was unfortunate because it has been reported[35] that in solution ketones form two types of 1:1 hydrogen-bonded complexes using the π system in one type and a lone-pair oxygen donor orbital in the other. In solution the enthalpy measured is an average of both adducts. Since it is well established that K's are very different in the gas phase than in solution, a different ratio of the two types of complexes in the gas phase and in solution could lead to a difference in enthalpy that is independent of solvation by CCl_4. Furthermore, if in nonpolar, nonbasic solvents (previously called "inert" by us, but more appropriately called innocent), the base were aggregated (say, an average molecular weight of a dimer), our E_B and C_B parameters would be for this dimer. If the base were a monomer in the gas phase, different E_B and C_B parameters might apply, and any differences could not be attributed to solvation by CCl_4. For this reason, we have been very careful to specify the solvents that should be employed to study the various bases in the E and C correlation. If the degree of aggregation were constant in a series of nonpolar solvents, the E and C parameters for the aggregate would be more relevant to the chemistry in solution than those of the individual molecules. If E_B and C_B changed with aggregation and different degrees of aggregation exist in different solvents, ESP will not work. Clearly, the combination of gas-phase and ESP studies are important for they can provide us with clues to the nature of the species in solution. Furthermore, if for *most* of the bases and acids in the E and C correlation the enthalpy in the gas phase were to differ from that in our innocent solvents by a constant amount, the data in solution would be related to the properties of the isolated donors and acceptors.

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Calculations of Rotatory Strengths in Chiral Chromophores: Cisoid Conjugated Dienes

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Abstract: Observation of the chiroptical effects of dissymmetrically disposed substituents has led us to reexamine the circular dichroism of the lowest $\pi \rightarrow \pi^*$ transition in nonplanar conjugated dienes. Oscillator and rotatory strengths of some skewed dienes with allylic substituents have been calculated, using both the CNDO/S and the CNDO/2 methods without configuration interaction. The CNDO/S method reproduces very well the experimental variation of the circular dichroism with changes in the allylic substituent. The reasons for the extreme sensitivity of the rotatory strength to the substituents are explored. Rotatory strengths for twisted butadiene are compared with those for model planar diene systems which are dissymmetrically substituted. The calculations confirm that the effect of the sense of twist does not always outweigh the effect of dissymmetric substituents.

Some years ago, an analysis of the relationship between the inherent diene chirality of nonplanar cisoid conjugated dienes and the sign of the Cotton effect associated with their lowest energy $\pi \rightarrow \pi^*$ transition led to the proposal of what has become known as the "diene chirality rule".[1] The rule states that a cisoid conjugated diene exhibits a positive or a negative circular dichroism (CD) depending on whether the diene is twisted about the central bond in a right- or left-handed sense (Figure 1), respectively. The sign of this band is attributed solely to the sense of helicity of the diene, and takes no account

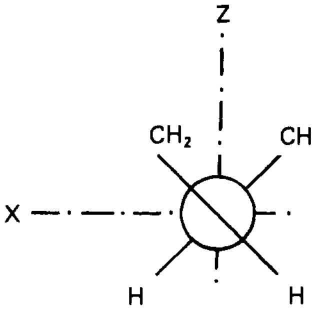


Figure 1. Definition of right-hand skew sense.

of dissymmetrically disposed substituents. The rule, predicted by Hückel calculations on twisted butadiene,[2] was found to be valid for more than 30 compounds in the original study and for many more since.[3] Observations made largely by Burgstahler and his associates[4] on various substituted dienes led to empirical rules which focused attention on the chirality relations between axial allylic substituents and the diene. Their efforts were very helpful in delineating the problem, but complete clarity was frustrated by the inability to account for all the observations or to establish unique general relationships. Very recently, a set of experimental observations[5] were made which seemed to provide an excellent opportunity to test the effect of dienic chirality and substituents on the CD of cisoid dienes. These results form the initial basis for the SCF calculations, which are the subject of this communication. Most, but not all, of the compounds for which the Hückel treatment was successful contained a common extended chromophoric system; namely, they contained at least one axial alkyl group allylic to the 1,4 carbons of the diene. These calculations show that in these compounds the rotatory strength arising from the skewed diene alone is of the same sign as that of the extended chromophore. An analysis of the relationship between these new results and the stereoregularity of dienic compounds will be published elsewhere.[6]

