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Calculations of Rotatory Strengths in Chiral Chromophores. Sensitivity to Structural Parameters in Dienes

Elliot Charney,* Che-Hung Lee, and Joan S. Rosenfield†

Contribution from the Laboratory of Chemical Physics, National Institute of Arthritis, Metabolism and Digestive Diseases, National Institutes of Health, Bethesda, Maryland 20205.

Received April 19, 1979

Abstract: The temperature dependence of the effective conformational distribution of the rotamers of the quasi-axial and quasi-equatorial conformers of the dienic molecule α-phellandrene has been calculated using the Westheimer approach as elaborated in the GEMO procedure of Cohen.[1] With the structural parameters obtained from the energy minimization procedure of this method, modified to restrict the distortion of the nominal double bonds of the diene, the rotatory strengths of individual rotamers have been calculated. Using the Boltzmann weighted distribution at 20 and −150 °C, the calculated values are found to be in excellent agreement with chiroptical measurements at these temperatures. The energy difference between the rotamer-averaged quasi-axial and quasi-equatorial conformations is also found to be in good agreement with the measured value. Three significant conclusions may be drawn from these results: (1) Structural parameters of chiral dienic hydrocarbons obtained by the Westheimer method are suitable for rotatory strength calculations. (2) Although the energy differences engendered are not large, the value 26.2 kcal $\mathrm{mol^{-1}\,rad^{-2}}$ heretofore utilized in the GEMO procedure as the double bond torsional constant does not sufficiently account for the stability of the planar structures of π-bonded carbon atoms when the π bond is part of a conjugated system. (3) The CNDO/S method without configuration interaction appears to be adequate to the task of predicting semiquantitatively the rotatory strength of these conformationally flexible dienes.

Introduction

Both empirical and theoretical attempts have been made to understand the chiral activity of the long-wavelength transitions of the dissymmetric diene chromophore. The successful application of the quantum mechanically derived diene rule to a large number of compounds[2] was followed by the discovery of notable exceptions and the derivation of the empirically derived allylic chirality concept.[3] Recently, a significant advance was made by utilizing the CNDO/S calculations for cyclohexadienes.[4] When applied, however, to the calculation of the conformationally mobile dienic compound α-phellandrene as a particularly exacting test of the method, the result was at best qualitatively correct. We have looked for the origin of the lack of better concordance of theory and experiment for this compound and have found that it resides in the extreme sensitivity of the rotatory strength to the molecular structural parameters. In the course of doing so, several very interesting and significant observations have been made with respect to both the utility of the CNDO/S method for this purpose and to the torsional distortion of π bonds in conjugated dienes.

Methods

Experimental data are taken from previous work as referenced. Values of experimentally observed *reduced* rotational strength are calculated from CD curves directly using the expression

$$[R] = 0.4396 \times 10^2 \Delta\epsilon(\Delta\lambda/\lambda) \qquad (1)$$

[where $\Delta\epsilon = [\theta]/3302$ and $[\theta]$ is the measured molar ellipticity, $\Delta\lambda$ is 1/2 the bandwidth at $0.368\Delta\epsilon_{\max}$ (or $[\theta]_{\max}$)], or indirectly from ORD curves using eq 1 and the expression

$$[\theta] = A/0.0122 \qquad (2)$$

(where A is 0.01 of the absolute value of the difference between the molar rotation at the peak and trough of the ORD curve).

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† Sigma Data Services, Goddard Space Flight Center, Greenbelt, Md. 20771.

Table I. Conformational Energies (kcal/mol) of α-Phellandrene

	quasi-axial			quasi-equatorial		
rotamer	A	B	C	A	B	C
			Energies			
set I[a]	16.79	20.95	30.63	8.56	12.83	11.93
set II[b]	5.32	5.66	6.14	5.11	5.01	4.84
set III[b]	5.82	5.76	6.38	5.60	5.58	5.38
			Dihedral Diene Angle			
set I	−18.0	−18.0	−18.0	18.0	18.0	18.0
set II	−17.2	−15.5	−17.5	15.1	16.3	15.2
set III	−20.9	−18.7	−19.4	20.0	19.5	19.1

[a] The computed energies for the molecules with the coordinates of set I without minimization. [b] The computed energies for the molecules obtained by energy minimization as discussed in the text.

