alternative method of resolution[14] which afforded the levorotatory enantiomer of **9** having substantively higher rotatory power, $[\alpha]^{25}_{D}$ −310° (*c* 0.15, hexane).

Whereas **5** belongs to the C_1 point group, **9** has C_2 symmetry; both molecules are therefore dissymmetric although **5** is also asymmetric.[15] Because the parent cyclooctatetraene ring system is achiral (D_{2d} symmetry), any chiral moiety contained therein must be balanced by an enantiomeric moiety, a common occurrence. Thus, if C_1-C_2-C_3-C_4-C_5 has left-handed helicity, the segment C_1-C_8-C_7-C_6-C_5 has the enantiomeric right-handed helicity. For this reason, the substituted derivatives **5** and **9** cannot be referred to as "inherently dissymmetric" hydrocarbons, a designation which would be appropriate only if the substituents caused the [8]annulene framework to distort significantly to a chiral geometry or if the methyl groups participated so significantly in the electronic transitions under consideration that they would have to be considered an integral part of the chromophore.

In the present circumstances, therefore, neither the homoannular diene helicity rule[16] nor the allylic chirality rule[17] apply. Twisting about individual double bonds[18] similarly cannot be playing a significant role. In actual fact, the two CD curves taken in conjunction with the UV spectra (which show minimal π-π interaction, Figure 3) clearly reveal that "conjugated" polyene systems with distinct near-UV absorptions are *not* being dealt with. Rather, these systems consist essentially of four virtually unconjugated ethylene chromophores coupled principally by the electrostatic potential between the $\pi \rightarrow \pi^*$ transition dipoles.

The CD spectra of the pair of optically active cyclooctatetraenes unmistakably reveal that antipodes of like sign belong to the same enantiomeric series. The curve due to **9** is more complex, however, perhaps because of a higher concentration of the bicyclo[4.2.0]octatriene valence tautomer.[5] Notwithstanding, it remains difficult to know at this time which CD band is pertinent for any given analysis. Obviously, further study of the matter is required, a goal currently being pursued in these laboratories.

Acknowledgment. This investigation was supported in part by the National Cancer Institute, DHEW (Grant No. CA-12115), and the National Science Foundation (Grant No. CHE7608764). The authors are indebted to Professors A. W. Burgstahler, S. Mason, K. Mislow, A. Moscowitz, and A. I. Scott for their helpful comments.

Supplementary Material Available: Fractional coordinates and temperature factors, bond distances, bond angles, and observed and calculated structure factors for **1b** (Tables 1–4, respectively) and **7b** (Tables 5–8, respectively) (24 pages). Ordering information is given on any current masthead page.

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Bond Fixation in Annulenes. 6. Equalization of Ring Inversion and Bond Shifting Energetics in Methyl-Substituted Cyclooctatetraenes. Use of Buttressing Effects for Comparing Transition-State Geometries[1]

Sir:

Cyclooctatetraenes are recognized to be capable of conformational ring inversion (RI) and bond shifting (BS).[2] While it is generally accepted that RI occurs through the D_{4h} planar alternate transition state **1** ($\Delta G^{\ddagger}$ = 12–15 kcal/mol for monosubstituted derivatives[3]), the mechanism for BS has remained controversial. The planar symmetric D_{8h} species **2** has been advanced to explain the permutation of ring carbon

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Table I. Rate Data for Bond Shifting in (±)-**4** and (±)-**5**

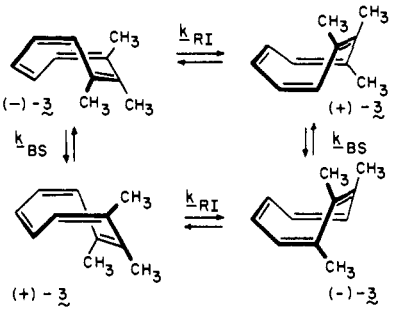
temp, °C	measd rate constants, s^{-1}	adjusted rate constants, s^{-1} [a]	activation parameters for **3**
50	1.08×10^{-5}	8.96×10^{-6}	E_{act} = 23.8 (±0.8) kcal/mol
70	1.26×10^{-4}	1.05×10^{-4}	ln A = 25.5 (±2.5)
90	6.3×10^{-4}	5.23×10^{-4}	$\Delta H^{\ddagger}_{(25°)}$ = 23.2 kcal/mol
			$\Delta S^{\ddagger}_{(25°)}$ = −7.9 eu
			$\Delta G^{\ddagger}_{(25°)}$ = 25.6 kcal/mol

[a] Assuming $k_H/k_D = 0.83$.[9]