Since the Hückel molecular orbital calculations of twisted butadiene,[2] there have been a number of calculations of the rotatory strength of the butadiene chromophore. Maestro et al.[7] performed calculations using a one-dimensional model with a periodic potential, and Nolte and Buss[8] applied the one-dimensional electron-gas model to a skewed diene. Cheong et al.[9] treated the π electrons of butadiene as a function of skew angle, using the Pariser-Parr-Pople scheme. A few all-valence-electron calculations of the rotatory strength of butadiene have been performed. Gould and Hoffmann[10] applied extended Hückel theory to butadiene as a function of skew angle. Hug and Wagniere[11] used the CNDO-CI method, with parameters very similar to those of Del Bene and Jaffé,[12] to calculate the rotatory strength of butadiene as a function of skew angle. Rauk et al.[13] have recently compared a number of computational methods; CNDO/2,[14] INDO,[15] a nonempirical approximate scheme they call ODIN, and the ab initio Hartree-Fock method with a minimal Slater basis, all without configuration interaction (CI). Their calculations were performed on butadiene at the three skew angles 45, 90, and 135°. In all the above calculations, with the exception of the CNDO/2 and INDO ones of Rauk et al.[13] at the angle of 45°, the rotatory strength associated with the lowest $\pi \rightarrow \pi^*$ transition in butadiene skewed in a right-handed sense is predicted to be positive, in agreement with the original diene chirality rule. To our knowledge, no calculations have been reported for systems in which the diene chromophore is incorporated in a larger molecule.

After describing the method of computation, we discuss the calculations which we have performed for model compounds in which the diene system is rigidly fixed in a nonplanar geometry. Then, in order to estimate the relative importance of the diene helicity and dissymmetric substituents to the rotatory strength of cisoid dienes, we present two sets of calculations. First the calculated rotatory strength of butadiene is considered as a function of skew angle. Then, we examine some calculations on the simplest model compounds having planar diene systems, but which have nonzero rotatory strengths by virtue of dissymmetrically disposed substituents. The effect of CI in two selected cases is examined. Finally, we discuss the conformationally mobile cisoid diene, α-phellandrene.

Methods of Calculation

The SCF-MO calculations were carried out using both the CNDO/S method, which was parameterized by Del Bene and Jaffé[12] to reproduce spectral properties of aromatic systems, and the CNDO/2 method, parameterized by Pople and Segal[14] to account for ground-state properties. Excited states were constructed in the single configuration approximation. The oscillator and reduced rotatory strengths for the electronic transition $|A\rangle \rightarrow |J\rangle$ were calculated according to the following formulas:

$$f(A \rightarrow J) = (8\pi^2 m/3he^2)\nu_{AJ}|\langle A|\mu|J\rangle|^2 \quad (1)$$

$$R(A \rightarrow J) = (100/\beta D)\mathrm{Im}[\langle A|\mu|J\rangle \cdot \langle J|\mathbf{m}|A\rangle] \quad (2)$$

where μ and $\mathbf{m}$ are the electric and magnetic dipole moment operators, respectively, m is the electron mass, ν_{AJ} is $(E_J - E_A)/h$, β is the Bohr magneton, D is the Debye unit, and Im denotes the imaginary part of the expression in brackets. The operators, μ and $\mathbf{m}$, are defined as follows:

$$\langle A|\mu|J\rangle = e\left\langle A\middle|\sum_i \mathbf{r}_i\middle|J\right\rangle \quad (3)$$

or

$$\langle A|\mu|J\rangle = -e\hbar^2\left\langle A\middle|\sum_i \nabla_i\middle|J\right\rangle \Big/ m(E_A - E_J) \quad (4)$$

