Chiroptical Properties and Optical and Molecular Orbital Calculations for Dictyopterenes A and B [1]

By **J. Cymerman Craig,*** **Peter A. Kollman,** and **S.-Y. Catherine Lee,** Department of Pharmaceutical Chemistry, University of California, San Francisco, California 94143, U.S.A.
Richard E. Moore and **John A. Pettus, jun.,** Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822, U.S.A.
S. Rothenberg, Information Systems Design, Santa Clara, California 95102, U.S.A.

Circular dichroism spectra of the optically active cyclopropane hydrocarbons (1a) and (2), measured over a range of temperatures, showed these compounds to be configurationally identical. The c.d. spectrum was found to consist of two overlapping exciton pairs, corresponding to an equilibrium mixture of two solution conformers, for which thermodynamic parameters were calculated.

Optical calculations using the exciton model were used to obtain the sign of the rotational strength for the long wavelength part of the exciton pair for different conformers. The result confirmed the absolute (*R,R*) configuration for (1a) obtained from oxidative degradation, and the conformational assignment made from spectral analysis showing that the *trans,trans*-conformer is responsible for the pair of exciton bands at shorter wavelength region. Both CNDO/2 and *ab initio* calculations confirmed that this conformer was of the lowest energy.

THE essential oil of Hawaiian *Dictyopteris* (Phaeophyta) contains a number of C_{11} hydrocarbons, two of which possess a *trans*-disubstituted cyclopropane ring. Dictyopterene A is *trans*-1-(hex-*trans*-1-enyl)-2-vinylcyclopropane (1a) [2] and dictyopterene B is *trans*-1-(hexa-

---

[1] Part 21, J. C. Craig, S.-Y. C. Lee, R. P. K. Chan, and I. Y.-F. Wang, *J. Amer. Chem. Soc.*, 1977, **99**, 7996.

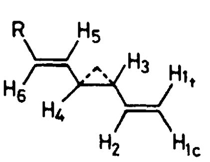
[2] R. E. Moore and J. A. Pettus, jun., *Tetrahedron Letters*, 1968, 4787.

trans-1,*cis*-3-dienyl)-2-vinylcyclopropane (2).[3] Both are optically active, having $[\alpha]_D$ +77 and −43° respectively.

The chiroptical properties of (1a) and (2) were examined in order to gain an understanding of their relation to conformational preferences and absolute configuration.

The long wavelength transitions of optically active molecules composed of two chromophores have usually been described by one of the following[4] two models: (I) the exciton model, for cases where coupling between the chromophores is weak, *e.g.* homo-conjugated dienes or (II) the 'inherently dissymmetric chromophore' model, for cases where coupling is strong, *e.g.* helicenes. In the case of the two hydrocarbons (1a) and (2), we will show that their spectra can best be analysed by a model which combines the features of both (I) and (II).

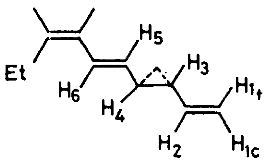
Cyclopropane has long been considered to conjugate with ethylene to a degree between that characteristic for saturated and unsaturated groups, and its presence in a molecule like (1a) or (2) provides an electronic linkage between the two ethylenic chromophores. In the case of vinylcyclopropane, rotation around the bond connecting the cyclopropane and the C=C bond is relatively easy. A similar situation is therefore expected for (1a) and (2), and CNDO and *ab initio* computations and optical calculations were undertaken for conformations which differed in the degree of rotation around the bond connecting the cyclopropane ring and the ethylenic group.



(1)

a; R = Bu

b; R = H



(2)

EXPERIMENTAL

C.d. measurements were made on a Jouan II Dichrograph at temperatures varying from −120 to +80 °C. Whereas Spectro-grade 2-methylbutane was used as solvent for low temperature studies (−120 to +20 °C), Spectro-grade n-heptane was employed for high-temperature studies (20—80 °C). U.v. data were obtained on a Cary 15. Overlapping c.d. bands were resolved on a Du Pont 310 Curve Resolver. The resolved curves were then used for the calculation of thermodynamic data.

