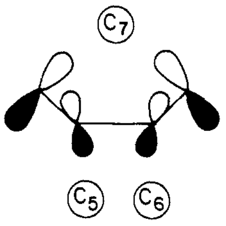

Figure 1. Schematic representation of the π_S orbital as obtained using the STO 3G method.

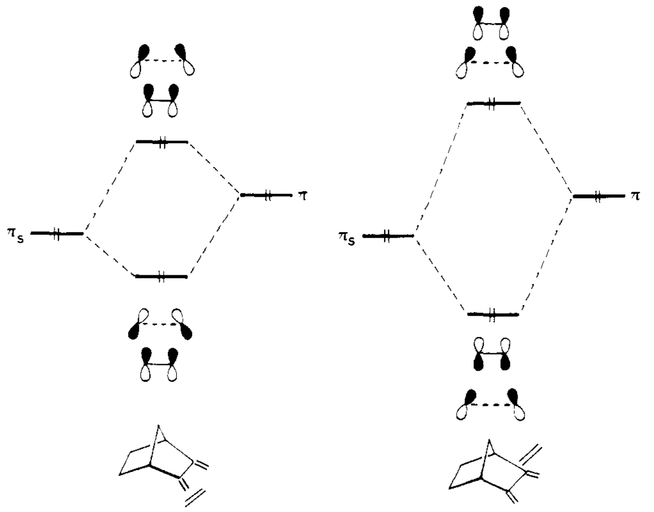

Figure 2. Qualitative diagram of the interaction between π_S of the diene unit and a π bond: left, approach from the direction anti to the methano bridge; right, corresponding syn approach.

to the ethano bridge in **29a** causes the proximal and distal methylene protons to be characterized by disparate chemical shifts (m at δ 1.61–0.60, 4 H). In **28a,** where such shielding does not operate, the four protons of the ethano bridge appear as a pseudosinglet at δ 1.62. Additionally, independent heating of **28a** and **29a** at 50 °C promoted the loss of ethylene with aromatization to provide diester **30a.** Likewise, **28b–29b** cleanly gave **30b** and **31–32** were transformed to dibenzonorbornadiene.[17]

The stereoselectivity observed above cannot be attributed to steric factors because C_1 and C_4 of each cyclopentadiene unit are too remote from either bridge.[18] Were such a working hypothesis adopted, the behavior of **1** and **3** would necessarily be contrasteric, an implausible premise. Steric attraction[2] and π-orbital hybridization arguments[2] are also considered by us to be inapplicable. Rather, rationalization of the observed stereoselectivity has presently been approached by performing extensive semiempirical (MINDO/3, SPINDO, EHT, modified INDO) and ab initio (STO 3G) calculations on 2,3-dimethylenenorbornane (**33**) and 2,3-dimethylenenorbornene (**34**) as simpler prototypes. These calculations, in combination with appropriate PE data, clearly indicate the π MO's in both compounds to reside above the σ MO's. More importantly, while the HOMO (π_A) of **33** and **34** is seen not to interact significantly with the σ framework, the π_S butadiene orbital admixes substantially, with the result that the terminal π lobes experience a disrotatory tilt which enhances electron density syn to the methano bridge ($S \neq 0$). Also, the π orbital associated with the central atoms of the butadiene unit rotate in the opposite direction as shown in Figure 1. As a direct result of this rotation, addition of a dienophile anti to the methano bridge can be predicted since the antibonding interaction between π_S of the butadiene moiety and the dienophile HOMO is considerably smaller for endo attack. This feature is indicated schematically in Figure 2.

The notable rotation of the π lobes, which arises because of a strong interaction between the semilocalized pure π_S orbital and a precanonical σ orbital[19] of the same symmetry, has also been observed computationally for **1** and **2**. Theory predicts a substantial reduction in stereoselectivity for **3**. These points will be elaborated upon in the full paper.[20]

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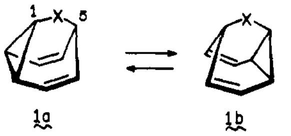
Optical Activity Associated with a Highly Fluxional Molecule. Absolute Configuration and Chiroptical Properties of 2(4)-Methylsemibullvalene

Sir:

Rigid constraint of a *cis*-divinylcyclopropane system into a folded conformation as in **1** results in appreciable canting of