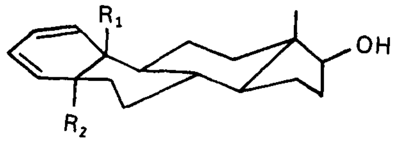
and

$$\langle A|\mathbf{m}|J\rangle = -ie\hbar\left\langle A\middle|\sum_i \mathbf{r}_i \times \nabla_i\middle|J\right\rangle \Big/ 2mc \quad (5)$$

All one- and two-center electric and magnetic dipole matrix elements were evaluated using symmetrically orthogonalized[16] Slater orbitals. Electric dipole matrix elements were calculated using both dipole length and dipole velocity operators. It has been shown that rotatory strengths calculated with the dipole velocity form of the operator are origin independent, unlike those calculated using the dipole length operator.[17] A test calculation on one of the model compounds in the CNDO/S parameterization provided a striking confirmation of this.[18] Consequently, only the results using the velocity operators are reported here.

Results and Discussion

Skewed 1,3-Cyclohexadienes. The particular exceptions to the diene chirality rule, which were the initial impetus for these calculations, are exemplified in the steroidal 5α 1,3-diene series I-III.[5] In these conformationally rigid molecules of known absolute configuration, the diene chromophore is skewed in a left-handed sense. However, the sign and magnitude of the



I, $R_1 = R_2 = H$
II, $R_1 = CH_3$; $R_2 = H$
III, $R_1 = R_2 = CH_3$

Table I. Oscillator and Rotatory Strengths of Skewed 1,3-Cyclohexadienes Calculated by CNDO/S Method

Compd	λ^a	f^a	R	R (obsd)	Diene rule sign
IV	238	0.19	12.0	14.9	−
V	241	0.18	−6.7	−8.4	−
VI			−7.9	c	−
VII	246	0.17	−27.0	−37.0	−
VIII	237	0.19	−2.6	-3.7^b	−

[a] Observed values for 1,3-cyclohexadiene: λ_{max} 248, f = 0.14. [b] Observed value for the enantiomer of palustric acid. [c] We are unaware of any compound corresponding to this structure for which experimental data exists.

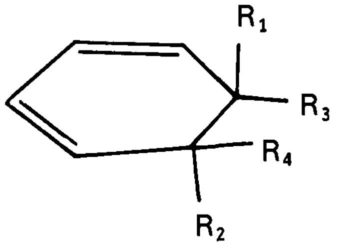
Table II. Oscillator and Rotatory Strengths of Skewed 1,3-Cyclohexadienes Calculated by CNDO/2 Method

Compd	λ^a	f^a	R	R (obsd)	Diene rule sign
IV	143	0.06	−84.8	14.9	−
V	144	0.06	−91.6	−8.4	−
VII	146	0.06	−101.2	−37.0	−
VIII	141	0.08	−88.7	-3.7^b	−

[a] Observed values for 1,3-cyclohexadiene: λ_{max} 248, f = 0.14. [b] Observed value for the enantiomer of palustric acid.

Cotton effect of the lowest energy $\pi \rightarrow \pi^*$ transition changes as the allylic axial methyl substituents are progressively replaced by hydrogen atoms. Compound III, with two axial methyls, has a negative CD, in agreement with the diene chirality rule, diene II has a negative CD which is markedly reduced in magnitude relative to III, while diene I exhibits a *positive* CD.

We have performed calculations of the rotatory strengths of some molecules, IV–VIII, which should serve as models for



IV, $R_1 = R_2 = H$; $R_3 = R_4 = CH_3$
V, $R_1 = CH_3$; $R_2 = H$; $R_3 = R_4 = CH_3$
VI, $R_1 = H$; $R_2 = CH_3$; $R_3 = R_4 = CH_3$
VII, $R_1 = R_2 = R_3 = R_4 = CH_3$
VIII, $R_1 = R_2 = R_3 = R_4 = H$

these steroidal dienes. Geometric parameters were taken from the x-ray diffraction study[19] of a related steroid which is also an exception to the diene rule. The skew angle for this geometry is 14.4°.