The proton n.m.r. spectra were determined on a Varian HA-100 spectrometer at temperatures ranging from −60 to +101 °C for dictyopterene A and −65 to +77 °C for dictyopterene B. Solutions of *ca.* 100 μg of hydrocarbon in 0.3 ml of chloroform were examined. Chemical shifts were measured as δ units using tetramethylsilane (δ = 0) as an internal reference. Spectral parameters were obtained directly from the spectra, except for δ_3 and J_{34} which were calculated with the aid of generalized multispin programs LAOCOON I and II.

Optical Activity Calculations.—Although models I and II mentioned above are different approaches to the c.d. spectral analysis, a number of calculations tend to show that they make similar predictions for the long wavelength part of the spectrum.[5] To simplify the problem, we chose to use the exciton model for the calculation of optical activity. Atomic co-ordinates were obtained from the COORD program.[6] Bond lengths and bond angles were taken from electron diffraction studies of vinylcyclopropane [7] and used as input for the COORD program. With a transformation of the co-ordinate system, rotational strength can be calculated using the formalism described [8] by Bosnich *et al.*

Since the electric transition moment for a pure conformer is not known, no attempt was made to calculate the exact magnitude of the rotational strength, rather its sign was estimated from the known geometry of the particular conformer. To get a general idea of the relationship between sign of optical rotation and molecular geometry, calculations were carried out for different conformations which differ by 30° rotation around the C(2)–C(3) and C(5)–C(6) bonds in (1b).

MO Calculations.—Since monovinylcyclopropane and 1,2-*trans*-divinylcyclopropane are closely related to dictyopterenes A and B, the former pair were chosen as model compounds for the MO calculations. Both CNDO/2 and *ab initio* calculations were carried out on monovinylcyclopropane, but only CNDO/2 calculations on *trans*-divinylcyclopropane. The input geometry was taken from electron diffraction studies of vinylcyclopropane and all parameters were held constant with the exception of the torsional angle of rotation around the C–C bond connecting the cyclopropane ring with the double bond. The CNDO/2 calculations [9] used QCPE program #91 and the *ab initio* calculations, employing a minimal STO-3G basis set,[10] were carried out using the MOLE quantum chemistry program.[11]

RESULTS AND DISCUSSION

U.v. Spectrum.—The maximum u.v. absorptions for structurally related compounds are listed in Table 1. Due to the presence of an additional double bond, dictyopterene A shows a bathochromic shift (*ca.* 15 nm) as compared to monovinylcyclopropane. This indicates that the cyclopropane ring transmits electrons although its ability to do so is less than that of a double bond (*cf.* buta-1,3-diene and hexa-1,3,5-triene). The effect of a conjugated double bond in dictyopterene B is of about the same magnitude as in conjugated alkenes: the maximum absorption undergoes a bathochromic shift from 207 to 245 nm, comparable to that observed for buta-1,3-diene and hexa-1,3,5-triene.

---

[3] J. A. Pettus, jun., and R. E. Moore, *Chem. Comm.*, 1970, 1093; E. R. Moore, J. A. Pettus, jun., and J. Mistysyn, *J. Org. Chem.*, 1974, **39**, 2201.

[4] K. Mislow, *Ann. N.Y. Acad. Sci.*, 1962, **93**, 451.

[5] W. Hug and G. Wagniere, *Tetrahedron*, 1972, **28**, 1241.

[6] Quantum Chemistry Program Exchange program 136 by M. J. S. Dewar

[7] A. de Meijere and W. Lüttke, *Tetrahedron*, 1969, **25**, 2047.

[8] B. Bosnich, A. de Renzi, G. Paiaro, J. Himmelreich, and G. Snatzke, *Inorg. Chim. Acta*, 1969, **3**, 175.

[9] Program available from Quantum Chemistry Program Exchange, University of Indiana, based on the papers of Pople *et al.* and summarized in 'Approximate Molecular Orbial Theory' by J. A. Pople and D. L. Beveridge, McGraw-Hill, New York, 1970.

[10] W. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1970, **51**, 2567.

[11] S. Rothenberg, P. Kollman, M. Schwartz, E. F. Hayes, and L. C. Allen, *Internat. J. Quant. Chem. III S*, 1969, 715.