1a 1b

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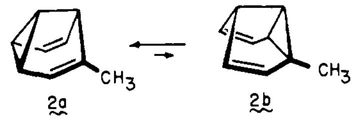
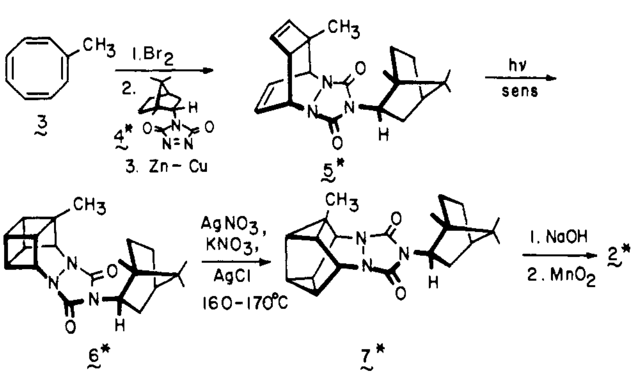
the internal cyclopropane σ orbital relative to the two π bonds. Electronic realignment via degenerate Cope rearrangement is thereby facilitated. Experimentally determined activation barriers for a number of such systems reveal the existence of a direct correlation between $\Delta H^{\ddagger}$ and the C_1–C_5 internuclear separation.[1] Accordingly, no organic molecule is likely to exceed the facility for [3,3] sigmatropy ($\Delta H^{\ddagger} = 4.8$ kcal/mol)[2] shown by semibullvalene (**1**, X = —). Despite the considerable attention which these highly fluxional molecules have attracted, no report describing the preparation of an optically active derivative has yet appeared. Consequently, factors which may contribute to the rotational strength of chiral semibullvalenes remain unknown. To provide insight into this question, we have devised a synthesis of optically pure 2(4)-methylsemibullvalene (**2***)[3] and have determined its absolute configuration and circular dichroic behavior.

To remove the C_s symmetry inherent in the parent hydrocarbon, a substituent must be placed at C_2 (C_4). An immediate result is alteration in the position of structural equilibrium to satisfy internal electronic requirements. The selection of methyl was predicated upon our knowledge of the equilibrium distribution of **2a** and **2b** at room temperature (85:15)[3] and other observations of methyl group influences.[4,5]



2a **2b**

The sequential reaction of methylcyclooctatetraene (**3**) with 1 equiv each of bromine and (−)-*endo*-bornyl-1,2,4-triazolinedione (**4***)[6] gave a mixture of Diels-Alder adducts which were directly debrominated with zinc-copper couple in dimethylformamide.[7] Florisil chromatography afforded **5*** as a mixture of diastereomers (46%). Irradiation of 0.5% solutions of **5*** in benzene-acetone (1:1) with a 450-W Hanovia lamp (Vycor filter) resulted in formation of the bishomocubane **6*** (61%), which was easily separated into appreciably enriched crystalline [mp 173–184 °C, $[\alpha]_D$ −23.0° (*c* 5.4, C_2H_5OH)] and oily diastereomers by simple column chromatography (Florisil). When an intimate mixture of solid **6*** and the silver salt eutectic, $AgNO_3 \cdot KNO_3 \cdot AgCl$ (59:38:3), was stirred[8] in the absence of light at 160–170 °C for 4 h, rearrangement occurred[9] to deliver dextrorotatory **7*** [mp 171–172 °C (from ethyl acetate-pentane), $[\alpha]_D$ + 1.1° (*c* 5.4, C_2H_5OH)] in high yield. Similar treatment of oily **6*** led to the isolation of (−)-**7***: $[\alpha]_D$ −11.5° (*c* 5.5, C_2H_5OH), mp 163–164 °C (from ethyl acetate). That diastereomeric purity had been attained in both samples was convincingly revealed by tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III) shifting (5.7 mol %) of their ^1H NMR spectra in $CDCl_3$ solution. Whereas the cyclopropyl-bound methyl signal for (+)-**7*** appeared at δ 1.25, that for (−)-**7*** was well separated (δ 1.30). No intercontamination of these singlets was seen in the individual spectra.