The results of the calculations performed according to the CNDO/S method are shown in Table I. Approximate experimental rotatory strengths are obtained from experimental $\Delta\epsilon$ values for the corresponding real compounds using the following expression:[20]

$$R = 43.956\ \Delta\epsilon(\Delta/\lambda) \qquad (6)$$

where Δ is the half width of the CD band assumed to be Gaussian in shape and λ its wavelength. The rotatory strengths are in remarkable agreement with experiment, when one considers how sensitive this property is to the quality of the wave functions. The trends of sign and magnitude are reproduced very well. The calculated oscillator strengths are in good agreement with the experimental value for 1,3-cyclohexadiene. For molecule VIII, we have chosen to compare the calculated results with the experimental values for the diterpenoid palustric acid, which has four corresponding allylic hydrogen atoms. Atomic models of palustric acid are conformationally flexible, indicating that the diene system could exist with either sense of helicity. However, recent measurements[21] indicate that the CD of this compound is not temperature dependent and therefore the barrier to the conformational conversion must be very high.

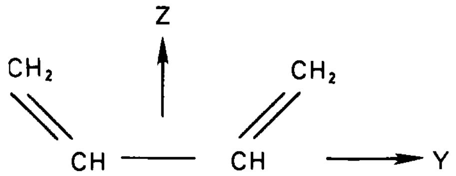


Figure 2. Cartesian coordinate system for diene chromophore.

The CNDO/2 results, presented in Table II, are less in accord with experiment. The magnitudes of the rotatory strengths are much too high, and the experimentally observed sign change between compound IV and the others is not reproduced. Oscillator strengths are similarly less well reproduced by the CNDO/2 method. This difference in the results produced by the two parameterizations must be related to the increased perturbing influence, in CNDO/2, of σ-type molecular orbitals on the π orbitals of the diene chromophore. In the CNDO/2 calculations on these molecules, the highest filled σ-type orbital is only about 1 eV lower than the highest filled orbital, which is a π-type orbital localized on the diene chromophore. In the CNDO/S calculations, the highest filled σ orbital is approximately 2 eV lower than the highest filled π orbital. Comparison of the coefficients of the orbitals obtained with the two methods of calculation shows that for both the π and π^* orbitals, but particularly the highest filled π orbital, the coefficients of the $2p_x$ AO's (see Figure 2 for definition of the coordinate axes) on the diene chromophore are reduced in the CNDO/2 orbitals, relative to the CNDO/S orbitals.

In planar *cis*-butadiene, which belongs to the point group C_{2v}, the lowest $\pi \rightarrow \pi^*$ state transforms as B_2, and is thus both electric and magnetic dipole allowed, but along mutually orthogonal axes; electric and magnetic dipole transition moments are in the y and x directions, respectively. The calculated electric moment is about 3 D and the calculated magnetic moment is about 0.5 μ_B. Thus, in chiral cisoid dienes the rotatory strength, determined by the scalar dot product given in eq 2, arises from a "borrowed" magnetic dipole transition moment in the y direction as well as a "borrowed" electric dipole transition moment in the x direction. In our calculations, *the x and y components of this scalar dot product are of comparable magnitude, and in the model compounds IV–VIII, they are of opposite sign.*[22] This seems to be the origin of the high sensitivity of the rotatory strength to the nature of the allylic axial substituent.