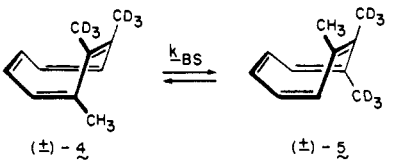
Table II. Rate Data for Racemization and Ring Inversion in **3**

temp, °C	racemzn rate constants, s^{-1}	extrapolated k_{BS}, s^{-1}	k_{RI}, s^{-1}	activation parameters
34.0	1.61×10^{-5}	1.43×10^{-6}	6.62×10^{-6}	E_{act} = 22.0 (±0.3) kcal/mol
42.3	4.12×10^{-5}	4.00×10^{-6}	1.66×10^{-5}	ln A = 24.1 (±0.9)
50.6	1.05×10^{-4}	1.06×10^{-5}	4.19×10^{-5}	$\Delta H^{\ddagger}_{(25°)}$ = 21.4 kcal/mol
				$\Delta S^{\ddagger}_{(25°)}$ = −10.6 eu
				$\Delta G^{\ddagger}_{(25°)}$ = 24.6 kcal/mol

Scheme I



Scheme II



connectivities, but the added $\Delta\Delta G^{\ddagger}$ increment (~2-3 kcal/mol)[3,4] is much less than that calculated by MINDO/2 and π approximations (13.9 and 15.4 kcal/mol, respectively)[5] and is contrary to most expectations concerning antiaromatic ($4n$) delocalization. We at this time present new experimental evidence in support of **2** as an acceptable representation of the BS activated complex and a theoretical explanation of its unusually low energetic requirements.

1 **2**

As concerns the response of (−)-1,2,3-Me_3COT[1] to thermal activation, enantiomerization will occur when either RI or BS operates (Scheme I).[6] Racemization will consequently obey

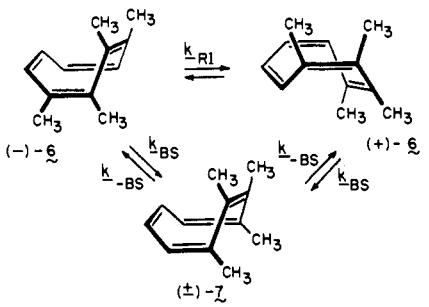
Table III. Rate Data for Racemization and Ring Inversion in (+)-**6**

temp, °C	racemzn rate constants, s^{-1}	k_{RI}, s^{-1}	activation parameters
120	1.956×10^{-5}	7.29×10^{-6}	E_{act} = 28.9 (±0.6) kcal/mol
140	1.172×10^{-4}	4.10×10^{-5}	ln A = 25.1 (±0.8)
160	5.867×10^{-4}	2.22×10^{-4}	$\Delta H^{\ddagger}_{(25°)}$ = 28.3 kcal/mol
			$\Delta S^{\ddagger}_{(25°)}$ = −8.7 eu
			$\Delta G^{\ddagger}_{(25°)}$ = 30.9 kcal/mol

Table IV. Rate Data for Bond Shifting in (±)-**6** and (±)-**7**

temp, °C	fraction of **7** at equilibrium	rate constants for **6** → **7**, s^{-1}	rate constants for **7** → **6**, s^{-1}	activation parameters for **6** → **7**
120	0.56	4.99×10^{-6}	3.92×10^{-6}	E_{act} = 28.4 (±2.0) kcal/mol
140	0.64	3.53×10^{-5}	1.99×10^{-5}	ln A = 24.3 (±2.4)
160	0.61	1.43×10^{-4}	9.14×10^{-5}	$\Delta H^{\ddagger}_{(25°)}$ = 27.8 kcal/mol
				$\Delta S^{\ddagger}_{(25°)}$ = −10.3 eu
				$\Delta G^{\ddagger}_{(25°)}$ = 30.9 kcal/mol

Scheme III



the rate law given by eq 1 and contain components of both processes. The factor 2 is obligatory because enantiomer production causes not only loss of the molecule undergoing dynamic change, but also negates the rotatory power of a second.

$$-(d\alpha/dt) = 2(k_{RI} + k_{BS})\alpha \quad (1)$$

To permit assessment of k_{RI}, k_{BS} was independently determined by subjecting the deuterium-labeled hydrocarbon (±)-**4**[7] to ^1H NMR kinetic analysis in diglyme-d_{14} solution. Advantage was taken of the different chemical shifts of the methyl groups in (±)-**4** and (±)-**5** (Scheme II).[4e] In order to utilize the measured BS rate constants (Table I) for interpretation of the racemization data, correction for the deuterium steric isotope effect was necessary. Drawing on the prior experiences of others,[8] we have deemed a k_H/k_D of 0.83 to be appropriate.