C.d. Spectrum.—C.d. measurements showed not only optically active absorption bands at 207 nm for dictyopterene A and 245 nm for dictyopterene B corresponding to the observed u.v. maxima respectively, but a long wavelength c.d. band was also observed for both compounds (see Figure 1). Although the additional c.d. band is much smaller in magnitude than the main peak, its existence is without doubt: the c.d. spectra of both compounds have the same shape except that for dictyopterene B the whole spectrum has undergone a bulk shift of 40 nm to longer wavelengths. Since the two compounds differ by one conjugated double bond, this bathochromic shift is understood on the basis of the conjugation effect. The identical shape of the spectra strongly suggests that electronic transitions in the observed wavelength region have the same origin and that the two compounds are configurationally identical. Compared to (2), (1) has a much simpler chromophore and will therefore be used as a model compound to discuss the spectroscopic properties.

TABLE 1

U.v. absorption of vinylcyclopropanes and related compounds

Compound	$\lambda_{max.}$/nm	$\varepsilon_{max.} \times 10^{-4}$/ l mol cm^{-1}
Vinylcyclopropane	192 [b]	1.0
Prop-1-enylcyclopropane	194.5 [b]	1.3
trans-1-(Hex-*trans*-1-enyl)-2-vinylcyclopropane (1a)	207 [a]	1.6
trans-1-(Hexa-*trans*-1,*cis*-3-dienyl)-2-vinylcyclopropane (2)	245 [a]	2.9
Buta-1,3-diene	217 [a]	2.1
	247.5 [b]	5.7
Hexa-1,3,5-triene	257.5	8.0
	267.5	6.7

Solvent: [a] EtOH: [b] C_6H_{12}.

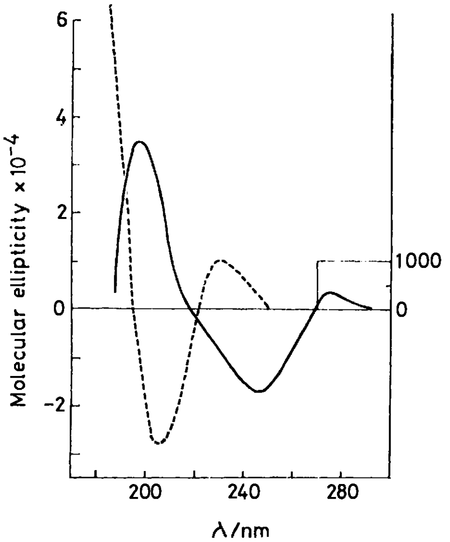


FIGURE 1 C.d. spectra of (+)-dictyopterene A (— — —) and (—)-dictyopterene B(——)

In general, c.d. and u.v. maxima coincide very well. If two electronic transitions are very close to each other but differ significantly in magnitude, the smaller u.v. band may be submerged in the absorption of the other and become indiscernible. However, c.d. bands can be either positive or negative. If the two ellipticity bands are of opposite sign, then although their rotational strengths may differ significantly the smaller band can still be observed although it is shifted far away from its original $\lambda_{max.}$[12] This could well be the reason for the presence of the long wavelength c.d. band at 230 nm in (1a). Since the n-butyl group in (1a) has only a slight inductive effect and does not absorb in the wavelength region under consideration, it is possible to neglect the n-butyl group and to consider the chromophore as a 1,2-*trans*-divinylcyclopropane (1b).