In an attempt to understand the physical significance of the observed sign change, we have examined further the $\langle\pi|\nabla_x|\pi^*\rangle$ matrix element in IV–VIII by breaking down this MO matrix element into one- and two-center atomic contributions. As one replaces allylic axial hydrogen atoms by methyl groups the matrix element $\langle\pi|\nabla_x|\pi^*\rangle$ increases in magnitude, and the sign of the scalar dot product (eq 2), made up of two terms of opposite sign, changes sign. The largest contribution to this effect seems to be a one-center term on the carbon atom of the axial allylic methyl group. Thus an induced atomic electric dipole transition moment appears to be responsible for

Table III. Oscillator and Rotatory Strength of Lowest B State in Butadiene as a Function of Skew Angle

	CNDO/S			CNDO/2		
Angle	λ	f	R	λ	f	R
0 (cis)	216	0.23	0	117	0.13	0
10	215	0.23	9.5	117	0.13	2.8
20	213	0.24	16.4	116	0.13	3.8
45	202	0.26	16.2	111	0.16	−8.9
70	188	0.26	2.6	106	0.17	−54.3
90	180	0.22	127.6	103	0.15	107.6
110	191	0.31	126.3	107	0.17	93.6
135	199	0.41	95.4	109	0.21	68.1
160	203	0.46	45.4	110	0.25	32.8
180 (trans)	203[b]	0.47[b]	0	110[b]	0.26[b]	0

[a] Right-hand skew sense. [b] Observed values for *trans*-butadiene: λ 209 nm, $f = 0.4$.

Table IV. Rotatory Strength Induced by Dissymmetric Substituents on Planar Diene System

			CNDO/2	
Compd	CNDO/S		No CI	With CI[a]
IX	17.7	"$\sigma \rightarrow \pi^*$"	14.0	−3.6
		"$\pi \rightarrow \pi^*$"	11.9	26.3
X	36.3	"$\sigma \rightarrow \pi^*$"	62.6	1.0[b]
		"$\pi \rightarrow \pi^*$"	−30.3	24.8
XI	17.4	"$\sigma \rightarrow \pi^*$"	10.5	−0.6
		"$\pi \rightarrow \pi^*$"	12.0	21.0

[a] Configuration interaction between two lowest excited states. [b] There is a large mixing of configurations in this case. The coefficient for the "$\sigma \rightarrow \pi^*$" configuration in this state is 0.87.

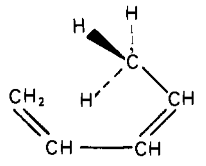
the changes observed in replacing methyl groups with hydrogen atoms.

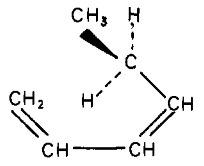
Skewed Butadiene. In order to compare that part of the rotatory strength which arises from the twisting of the butadiene chromophore about the central bond with that which arises from dissymmetrically disposed substituents outside the butadiene chromophore, we have calculated the optical properties of butadiene as a function of skew angle. These results will be compared in the next section with calculations performed for model planar diene systems, which are dissymmetrically substituted. The optical properties of butadiene as a function of skew angle have been computed before, but we believe it necessary to make these comparisons using wave functions obtained by the same computational scheme.

When the four atom system is skewed, the symmetry of *cis*-butadiene is reduced from C_{2v} to C_2, and the lowest $\pi \rightarrow \pi^*$ state, which transforms as B_2 in the planar cis case, correlates with a B state in the skewed conformer, finally transforming as B_u in the C_{2h} point group of the planar trans configuration. Table III shows the oscillator and rotatory strengths calculated using both the CNDO/S and CNDO/2 methods for butadiene at a number of right-handed skew angles ranging from 0 (cis) to 180° (trans). The calculated CNDO/S oscillator strength for the trans case agrees well with experiment. The ratio $f(\text{trans})/f(\text{cis})$ is calculated by all the methods to be about two, in agreement with the calculations of Allinger and Miller,[23] Hug and Wagnière,[11] Charney,[2] and Cheong et al.[9] The experimental estimate for this ratio is three. The trend of the oscillator strength as a function of skew angle follows closely the π-electron calculations of Cheong et al. when CI is omitted. With CI, these authors calculate $f = 0$ at 90°, as do Allinger and Miller, whose π-electron calculations include CI. Hug and Wagnière, with CNDO calculations including CI, do not obtain $f = 0$ at 90°. The Hückel calculation gives a value of about $f = 0.4$.