Racemization rates were likewise determined in diglyme solution and plots of −ln α vs. time gave straight lines whose slopes equalled $2(k_{RI} + k_{BS})$. These data are summarized in Table II[9] together with extrapolated values of k_{BS}, the computed values of k_{RI}, and the activation parameters.

The rate law governing the racemization (Table III) of (+)-1,2,3,4-Me_4COT[1] (eq 2) takes a somewhat different form because only RI leads to enantiomerization (Scheme III). Isomer **7** is a meso compound and, although its production does result in racemization, additional rotatory power is not lost. Bond shifting measurements on (±)-**6** in diglyme-d_{14} solution utilizing ^1H NMR techniques were made possible by the

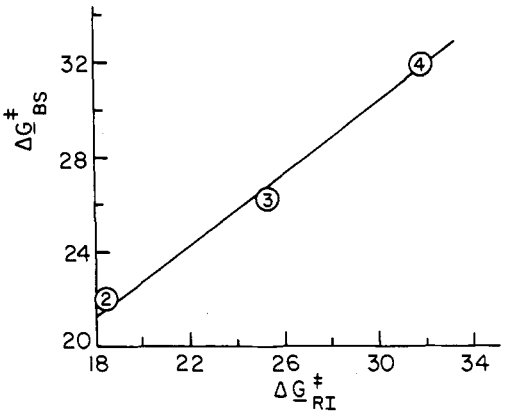


Figure 1. Plot of $\Delta G^{\ddagger}_{BS(122°)}$ vs. $\Delta G^{\ddagger}_{RI(122°)}$ as a function of the level of alkyl substitution. The encircled numeral relates to the number of pendant groups.

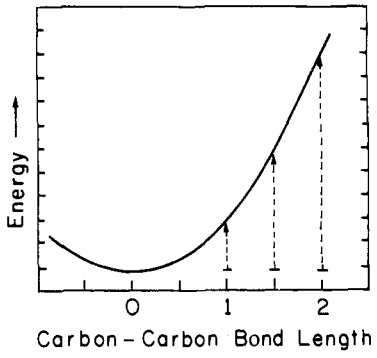


Figure 2. Morse curve relating strain energy to Me-Me separation in transition states **1** and **2**.

Table V. Summary of $\Delta\Delta G^{\ddagger}_{(122°)}$ Values as a Function of Alkyl Substitution

substn plan	$\Delta G^{\ddagger}_{RI(122°)}$	$\Delta\Delta G^{\ddagger}$	$\Delta G^{\ddagger}_{BS(122°)}$	$\Delta\Delta G^{\ddagger}$
1,2-Me_2	18.4[a]		21.1	
		7.2		5.2
1,2,3-Me_3	25.6		26.3	
		6.1		5.6
1,2,3,4-Me_4	31.7		31.9	

[a] Measured at 70 °C (NMR experiment) for 2-methylcyclooctatetraenylmethyl *O*-methylmandelate.

presence of distinctive methyl resonances in the two isomers[4c] (Table IV).

$$-(d\alpha/dt) = (2k_{RI} + k_{BS})\alpha \qquad (2)$$

When the free energies of activation determined above are taken together with the $\Delta G^{\ddagger}_{RI(70°)}$ measured for 2-methylcyclooctatetraenylmethyl *O*-methylmandelate[4a,10] and the $\Delta G^{\ddagger}_{BS(122°)}$ assessed for 1,2-Me_2COT,[11] two important points emerge. The first and most obvious one is the progressively heightened barrier to both RI and BS as the level of vicinal alkyl substitution is increased (Table V). For **6**, *the two processes are equally energy demanding!* More informative are the differing incremental energy changes ($\Delta\Delta G^{\ddagger}$) observed for the two reaction channels. In the RI mode, the di → tri and tri → tetra progressions generate $\Delta\Delta G$'s of 7.2 and 6.1 kcal/mol, values which are larger than those associated with BS (5.2 and 5.6 kcal/mol, respectively).[12] These effects are best viewed by plotting $\Delta G^{\ddagger}_{BS}$ vs. $\Delta G^{\ddagger}_{RI}$ (Figure 1). A straight line is obtained having a positive slope (0.809), thereby denoting that the impact of cumulative substitution is greater on RI energetics.

These results are cogently accommodated by transition-state structures **1** and **2**. Using the degenerate behavior of **3** as an example, one sees that flattening of the tub to give 1,2,3-Me_3-**1** generates a transition state having one Me-Me double-bond interaction and one Me-Me single-bond interaction. In contrast, passage through 1,2,3-Me_3-**2** causes two Me-Me 1,5-bond interactions to develop. As the Morse curve in Figure 2 graphically illustrates, the sum of the interactions in the planar alternate form should exceed those that develop in the planar delocalized species.