The divinylcyclopropane chromophore has a point group symmetry of C_2; therefore all the electronic transitions in this molecule belong either to the irreducible representation (A) or (B). In the first case (A) it is polarized parallel to the twofold symmetry axis, in the second case (B) perpendicular to it. Molecules of symmetry C_2 (*e.g.* twisted dienes) may conveniently be viewed as composed of two equivalent parts. If the coupling between these two parts is relatively weak an exciton model (model I)[4] may be applied to describe the resulting long-wavelength transitions, which are viewed as combinations of two local excitations. One resulting transition is of symmetry A, the other of symmetry B and the rotational strengths are opposite in sign.[5] If, on the other hand, the coupling between the two fragments is strong, the whole chromophore must be considered as inherently dissymmetric, *e.g.* helicenes.[13] A description by molecular orbitals extending over the complete chromophore is more suitable (model II). In the case of divinylcyclopropane, the existence of the cyclopropane ring constitutes a moderate electronic linkage[14] between the two vinyl groups. This makes it an unique example in producing optical activity which resembles ***both models I and II***. As a wide variety of LCAO-MO calculations, including configuration interaction, tend to show[5] that models I and II predict similar patterns of the c.d. spectrum, divinylcyclopropane may, therefore, be expected to show the same type of c.d. as *e.g.* a twisted diene. In a molecule with rigid structure, exciton bands of equal intensities but opposite signs will be observed in the absence of interference from a neighbouring transition. For divinylcyclopropane, it is noted that rotation around the C–C single bonds connecting the cyclopropane ring and the two double bonds is easy. If conformational equilibrium exists in the solution under study, it would complicate the appearance of the spectrum. Since one conformation is related to one pair of exciton bands, spectral analysis would be particularly difficult in this case. For monovinylcyclopropane rotational isomers have been detected

---

[12] K. M. Wellman, P. H. Laur, W. S. Briggs, A. Moscowitz, and C. Djerassi, *J. Amer. Chem. Soc.*, 1965, **87**, 66.

[13] S. F. Mason, W. S. Brickell, A. Brown, and C. M. Kemp, *J. Chem. Soc.* (*A*), 1971, 756.

[14] R. S. Brown and T. G. Traylor, *J. Amer. Chem. Soc.*, 1973, **95**, 8025; C. F. Wilcox, L. M. Loew, and R. Hoffmann, *ibid.*, p. 8192.

by n.m.r. and electron diffraction studies.[7,15-17] Generally, it is agreed that the *trans*-conformer is the most stable species, but the higher energy conformer(s) have not been unequivocally identified, although the evidence from n.m.r. measurements indicates that a *gauche* conformer is next in energy to the *trans* (*vide infra*). In the structurally closely related divinylcyclopropane, the most stable conformer is also expected to be the *trans*, *trans*-form. To investigate the geometry dependence of chiroptical behaviour of divinylcyclopropane, we carried out a series of c.d. measurements at variable temperatures. The c.d. at room temperature (Figure 1) showed three bands: Band I (positive) approaching a maximum at 185 nm, Band II (negative) at 207 nm, and Band III (positive) at 232 nm. Band I and Band II were found to increase rapidly with decreasing temperature while Band III decreased sharply at the same time (Table 2).

TABLE 2

Circular dichroism of (+)-dictyopterene A at variable temperatures between 80 and −120 °C[a]

Temp. (°C)	Band III $[\theta]_{max.}$	$\lambda_{max.}$/nm	Band II $[\theta]_{max.}$	$\lambda_{max.}$/nm	Band I $[\theta]_{185}$/nm
Solvent: 2-methylbutane					
20	+5 280	231.5	−28 050	205	+69 300
−120	+330	241.5	−138 600	210.5	+188 100
Solvent: n-heptane					
	$[\theta]_{max.}$, 225—230 nm		$[\theta]_{max.}$, 205 nm		
20	+6 188		−30 250		
80	+12 375		−9 625		

[a] Only the values at the highest and lowest temperatures and at room temperature are given.