The absolute configuration of (+)-**7*** was ascertained by three-dimensional X-ray analysis (Figure 1). A crystal of this substance proved to be orthorhombic, space group $P2_12_12_1$, with $a = 12.013$ (4), $b = 12.043$ (4), $c = 12.735$ (4) Å; $d_{\text{calcd}} = 1.274$ g cm^{-3} for $Z = 4$. The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse height discrimination). A crystal measuring approximately 0.15 × 0.25 × 0.35 mm was used for data collection. A total of 1439 reflections were measured for $\theta < 57°$, of which 1369 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple solution procedure[10] and was refined by full-matrix least squares. In the final refinement, anisotropic thermal parameters were used for the heavier atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indices are $R = 0.038$ and $wR = 0.044$ for the 1369 observed reflections. The final difference map has no peaks greater than ±0.2 eÅ^{-3}. Tables describing the final fractional coordinates and temperature factors, bond lengths, and angles have been placed in the microfilm version of the journal. With knowledge of the absolute configuration of the *endo*-bornylamine moiety,[6,11] that of the snoutane segment[12] can be assigned with confidence.

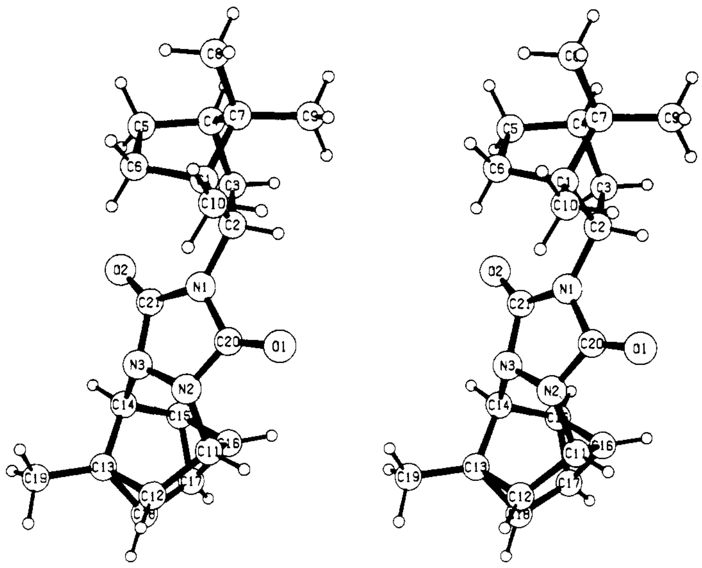


Figure 1. Three-dimensional view of (+)-**7*** as determined by X-ray analysis.

Hydrolysis-oxidation[3,6,13] of pure (−)-**7*** delivered the labile semibullvalene, $[\alpha]_D$ +11.7° (*c* 5.2, C_2H_5OH), whose absolute configuration therefore corresponds to that shown in **2**. The electronic and circular dichroic spectra of (+)-**2*** which appear in Figure 2 reveal the typical intense UV end absorption of the system and a reasonably intense negative $\pi \rightarrow \pi^*$ Cotton effect near 237 nm.

Although capable of rapid valence isomerization, semibullvalenes are otherwise conformationally rigid because of geometric constraints. Since it has previously been shown that the equilibrium for **2** is dominated largely by **2a**,[3] the chiroptical properties of (+)-**2*** are analyzed in terms of this tautomer. The methyl substituted π bond in (+)-**2a*** is seen to be embedded in an asymmetric environment formed by a "loop" consisting of a second vinylcyclopropane moiety. The rotatory contributions of such an array have been paid no attention in previous calculations on the rotational strengths of olefinic transitions. As Hudec and Kirk have succinctly pointed out, any attempts to calculate, from known group increments, values of $\Delta\epsilon$ for entirely new types of olefins, particularly those containing strained and five-membered rings, are unlikely to produce reliable results.[14] This conclusion was founded chiefly on the premise that these subunits would be apt to introduce