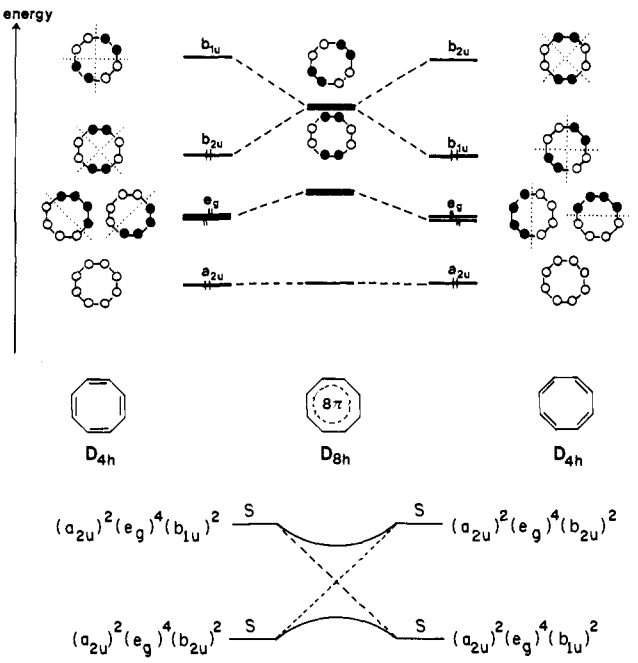


Figure 3. Correlation (top) and state diagrams (bottom) for bond shifting in COT.

The causative factor underlying the relatively low energetics of bond shifting can be seen from a correlation diagram of the occupied MO's and LUMO of both planar COT bond shift isomers (Figure 3). As with cyclobutadiene, an orbital crossing is required and the interconversion is therefore "forbidden", a fact which is also apparent from the state diagram shown. Two of the three possible singlet configurations of D_{8h} COT possess the same energy and thus repel each other strongly. This leads to a net lowering of the activation energy.[13,14]

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(9) Because our original sample of optically active **3** is now recognized to have been impure,[1] the racemization data reported earlier[4e] is in error and should not be considered relevant.
(10) Anet and Bock[4a] observed that the diasterotopic methyl signals which appear at δ 1.73 and 1.62 (60 MHz) coalesce at 70 °C. Through use of the formula $k_{coal} = \pi\Delta\nu/\sqrt{2}$ to approximate the rate constant for ring inversion and substitution of this value into the Eyring equation,[8] we have obtained the $\Delta G^{\ddagger}_{R(70°)}$ value cited in Table V.
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(14) This investigation was supported in part by the National Cancer Institute, DHEW (grant No. CA-12115), the National Science Foundation (Grant No. CHE7608764), the Deutsche Forchungsgemeinschaft, and the Fonds der Chemischen Industrie. Enlightening exchanges of information were had with Professors Jack Hine and Gerhard Binsch.
(15) The Ohio State University Dissertation Fellow, 1977–1978.

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Configuration and Planarity of Fluorescent and Nonfluorescent 1,5-Diazabicyclo[3.3.0]octadienediones (9,10-Dioxabimanes) by X-ray Crystallography

Sir:

We have recently described the synthesis and some properties of an essentially new class of compounds, the 1,5-diazabicyclo[3.3.0]octadienediones (briefly, 9,10-dioxabimanes or "bimanes").[1] We now confirm that strongly fluorescent bimanes are syn isomers and weakly fluorescent bimanes are anti isomers (see formulas below). We further report that some *syn*- and *anti*-bimanes are planar and that others are nonplanar, including an unusual dicyanomethylene bridged bimane. These facts are established by X-ray crystallography from data recorded on a four-circle diffractometer with structures solved by direct methods. There is no obvious relationship between the planarity and the photophysical properties as will be described in more detail elsewhere.[2]

Single crystals of the strongly fluorescent $(C_6H_5,Cl)B$ isomer were grown from acetonitrile solution. The crystal data are $a = 6.822$ Å, $b = 10.614$ Å, $c = 11.589$ Å, $\alpha = 100.79°$, $\beta = 81.98°$, $\gamma = 102.16°$, space group $P\bar{1}$, and $Z = 2$. An anisotropic least-squares refinement of the structural model converged to $R = 0.069$. The structure reveals a diazabicyclooctanedione system with both carbonyl groups on the same side: a *syn*-bimane. The central part of the molecule is slightly bent about the N–N bond, the dihedral angle between the adjacent five-atom rings being 171.6°. The crystal packing seems to be affected by strong dipolar interactions between molecules related to each other by the inversion center with overlap and interplanar distance closely resembling those for heteromolecular π complexes (Figure 1). The shortest interatomic contact between the overlapping moieties is the N···N distance of 3.18 Å. The distances of the atoms in one diazabicyclooctane unit from the mean plane of the framework of the second unit are in the range of 3.22–3.50 Å and average 3.34 Å. (Fluorescent $(CH_3,H)B$ has a "π-complex" syn structure similar to that of the $(C_6H_5,Cl)B$ described above.[3])