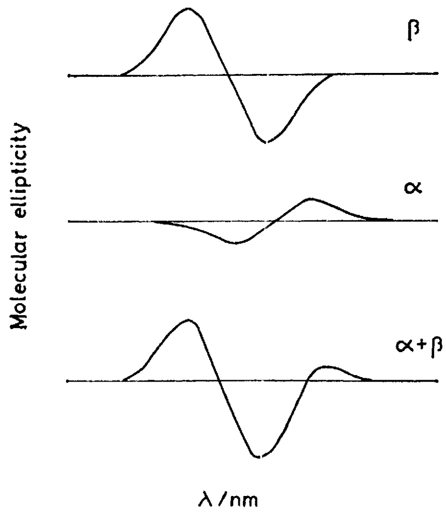


FIGURE 2 Overlapping pairs of exciton bands (α) and (β) and their summation

From the fact that the short wavelength band I changes in the same manner as the 207 nm band while opposite to the 232 nm band, it is clear that the 232 nm band cannot be the tail of the short wavelength band I. This suggests that the three bands observed may be the result of two overlapping pairs of exciton bands: one pair (α) which appears at long wavelength region has a positive long wavelength exciton band, and the other (β) which appears at shorter wavelength region has a negative long wavelength exciton band (Figure 2). The two pairs of exciton bands can best be related to two conformational species in equilibrium. According to the Boltzmann distribution law, the population of the lower-energy species increases with decreasing temperatures and *vice versa*. Apparently the shorter wavelength pair is associated with the more-stable conformer which according to the conformational analysis mentioned earlier is likely to have the *trans,trans*-geometry. The possible conformation(s) related to the higher wavelength pair are uncertain.

A possible way to analyse the energy difference between the *trans,trans*-conformer and higher energy conformers is as follows.[18] Using the ellipticity values obtained at different temperatures (Table 2) in the Boltzmann equation (1) where R_T = apparent rotational

$$R_T = (R_a - R_b)\,\frac{1}{1 + n.\ \exp\,(-\Delta E/RT)} + R_b \quad (1)$$

strength, R_a = rotational strength of the more stable conformer (*trans*-form), R_b = rotational strength of the less-stable conformer (*gauche* form), and n = degeneracy of the less-stable conformer, and plotting R_T against

$$\frac{1}{[1 + n.\ \exp\,(-\Delta E/RT)]}$$

a straight line was obtained which gives R_b as the intercept and $(R_a - R_b)$ as the slope. Least-square fitting of the data yields ΔE values for n = 1—4 of 610, 1 010, 1 250, and 1 400 cal mol^{-1}. If this higher-energy conformer is ***trans,cis***, then $n = 2$. If the higher-energy conformer is ***trans,gauche***, we expect $n = 4$ (if ***trans,gauche*** with $\theta_2 = 90°$ is equal in energy to ***trans,gauche*** $\theta_2 = 270°$). If we assume two ***trans,gauche*** ($\theta_2 = 90°$) and two ***trans,gauche*** ($\theta_2 = 270°$) conformers which differ in energy by 300 cal mol^{-1}, with ***trans,gauche*** ($\theta_2 = 270°$) more stable (see later section on MO calculations), the denominator in equation (1) becomes

$$1 + 2e^{-\Delta E/RT} + 2e^{-(\Delta E + 300)/RT}$$

ΔE Is then predicted to be 1 250 cal mol^{-1} and represents the energy difference between the ***trans,trans*** and ***trans,gauche*** (270°) conformers. All values for ΔE (with $n \neq 1$) are in respectable agreement with the ΔE value derived from n.m.r. studies of vinylcyclopropane [16,17] ($\Delta E = 1.1 \pm 0.2$ kcal mol^{-1}).

The following values of R_a and R_b were obtained in this manner: $R_a = 3.5 \times 10^{-38}$ c.g.s. and $R_b = -1.5 \times 10^{-38}$ c.g.s.

---

[15] W. Lüttke and A. de Meijere, *Angew. Chem. Internat. Edn.*, 1966, **5**, 512.

[16] H. Günther and D. Wendisch, *Angew. Chem. Internat. Edn.*, 1966, **5**, 521.

[17] G. R. de Mare and J. S. Martin, *J. Amer. Chem. Soc.*, 1966, **88**, 5033.

[18] W. W. Wood, W. Fickett, and J. G. Kirkwood, *J. Chem. Phys.*, 1952, **20**, 561; A. Moscowitz, K. Wellman, and C. Djerassi, *J. Amer. Chem. Soc.*, 1963, **85**, 3515.

From these values it is then possible to calculate the population of the most-stable conformer (*S-trans*) when $n = 1$ as 56% at 100 °C, 65% at 20 °C, and 72% at −30 °C.*

Variable-temperature c.d. measurements were also carried out for compound (2) (dictyopterene B) and showed that it behaved in exactly the same manner as (1a) (Table 3).