Looking now at the calculated rotatory strengths, the CNDO/S method predicts a positive sign for all the right-handed skew angles, *in agreement with the diene rule*, but does not reproduce the monotonic increase in magnitude from 0 to 90° calculated by other authors. However, when Gould and Hoffmann,[10] and Cheong et al.[9] include CI, sign changes are observed in this range of angles. With the CNDO/2 calculations, we see sign changes at 45 and 70°, in agreement with the CNDO/2 and INDO calculations at 45° of Rauk et al. All methods predict a monotonically decreasing rotatory strength on going from 90 to 180°. We would caution against putting much credence in the calculations performed for the larger angles of twist, particularly in the 70–110° range. The near orbital degeneracies which occur make it hard to justify the omission of CI in these cases.

Planar Butadiene with Dissymmetric Substituents. Table IV shows the rotatory strengths calculated for the following model compounds (IX–XI). In these molecules the only atoms which


IX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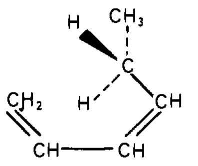

XI

are out of the plane of the diene chromophore are the hydrogen substituents and the hydrogen and methyl substituents on the methyl carbon in IX, X, and XI. The geometries chosen are those that would mimic an axial allylic hydrogen or methyl (IX and X, respectively) or an axial hydrogen and equatorial methyl (XI) in 1,3-cyclohexadiene. To facilitate comparison with these calculations, the geometric parameters for compounds IV–XI are available in the microfilm edition. What is immediately striking in the CNDO/S calculations is that the rotatory strength for IX, where the only out-of-plane atoms are hydrogens, is as large as that for butadiene with a skew angle of 20°. In X, with an out-of-plane methyl, the rotatory strength increases by about a factor of 2. Compound XI, with an out-of-plane methyl mimicking an equatorial methyl in cyclohexadiene, shows magnitudes differing little from that of IX, as expected, since the equatorial carbon lies only slightly off the nodal plane of the π-electron system. In the CNDO/2 computations, the lowest energy configuration was "$\sigma \rightarrow \pi^*$", and we report the results for this transition as well as the "$\pi \rightarrow \pi^*$". When these two configurations are allowed to interact, sign changes are observed. In X, there is a large interaction between the two configurations. Again, with the CNDO/2 results, the magnitudes relative to those of skewed butadiene are surprisingly large. These calculations show that the contribution of dissymmetric substituents to the rotatory strength of chiral cisoid dienes may be comparable to and even outweigh the contributions arising from the intrinsic dissymmetry of the diene.

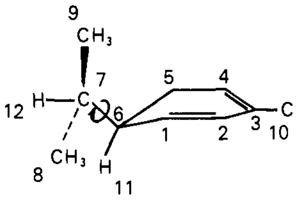
Effect of Configuration Interaction. Although not always found to be true, configuration interaction is generally expected in semiempirical MO schemes to improve the values of computed parameters. We have studied the effect of configuration interaction on the optical properties of the lowest $\pi \rightarrow \pi^*$ transition of butadiene at a skew angle of 20°, using the CNDO/S method. At this time we have been able to include only 55 out of a total of 61 singly excited B configurations. Nevertheless, this seems to be sufficient to indicate what would

Table V. Effect of Configuration Interaction in Twisted Butadiene (dihedral angle 20°) CNDO/S