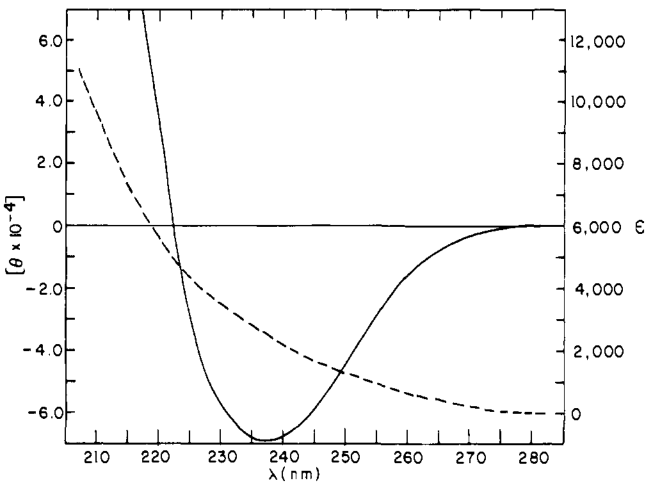
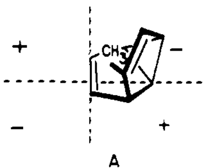


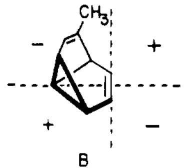
Figure 2. UV (- - -) and CD (—) spectra of (+)-**2*** (hexane solution).

deviations which are not predictable at our present state of knowledge.

The principal absorption band in (+)-**2a*** shall be considered in the present discussion as due to a $\pi \rightarrow \pi^*$ transition, although its precise spectroscopic assignment remains uncertain. Analysis of Figure 2 indicates that the sign of the CD curve due to this transition can be predicted by applying the Scott and Wrixon octant rule[15] to the outer semibullvalene framework in either of the two projection formulas (A and B) which do not position the methyl group in the noncontributory z plane of a left-handed Cartesian coordinate diagram. In A, the methyl group and its attached double bond are positioned in a front octant which is negative; the rear octant features which characterize B generate the identical result. Thus, the effect of methyl perturbation on the chiroptical properties of the semibullvalene nucleus is dissignate.[16]



A
(front octant)



B
(rear octant)

Although this analysis nicely correlates the negative Cotton effect of (+)-**2a*** with its absolute configuration, it has assumed that the double bonds in semibullvalene behave as isolated olefinic linkages. However, at least one theoretical analysis has raised the issue of dominant through-space interaction in molecules of this type.[17] Consequently, as additional chiral semibullvalenes become available, it may prove necessary to refine matters through application of coupled oscillator theory.[18,19]

Acknowledgment. This work was supported in part by the National Institutes of Health and the National Science Foundation.

Supplementary Material Available: Final atomic (Table I) and anisotopic thermal parameters (Table II), bond lengths (Table III), and bond angles (Table IV) for (+)-**7*** (3 pages). Ordering information is given on any current masthead page.

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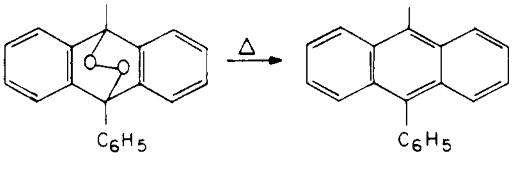
Magnetic Isotope Effect on the Thermolysis of 9,10-Diphenylanthracene Endoperoxide as a Means of Separation of ^{17}O from ^{16}O and ^{18}O

Sir:

In principle, magnetic fields will influence any chemical process involving a change in electron spin multiplicity.[1] The experimental question to be answered involves the magnitude of magnetic effects in cases of interest. Intersystem crossing (ISC, singlet-triplet or triplet-singlet) of organic radical pairs[2] (or diradicals)[3] has been shown to be sensitive to magnetic fields resulting from laboratory fields[4] and from nuclear magnetic moments.[5] When ISC of a radical pair is competitive with chemical or physical processes (which do not involve ISC), the efficiency of these processes will depend on magnetic fields. The observation of a magnetic isotope and/or a magnetic field effect on a chemical reaction is impressive evidence in support of radical pair or a diradical intermediate along the reaction pathway. A significant laboratory magnetic field effect was observed[6] on the relative yields of singlet ($^1O_2$) and triplet ($^3O_2$) oxygen produced from the thermolysis of 9,10-diphenylanthracene endoperoxide (DPA-O_2) as shown in eq 1.



$$+\ \alpha\,{}^1O_2 + (1-\alpha)\,{}^3O_2 \qquad (1)$$

The (simplified) mechanism shown in eq 2 was employed to interpret the basis of the influence of magnetic fields on the

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