TABLE 3

Circular dichroism of (−)-dictyopterene B at variable temperatures between 20 and −120 °C [a]

Temp. (°C)	Band III $[\theta]_{max.}$	$\lambda_{max.}$/nm	Band II $[\theta]_{max.}$	$\lambda_{max.}$/nm	Band I $[\theta]_{max.}$	$\lambda_{max.}$/nm
Solvent: 2-Methylbutane						
20	+748	273.5	−16 790	247	+35 100	197.5
−120	+92	282	−80 890	246	+147 285	202

[a] Only the values at the highest and lowest temperatures are given.

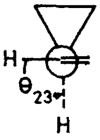
N.m.r. Studies.—In the n.m.r. spectrum of dictyopterene A the chemical shifts of 1-H, 2-H, and 5-H and the coupling constants J_{23} and J_{45} are strongly temperature dependent whereas the chemical shift for 6-H is only slightly affected (Table 4). A plot of δ_1 and δ_2 gives a straight line whose slope, $\Delta\sigma_1/\Delta\sigma_2$, is −0.17. From a graph[17] of the computed shielding arising from ring anisotropy, the dihedral angle θ_{23} for the upper state *gauche* conformation of the vinylcyclopropane moiety is estimated to be 82°. The shift ratio $\Delta\sigma_6/\Delta\sigma_5$ on the other hand is roughly −0.02 and therefore θ_{45} is *ca.* 95°. If J_{23} or J_{45} is assumed to be 12.5 Hz for the *s-trans* conformers and 1.5 Hz for the *gauche* conformers[17] then the fractional population in the upper state is 0.47 at 101 °C and 0.38 at −30 °C for the vinylcyclopropane moiety and 0.51 at 101 °C and 0.36 at −30 °C for the hexenylcyclopropane moiety. These values are in reasonable agreement with those calculated from n.m.r. and c.d. data for vinylcyclopropane.

TABLE 4

Proton n.m.r. spectral parameters for dictyopterene A at variable temperatures [a]

Temp. (°C)	Chemical shift (p.p.m.) δ_{1t}	δ_2	δ_6	δ_6	Coupling constant (Hz) J_{23}	J_{45}
−59.3	5.051	5.276	4.877	5.524	8.5	
+29.2	5.022	5.418	5.033	5.508	7.8	7.7
+101.0	5.011	5.523	5.148	5.520	7.3	6.9

[a] Only the values at the highest and lowest temperatures and at room temperature are given.



(3)

For dictyopterene B $\Delta\sigma_1/\Delta\sigma_2$ and $\Delta\sigma_6/\Delta\sigma_5$ are −0.12 and −0.3, respectively, corresponding to dihedral angles of 88° for θ_{23} and 70° for θ_{45} (Table 5).

TABLE 5

Proton n.m.r. spectral parameters for dictyopterene B at variable temperatures [a]

Temp. (°C)	Chemical shift (p.p.m.) δ_{1t}	δ_2	δ_5	δ_6	Coupling constant (Hz) J_{23}	J_{45}
−65	506.9	530.0	504.0	644.2		8.2
+30	504.6	543.5	514.3	640.2	7.9	
+77	504.4	550.3	520.1	639.4	7.2	

[a] Only the values at the highest and lowest temperatures and at room temperature are given.

Optical Activity Calculations.—To obtain further support for our spectral analysis, theoretical calculations of (1) the optical activity of different conformations and (2) the energies of these conformers were carried out using divinylcyclopropane as model compound.

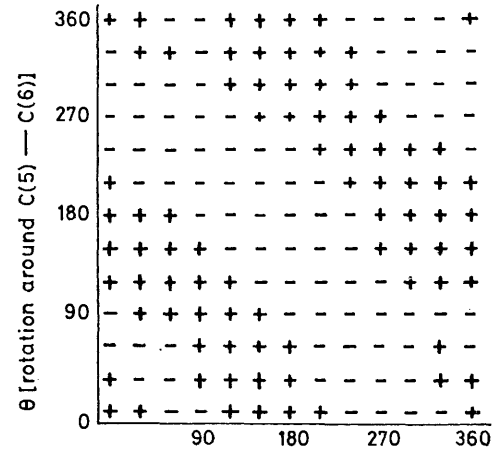
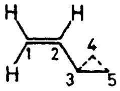
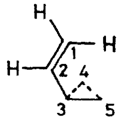