The weakly fluorescent $(C_6H_5,Cl)B$ crystallized from dichloromethane and diethyl ether in space group $P2_1/n$ and

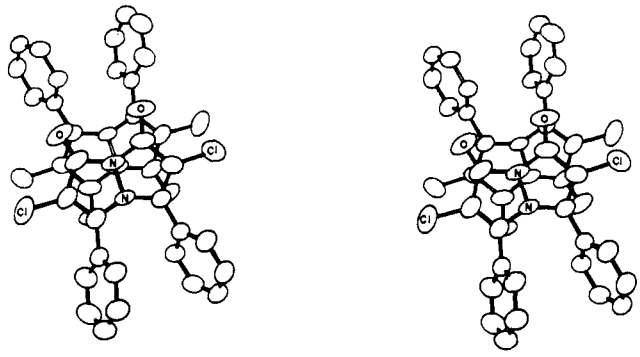
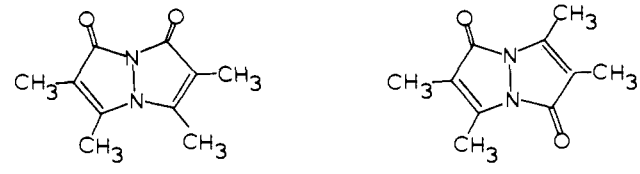


Figure 1. Computer generated (stereo-) drawing of *syn*-$(C_6H_5,Cl)B$ (*syn*-"phenylchlorobimane") illustrating the close approach of pairs of molecules suggestive of π-complex formation.

with $a = 9.942$ Å, $b = 16.132$ Å, $c = 10.529$ Å, $\beta = 110.88°$, $Z = 4$. The structure has been refined to $R = 0.050$. It shows an anti arrangement of the carbonyl groups and phenyl substituents with respect to the molecular framework. The diazabicyclooctane units deviate strongly from planarity, the dihedral angle around the central N–N bond being 147.3°.

The correspondence found between the molecular configuration and fluorescence for the "phenylchlorobimane" isomer pair also holds for the "methylmethylbimane" isomeric pair (formulas shown).

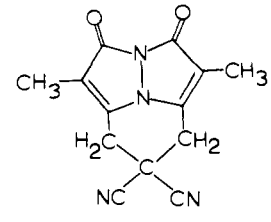


syn-$(CH_3,CH_3)B$ — strongly fluorescent

anti-$(CH_3,CH_3)B$ — weakly fluorescent

The data for crystals of the two "methylmethyl" bimanes follow: (a) *syn*-$(CH_3,CH_3)B$, $a = 6.608$ Å, $b = 6.043$ Å, $c = 13.300$ Å, $\beta = 113.71°$, space group Pc with $Z = 2$; (b) *anti*-$(CH_3,CH_3)B$, $a = 3.953$ Å, $b = 10.783$ Å, $c = 11.499$ Å, $\beta = 92.81°$, space group $P2_1/c$ with $Z = 2$. The tetramethyl substituted *anti*- and *syn*-diazabicyclooctadienone structures have been refined anisotropically to $R = 0.054$ and $R = 0.041$, respectively. The former is planar since it occupies a crystallographic inversion site of symmetry; the latter, occupying a general crystallographic position, is planar within experimental error. In the anti isomer, molecules are stacked along the a axis of the crystal unit cell, the separation perpendicular to the molecular plane being only 3.54 Å. For the syn isomer, the molecules are stacked along the b axis in two types of columns related by the glide plane. A "π-complex" arrangement is not present in the crystal; there is little overlap between adjacent units in the stack, and the corresponding perpendicular distance between molecular planes is also relatively large (3.65 Å). A single structure of an *anti*-bimane has previously been reported, but it is not sufficiently accurate to allow detailed comparison with our work.[4]

Crystal data for the bridged *syn*-bimane, the μ-$[(CN)_2C]$-*syn*-(CH_2,CH_3) (formula shown), follow: $a = 9.956$ Å, b



μ-$((CN)_2C)$-syn-$(CH_2,CH_3)B$

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