Table II. Calculated Rotatory Strength of α-Phellandrene Rotamers

	quasi-axial			quasi-equatorial		
rotamer	A	B	C	A	B	C
set I	−24.8	15.6	17.4	−2.7	−3.7	−5.5
set II	−16.6	−6.1	−12.2	−10.9	−10.4	−11.1
set III	−25.5	−9.1	−29.6	−1.0	−1.6	−1.5

The calculation of the rotational strength utilized the SCF-MO method, CNDO/S, and proceeded exactly as described in ref 4. Structural parameters required for the CNDO/S calculation were obtained by an energy minimization concept originating with Westheimer[5] and elaborated in the GEMO procedure of Cohen.[1] The values of the energy or force constants were taken from ref 1 except that, as indicated below, in one calculation the torsional bond energy constant for the nominal double bonds of the diene was essentially made very large by prohibiting distortions from planarity of the hydrogen atoms attached to each nominal double bond of the diene. No configuration interaction is used to obtain the CNDO/S results.[4,6]

Results and Discussion

In the earlier CNDO/S calculation[4] of the rotatory strength of the assumed minimum-energy rotamers of quasi-axial and quasi-equatorial α-phellandrene, the structural parameters (I) were taken from those experimentally derived for cyclohexadiene by Traetteberg[7] for the ring atoms and standard bond lengths and angles were used for the substituent atoms. The skew (dihedral) angle of the diene for this geometry is 18.0° and the rotamer angles were fixed by rotating the isopropyl group about the C(7)-C(6) bond in 120° intervals.

To examine the effect of structural parameters, two additional calculations have now been made, for which the atom coordinates have been obtained from the energy minimization procedure noted above. Starting with the earlier structure, the GEMO minimization was permitted to generate a new set of coordinates (II) without restriction as to rotamer dihedral angles and based on the minimized total conformational energy described by

$$E_{\text{conf}} = E(\text{l}) + E(\theta) + E(\phi) + E(\text{nb}) \qquad (3)$$

where $E(\text{l})$, $E(\theta)$, $E(\phi)$, and $E(\text{nb})$ are the energies for bond stretching, valence angle bending, torsional strain, and van der Waals energy, respectively. Monopole electrostatic energies were not included[8] as they play a minor part in compounds of this type and in any event the extent to which they are partially included in the other interactions is open to question. All atoms were allowed to find their optimum structural coordinates. In the energy-minimized optimal structures the dihedral angle of the bonds C(5)-C(6), C(7)-C(8) (see Figure 1) which fixes the rotamer conformations remained close to the angles used in set (I). For the quasi-equatorial conformers, these angles are 57.6, −60.7, and 175.4°, respectively, for the rotamers designated A, B, and C and for the quasi-axial conformer the angles were 62.4, −58.8, and 179.0° for the A, B, and C rotamers. [Note that in ref 4 the angle is defined with respect to C(6)-H(11) and C(7)-H(12) bonds. The corresponding angles to those used in this paper would be 60, −60, and 180° for A, B, and C conformers.]

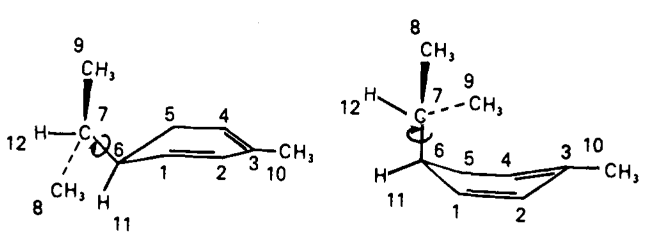

Figure 1. Quasi-equatorial (left) and quasi-axial (right) conformers of α-phellandrene.

Table III. Conformational Energy Difference (kcal/mol): E (Quasi-equatorial) − E (Quasi-axial)

	20 °C	−150 °C
set I	>−10	>−10
set II	−0.57	−0.46
set III	−0.38	−0.33
	obsd = −0.46[a]	

[a] From observations[12] in the temperature range of +100 to −196 °C.

The final calculation used precisely the same procedure, but the hydrogen atoms bonded to carbons 1, 2 and 4, and the methyl carbon 10, were held fixed relative to the double bond to which they are bonded, so that each of the nominal double bonds and its substituents retains a planar conformation. The set of coordinates (III) resulting from the subsequent energy minimization, therefore, include what we have labeled as "undistorted" double bonds. As in set (II), the rotamer angles remained close to the set (I) angles. In Table I, the calculated values of the total conformational energies for each rotamer and the values of the associated diene twist angles for structural coordinate sets (I), (II), and (III) are listed. The dihedral angles of the diene become slightly larger when the individual bonds are held planar but the remaining atoms and the diene are permitted to take their optimum coordinate positions. In Table II, the values of the rotational strengths calculated for each set of coordinates are given. Using the conformational energies of Table I, we have calculated the Boltzmann weighted averages of the energies of the quasi-axial and quasi-equatorial conformers. The energy difference between these are compared to an experimental value obtained from a photochemical investigation in Table III. The van't Hoff plot[9] leads to a temperature-independent value of −0.46 kcal/mol for the energy difference between the axial and equatorial conformers. The slight curvature apparent in that van't Hoff plot is probably due to changes in the rotamer distribution when the temperature is changed. It is apparent that the agreement between the values calculated for sets (I) and (II) and the observed values is extraordinarily good. Note the very large difference between set (I) and the GEMO minimized sets (II) and (III). The difference between the calculated energies of the two conformers based on sets (II) and (III) is not large. Nevertheless, there is a very substantial difference between the rotatory strengths calculated from these sets and from set (I), as may be observed in Table IV, where the Boltzmann weighted values of the predicted rotational strengths at 20 and −150 °C are compared, and also compared to available ex-