FIGURE 3 Sign of rotational strength for the long wavelength part of the exciton pair for different conformations

The signs of the long wavelength part of the exciton pairs for different conformations are shown in Figure 3. The calculations showed that the *trans,trans* conformer (4) (θ = 180°) does indeed give the minus sign in agreement with the experimental results (Table 2). This result establishes not only that (4) is the conformation responsible for the pair of exciton bands at shorter wavelength region (β), but also that the configuration of (1a) and (1b) as drawn, and on which this calculation is based, is the correct one *since otherwise all signs in Figure 3 would be reversed*. The absolute configuration shown in (1a) is, therefore, (*R*,*R*), confirmed by oxidative treatment of dictyopterene A and B, both of which



(4)



(5)

---

* When $n = 2$ or 4 these populations become 49 and 40% at 100 °C, 65 and 64% at 20 °C, and 75 and 78% at −30 °C respectively.

afforded (+)-(*S*,*S*)-*trans*-cyclopropane-1,2-dicarboxylic acid on Lemieux oxidation. Further support for these conclusions can be drawn from molecular orbital calculations (*vide infra*) which find the *trans,trans*-conformation to have the lowest energy, in agreement with the experimental results.

Molecular Orbital Calculations.—Molecular orbital calculations on both vinylcyclopropane and divinylcyclopropane were carried out. For vinylcyclopropane, CNDO/2 calculations found only a *trans* ($\theta = 180°$) and a *cis* ($\theta = 0°$) minimum energy for rotation around the C(2)–C(3) bond, corresponding to the conformations (4) and (5) respectively; ΔE(*cis,trans*) = 1.57 kcal mol^{-1} (Figure 4). Since there was considerable experimental evidence favouring a secondary '*gauche*' minimum, *ab initio* STO-3G calculations were carried out on the same surface, finding *trans-*, *gauche*, and *cis*-minima with the energy difference ΔE(*gauche,trans*) = 3.07 kcal mol^{-1} and ΔE(*cis,trans*) = 2.86 kcal mol^{-1} (Figure 5). These energy differences are qualitatively (although not quantitatively) in line with the experimental interpretations of energy differences between the conformers. While this study was in progress, we learned of the work of Hehre [19] who carried out more accurate 4-31G *ab initio* calculations on the vinylcyclopropane surface. He found [19] that these calculations supported only a *trans-* and a *gauche* minimum, with the *gauche* minimum at $\theta = 60°$ and a ΔE(*gauche,trans*) = 1.36 kcal mol^{-1}. Our CNDO/2 calculations on *trans*-divinylcyclopropane showed only *trans-* and *cis*-minima, with the two rotors effectively independent. The *trans,trans*-conformer was lowest in energy, with the *trans,cis* the next lowest minimum, 1.57 kcal mol^{-1} above the *trans,trans*. There was no minimum corresponding to the *trans,gauche* forms (6a) ($\theta = 90°$) or (6b) ($\theta = 270°$) but both these conformers were about 2.95 kcal mol^{-1} above the *trans, trans*-conformer. In view of the difference between the CNDO/2 and *ab initio* calculations on monovinylcyclopropane, we expect the *trans,gauche* (90°) and *trans,gauche* (270°) forms to be competitive in energy, with the exciton model calculations not definitive on this point. It may be that the higher energy c.d. band is a mixture of the *trans,gauche* (90°) and *trans,gauche* (270°) conformers (6a) and (6b). From Figure 3, we find these two conformers have opposite signs of rotation. Since the *trans,gauche* (270°) form is 0.3 kcal mol^{-1} energetically more favoured than the *trans,gauche* (90°) conformer, the net contribution to optical rotation from these would be expected to be positive for the long wavelength part of the exciton band. This is in agreement with the observed spectra. In view of Hehre's calculations,[19] we would expect 2-cyano-substitution to increase the c.d. contribution from the second lowest-energy conformer.

