likewise gave an oil (*m/e* 210.1411) whose ^1H NMR spectrum (in CCl_4) consisted of two broad multiplets at δ 5.02–6.18 (9.8 H) and 1.90–3.12 (8.3 H).[15]

The present results demonstrate that tetraanion formation in **1** is indeed feasible.[16] The possibility that similar levels of reduction can be effected in systems which can attain a bisected conformation less readily or not at all is being explored. A quantitative correlation between multiple electron affinity and anion conformation might thereby be realized. We are also evaluating those effects on reducibility introduced by alterations in the annulene perimeter.[17]

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(17) The authors thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support. We are particularly indebted to Professor Larry Anderson and Mr. Davis Taggart for the use of their electrochemical equipment and for valuable comments and suggestions.

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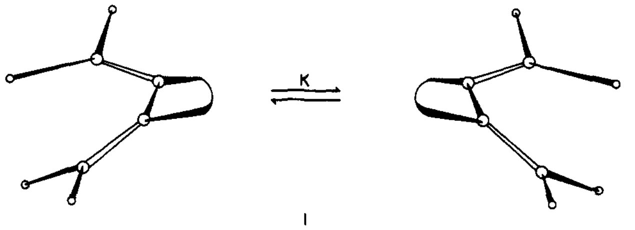
Dissymmetric 1,3-Dienes. III.[1,2] Enantiomerization Barriers in Some Cyclic *vic*-Dialkylidene Compounds

Sir:

Substitution of isopropylidene groups on adjacent carbon atoms gives rise to large energy barriers to rotation about the bond between the two carbon atoms in both cyclic[1] (**1**) and acyclic[2,3] (**2**) compounds, causing such dienes to adopt severely skewed conformations[2,4] which are dissymmetric and thus, in principle, resolvable.[5] The recent flurry of activity involving this class of compounds has included the isolation of both cyclic[6] and acyclic[7] examples in optically active form.



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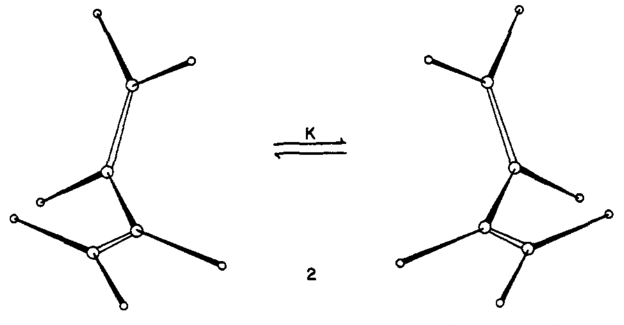

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We wish to communicate our results to date on a dynamic NMR investigation of a series of compounds related to our original model (**3**),[1] and to Pasto's alkylidenecyclopropane adducts (**4**),[6] which suggest that seemingly minor structural variations in **1** can produce large changes in the apparent enantiomerization barrier.

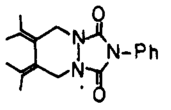
Compounds **5–7** possess temperature-dependent NMR spectra[8] enabling calculation of free energies of activation at the coalescence temperature using either complete line-shape analysis or the Eyring rate equation[9] (cf. Table I).

In contrast to Pasto's compounds (**4**) which are optically stable at room temperature[6] (thus requiring $\Delta G^{\ddagger} \approx 25$ kcal/mol), the similarly constituted **5b** enantiomerizes rapidly at room temperature,[10] and yields $\Delta G_c^{\ddagger} = 10.0$ kcal/mol at −78°. In order to reconcile these data one must assume either (a) that the $\Delta G^{\ddagger}$ value determined by NMR does not reflect the true enantiomerization process in **5b**, or (b) that apparently minor structural changes can give rise to large differences in $\Delta G^{\ddagger}$; i.e., that the repulsive van der Waals potential function leading to enantiomerization is very steep in this region.

Table I

Compound	R	T_c, °C[8]	$\Delta G_c^{\ddagger}$, kcal/mol[9]	Method of preparation
5a	$R_1 = R_2 = R_3 = R_4 = CH_3$	48	16.0	*a*
5b	$R_1 = R_2 = CH_3$, $R_3 = Ph$, $R_4 = H$	−78	10.0	*a*
5c	$R_1 = R_2 = CH_3$, $R_3 = H$, $R_4 = Ph$	—	—	*a*
5d	$R_1 = R_2 = H$, $R_3 = R_4 = Ph$	—	—	*a*
6a	O	−109	8.0	*b*
6b	$C(CO_2Et)_2$	−46	11.1	*c*, *t*-BuOK, $CH_2(CO_2Et)_2$
6c	S	30	15.0	*c*, Na_2S
6d	SO	30	15.1	*d*
6e	SO_2	36	15.3	*d*
6f	NCH_2Ph	−95	8.7	*c*, $PhCH_2NH_2$
6g	NCH_3	<−100	<8.4	*c*, CH_3NH_2
7a	CH_2Ph	−46	11.0	*c*, $(PhCH_2NH-)_2$
		131	20.4	
7b	CH_3	−31	11.9	*c*, $(CH_3NH-)_2$
		109	19.1	

[a] Heating to ~50° the product obtained by reaction of corresponding dimethyl dialkylidenesuccinate with excess CH_3Li. [b] Reaction of 2,3-diisopropylidene-1,4-butanediol[2] with NaH and *p*-TsCl. [c] Reaction of the indicated reagent with 2,3-diisopropylidene-1,4-dibromobutane (prepared in ca. 30% yield from 2,3-diisopropylidene-1,4-butanediol[2] and Ph_3PBr_2). [d] Compound 6c plus the theoretical amount of *m*-chloroperbenzoic acid.



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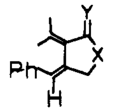
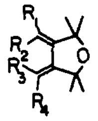


4a X = O, Y = NSO_2Cl

4b X = NSO_2Cl, Y = O



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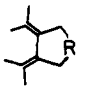

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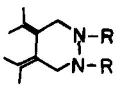

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Compound **5a** exhibits a large increase of ~8 kcal/mol caused by the saturated *gem*-dimethyl groups (termed a "buttressing effect" by Mannschreck et al.[5] in acyclic analogues) in comparison to **6a**, which again emphasizes the importance of *overall* deformational freedom in the molecular racemization process.

The substantial increase in $\Delta G^{\ddagger}$ as R descends the periodic table from R = O in **6a** to R = S in **6c** can be attributed to an increase in bond lengths and a decrease in the C–R–C bond angle. Both of these effects result in a closer approach of the methyl on the "inside" of the diene system in the planar transition state for enantiomerism for compound **6c**.