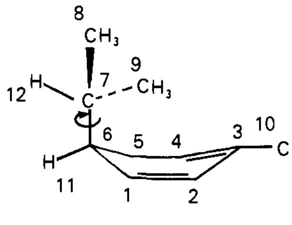
No. of B configurations	λ	*f*	*R*
1	213	0.24	16.3
10	214	0.22	−15.7
20	215	0.17	−26.4
30	226	0.09	1.2
40	243	0.10	−1.3
50	251	0.10	6.7
55	253	0.11	6.2

be obtained by including all singly excited configurations. The results are presented in Table V. The striking sign changes observed in the calculated rotatory strength as a function of the number of configurations raises serious reservations about semiempirical calculations of rotatory strengths with limited CI. It does appear that the optical properties are converging as the limit of all singly excited configurations is approached. The calculated rotatory strengths *appear to be approaching the results calculated without CI* both with respect to sign and magnitude. Bouman and Lightner[24] have found a similar erratic behavior of the rotatory strength of the ketones as a function of CI, and found that the CNDO/S method without CI reproduces well the rotatory strengths of the $n \rightarrow \pi^*$ transition in this class of molecules. For dienes larger than butadiene, and in particular the substituted cyclohexadienes with which we have been concerned, the number of singly excited configurations becomes prohibitively large in the context of semiempirical calculations. In a study of the effect of the inclusion of 10, 20, and 30 configurations on the rotatory strength of compound IV, we found that the agreement with experiment becomes progressively worse as the number of configurations is increased up to 30. It appears from these results that, in dienes of low symmetry where it would be impractical to include all singly excited configurations, rotatory strengths calculated by the CNDO/S procedure without CI are likely to be in better accord with experiment than those calculated with limited single excitation CI. Even the inclusion of all singly excited states would not necessarily improve the agreement with experiment. It remains to be seen whether this is generally characteristic of rotatory strengths.[25]

α-Phellandrene. An interesting and particularly exacting test of the applicability of the considerations discussed above is the calculation of the rotatory strength of the conformationally flexible molecule α-phellandrene, whose chiroptical properties have been studied by several investigators.[26] The molecule can and does exist in two conformers at room temperature. In one, the isopropyl group is in a quasi-equatorial position (XII) and in the other a quasi-axial one (XIII). Experimental data[26d,e] show that the CD is temperature dependent, with a $\Delta\epsilon$ of −10.03 at 20 °C and a $\Delta\epsilon$ of 5.5 at −177 °C. Photochemical investigations[26f] indicate that the quasi-equatorial conformer is more stable than the quasi-axial one by 0.46 kcal/mol. In XII, where the isopropyl group is equatorial, the diene system is skewed in a right-handed sense, while in XIII, the diene helicity is left-handed. Thus, the experimental data are consistent with the diene helicity rule, provided that the axial conformer has a significant population at room temperature and/or has a very much larger rotatory strength than the equatorial conformer.



XII



XIII

Table VI. Rotatory Strength of α-Phellandrene[a]

	CNDO/S	CNDO/2	"Diene rule" sign
	Quasi-Equatorial Isopropyl Conformation		
XII A	−2.7	71.6	+
B	−3.7	75.7	+
C	−5.5	74.5	+
	Quasi-Axial Isopropyl Conformation		
XIII A	−24.8	−80.1	−
B	15.6	−51.1	−
C	17.4	−46.6	−

[a] Observed rotatory strength: −35 (20°), 19 (−177°).

Since the precise geometric coordinates of α-phellandrene are not known, we have used the experimental 1,3-cyclohexadiene parameters[27] for the ring geometry, and standard bond lengths and angles for the remaining atoms. The skew angle for this geometry is 18.0°. In the case of α-phellandrene the situation is made even more difficult by uncertainty in the isopropyl rotamer populations. For each of the ring conformers, XII and XIII, three rotamers of the isopropyl group about the C(6)-C(7) bond have been considered. For XII, the H(11)-C(6), C(7)-H(12) dihedral angle was taken as 180, 300, and 60°, in A, B, and C, respectively. For XIII, the H(11)-C(6), C(7)-H(12) dihedral angles used were 180, 60, and 300°, in A, B, and C, respectively. The calculated optical properties were not sensitive to the conformation of the hydrogens on C(10).