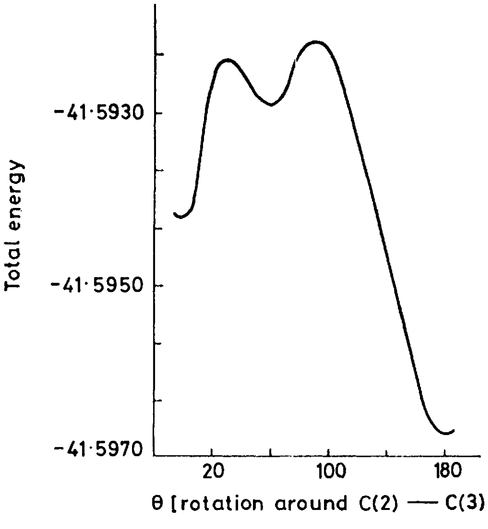


FIGURE 4 CNDO/2 calculation for vinylcyclopropane

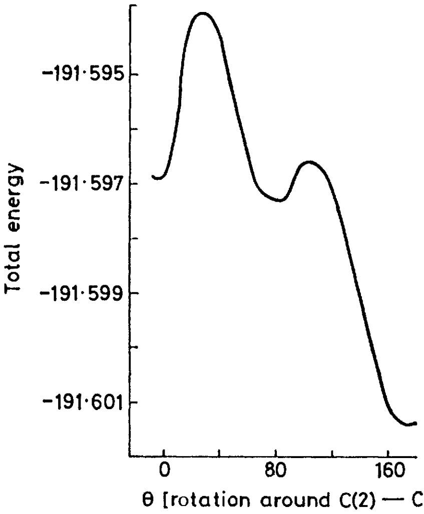
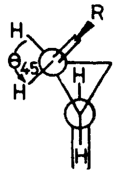
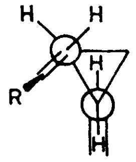


FIGURE 5 *Ab initio* STO-3G Calculation for vinylcyclopropane



(6a)



(6b)

As expected from a simple Walsh model for cyclopropane [19] the electronic interaction between the vinyl and cyclopropane groups is larger for the *cis-* and *trans*-conformation than for the *gauche*, with the total π population on the ethylene group reflecting the amount of interaction between the vinyl group and the cyclopropane ring. In the *cis*-conformation, this interaction is largest since the two groups are closest together in this conformation and the most charge is transferred from the *e* orbitals of cyclopropane to the ethylenic π^*. As expected, this charge transfer is minimum at $\theta = 90°$, when only the a_1 orbital of the cyclopropyl group can interact with the ethylene π^* orbital. The π charge is

---

[19] W. J. Hehre, *J. Amer. Chem. Soc.*, 1972, **94**, 6592.

polarized to place more of it on the carbon (C-1) further from the cyclopropyl ring and the population on this carbon is maximum for *trans*- and *cis*-conformations.

Assuming the n.m.r. and the most accurate theoretical calculations are correct and the most stable conformations are *trans* and *gauche*, it is interesting to enquire why the *cis* is less stable than the *gauche* or *trans* form. There appear to be two physical effects which contribute to the observed conformation profile: the first is the conjugative interaction discussed above, which stabilizes *cis* and *trans* conformers. The second is due to non-bonded repulsions between groups that are eclipsed, as is observed in ethane-like molecules. This effect favours a *gauche* ($\theta = 90°$ or $270°$) conformation and strongly disfavours the *cis*-structure, where H · · · H interactions are maximal. CNDO/2 and minimal basis set *ab initio* calculations, by tending to underestimate these repulsive effects, may thus predict the *cis*-conformation to be more stable than it really is.

Conclusion.—From both theoretical and experimental considerations, the c.d. spectrum of dictyopterene A can be assigned as follows: the long wavelength positive band is associated with the *trans,gauche* form ($\theta = 270$—$280°$) and the 207 nm band is mainly associated with the *trans,trans*-form. Both these absorptions originate from $\pi\rightarrow\pi^*$ transitions of the ethylenic chromophore. The short wavelength band I is a combination of the positive half of the exciton pair at short wavelength region (β) and some other transitions, presumably due to cyclopropane ring absorption below 200 nm. The assignment for the c.d. spectrum of dictyopterene B would have the same interpretation, with the appropriate red shift.

[8/937 *Received*, 8th *March*, 1978]