Table IV. Rotatory Strength of α-Phellandrene

	set I	set II	set III
20 °C calcd	−2.7	−11.31	−7.11
obsd^a = −8.5			
−150 °C calcd	−2.7	−11.18	−4.88
obsd^b = −2.0			

^{a} This is the average of values obtained at this temperature from the data of ref 8-10. ^{b} From the data of ref 9.

perimental values.[10-12] One experimental value (+5.5) obtained by Snatzke et al.[12,13] in a rigid glass at −177 °C is not included in the table. Neither the optical rotation data of Ziffer et al.[10] done at temperatures of 82, 18, and 10 °C nor of Horseman and Emeis[11] at 20 and −150 °C extrapolate to positive values of the rotational strength at −177 °C. It is possible that the optical purity of the Snatzke et al. sample is slightly higher than that of the other two sets of investigators but optical artifacts in chiral measurements in rigid glasses are well known. The value (−10.3) that they obtained at room temperature is included in the data of Table IV. What is quite clear from the calculated values of $[R]$ for the long-wavelength diene transitions is that the energy-minimized coordinates of set (III) result in far better agreement with experiment than sets (I) and (II). With set (I) the rotational strength is predicted to be independent of temperature because only one rotamer is stable. The temperature dependence of set (II) is also predicted to be very small, in this case, because of the very similar values of the rotamer rotational strengths. The restriction of the coordinates of the diene substituents at the carbon atoms of the diene moiety to prevent distortion of the double bond makes a very significant improvement in the agreement between experiment and theory. It appears highly likely that the generally accepted value of 26.2 kcal mol^{-1} rad^{-2} as the torsional constant about the double bond is too small when the double bond is part of a conjugated system.

Summary

The rotatory strength of the rotamers of the quasi-axial and quasi-equatorial conformers of α-phellandrene has been calculated by the CNDO/S method without configuration interaction using coordinates obtained by energy minimization based on Westheimer concepts. This paper clearly demonstrates how sensitive the chiral activity of the allowed transition of a molecule is to its fine structure. Semiempirical potential energy calculations are shown to generate values of the structural parameters which produce excellent agreement with chiral measurements.

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A Quadrant Rule for the Prediction of Chiroptical Effects of Optically Active Homoannular Cisoid Dienes

Robert M. Moriarty,[*1a] **Herbert E. Paaren,**[1a] **U. Weiss,**[1b] **and W. Basil Whalley**[1c]

Contribution from the Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680, the National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, Bethesda, Maryland 20014, and The School of Pharmacy, London WC1N 1AX, England.

Received April 13, 1979

Abstract: An empirical analysis for the chiroptical effects of cisoid homoannular dienes called the diene quadrant rule is presented. This regional rule uses a cubic space divided into quadrants in order to assign relative signs of the rotatory contribution of the diene and axial allylic substituents. The magnitude of the contribution of axial allylic substituents is estimated from their stereochemical relationship to the adjacent double bonds. Assumptions are made about the relative contributions of axial allylic hydrogen vs. methyl. The total $\Delta\epsilon$ is considered to consist of $\Delta\epsilon = \delta_{\text{diene}} - [\delta_X \sin^2 \omega + \delta_{X'} \sin^2 \omega]$, where δ_{diene} is the contribution of the diene, and δ_X and $\delta_{X'}$ are substituent contributions at torsional angle of ω to the adjacent olefinic unit. The algebraic sum derives from the orientation of the diene and axial allylic moieties inscribed within the cubic space. The diene quadrant rule is applied successfully to known exceptions to the original diene chirality rule.

In 1961 a rule was proposed for the relationship between the sign of the Cotton effect for the lowest energy $\pi \rightarrow \pi^*$ transition and the skew sense of a cisoid homoannular diene.[2a,b] A positive or negative Cotton effect results from a right- or left-handed diene, respectively. The chiroptical contribution of substituents in the vicinity of the diene was considered to be negligible compared to that associated with the inherent dissymmetry of diene chromophore. The original rule was based on HMO calculations on twisted butadiene[2c] and more elaborate calculations have confirmed the relationship between helical sense and chiroptical effect.[3a-g,4] The rule successfully predicted the sign of the CD for many compounds.[5] Unfortunately, a number of exceptions have come to light, and apparently the twist sense of the diene alone does not control the chiroptical effect.

Illustrative of such exceptions, which will be treated sub-

0002-7863/79/1501-6804$01.00/0