The CNDO/S calculated rotatory strengths are presented in Table VI. The rotatory strengths of the equatorial conformer are relatively independent of the isopropyl rotamer chosen. For the axial conformer XIII, even the signs of the rotatory strengths are dependent on the rotamer. Rotamer A, which appears to be the most stable from an examination of space filling models, gives a negatively signed rotatory strength, in accord with experiment. The magnitudes for XIII are significantly larger than those for XII, also in accord with experiment. For comparison purposes the CNDO/2 results are also reported in Table VI. The signs are correctly predicted, but the relative magnitudes are at variance with experiment. We must conclude that in the case of α-phellandrene, the calculations do not give a completely consistent interpretation of the experimental data and in this respect these calculations fail in this particularly exacting case. We would point out, however, that the rotatory strength is of such a small magnitude for the quasi-equatorial conformers that very slight changes in geometry could effect a change in sign.

Summary

We have performed CNDO/S and CNDO/2 calculations of the optical properties of the lowest $\pi \rightarrow \pi^*$ transition in chiral cisoid conjugated dienes, and have shown that the CNDO/S method without configuration interaction yields rotatory strengths in good agreement with experiment for substituted 1,3-cyclohexadienes of fixed conformation. The calculations have demonstrated that dissymmetrically disposed substituents must be considered an integral part of the diene chromophore in attempting to predict the chiroptical properties of dienic compounds. Rotatory strengths of the same order of magnitude arise from the asymmetry of the substituents as from the skewed isolated π-electron system. The relative contributions depend on the nature of the substituents, their precise structural relationships, and the skew angle of the four dienic carbons.

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Supplementary Material Available: The Cartesian coordinates for compounds IV-XI (1 page). Ordering information is given on any current masthead page.

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Acid-Base Properties of Molecules in Excited Electronic States Utilizing Ion Cyclotron Resonance Spectroscopy

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Abstract: A general method is described for obtaining excited state acid-base properties of molecules and ions in the gas phase which utilizes ion cyclotron resonance spectroscopy for studying photochemical processes involving ions. These processes, including photodissociation and photodetachment, yield in favorable instances electronic excitation energies of ions. A comparison of the excitation energies of a base B with the corresponding acid-base complex AB yields the excited state basicity of B. Similarly, a comparison of the excitation energies of a chromophoric acid A with the complex AB yields information about the excited state acidity of A. Studies of the first type are described using the reference acids H^+ and Li^+ with the bases C_6H_5X ($X = H, CN, NH_2, CHO, COCH_3, NO_2, OCH_3, O^-$, and S^-), pyridine, and ferrocene. In several instances photodissociation spectra of solvated acid-base complexes of the type B_2Li^+ have been obtained and analyzed to determine the effects of further solvation on the excitation spectra of these complexes. A comparison of the gas-phase excitation spectra of a number of ions to their solution absorption spectra is made. Studies of the second type (excited state acidities) are described using the reference base H^- with the acids $C_6H_5CO^+$ and $C_6H_5CHOH^+$. Calculated changes in acidity and basicity are used to infer changes in electron distributions and dipole moments for excited states, and yield insight into the types of transitions involved. In particular these studies are used to assess the controversial role played by intramolecular charge transfer in the lowest two singlet $\pi \rightarrow \pi^*$ transitions of monosubstituted benzenes. These results are compared with findings from related experiments and calculations when available.

One of the most important and useful concepts in chemistry is that of the acid-base properties of molecules. Several treatises have been written on the subject, including classic papers by Brønsted and Lewis among others.[2] Despite different points of view, a general description emerges: a base is a species which is electron donating and an acid is one which is electron accepting. This definition alone suggests an intimate relationship between the acid-base properties of a molecule and its charge distribution. Since charge densities are often modified by electronic excitation, it is expected that the acid-base