59, 85048-58-4; **59** (ethyl ester), 85048-57-3; **59** (methyl ester), 85048-60-8; **60**, 85048-59-5; **61**, 85048-61-9; **62**, 85048-62-0; *tert*-butyl (trimethylsilyl)acetate, 41108-81-0; *tert*-butyl acetate, 540-88-5; trimethylsilyl chloride, 75-77-4; triethyl phosphonoacetate, 867-13-0; methyltriphenylphosphonium bromide, 1779-49-3; methylenetriphenylphosphorane, 3487-44-3; *p*-bromophenacyl bromide, 99-73-0; (±)-2-methylcyclohexanone, 24965-84-2; (2*S*)-(+)-2-methylcyclohexanone, 22554-27-4; (*S*)-(−)-1-phenylethylamine, 2627-86-3; succinic anhydride, 108-30-5; ethoxyacetylene, 927-80-0; *l*-menthol, 2216-51-5; 1-(2-ethoxyacetylenyl)-2-isopropyl-5-methylcyclohexanol, 85048-56-2.

Supplementary Material Available: Tables IA–C listing bond angles, bond lengths, and torsion angles for compound **20** (3 pages). Ordering information is given on any current masthead page.

Chiroptical Properties of Planar Acyclic 1,3-Dienes and α,β-Unsaturated Aldehydes: A Planar Diene Rule

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Abstract: Cotton effects in circular dichroism (CD) and optical rotatory dispersion (ORD) spectra of 1,3-dienes and α,β-unsaturated carbonyl compounds, for their $\pi-\pi^*$ transitions, are believed to arise from inherent dissymmetry of the chromophore as well as dissymmetric substituents. A selected number of chiral acyclic 1,3-dienes and α,β-unsaturated aldehydes whose chromophores are transoidal and planar have been studied. Ultraviolet (UV) and CD spectra were measured for these molecules and their long wavelength $\pi-\pi^*$ Cotton effects interpreted in terms of a "planar diene rule".

Chiroptical properties of 1,3-dienes and their molecular origin have been interesting modern stereochemical problems.[1] A relationship between the long wavelength $\pi-\pi^*$ Cotton effect in optical rotatory dispersion (ORD) and circular dichroism (CD) spectra of homoannular cisoid 1,3-dienes and the helicity of the diene chromophore was proposed as the "diene chirality rule".[2] According to this rule (Figure 1a) a homoannular cisoid diene skewed in a right-handed sense will give a positive Cotton effect and in a left-handed sense will give a negative Cotton effect for the long wavelength $\pi-\pi^*$ transition. Such a rule was also supported[3] by the Hückel molecular orbital (HMO) calculation[4] of butadiene as an inherently dissymmetric chromophore. For heteroannular cisoid dienes, an inverse rule was proposed;[5a] the inversion of sign is attributable to changes in electronic properties of the diene when the dihedral angle about the central bond is very large compared with that of homoannular dienes.

The HMO theoretical treatment was also extended to skewed transoid dienes and a rule was proposed[5b] (Figure 1b). This rule states that if the diene is oriented in such a way that its carbon atoms 1, 2, and 3 define a plane in a right-handed coordinate system as shown, the sign of the Cotton effect is determined by the position of the carbon atom 4: the sign will be positive or negative respectively if the coordinate of carbon atom 4 is positive or negative.

The various diene chirality rules were also tested on α,β-unsaturated carbonyl compounds for their long wavelength $\pi-\pi^*$ transition Cotton effects.[6,7] Originally it was argued that the contribution from the twist of the chromophore will outweigh the effects due to asymmetric substituents.[2] Exceptions to this theory were noted,[8-11] and it was observed that substituents, by interacting with the chromophore, play a major role. Allylic oxygenated systems were interpreted in terms of a helical chromophore containing the allylic oxygen.[12]

In order to explain the exceptions[9] to the diene chirality rule Burgstahler has introduced the concept known as "allylic axial chirality" to the 1,3-diene chromophore[9] especially in homoannular cisoid dienes[13a] (Figure 1c). The allylic axial bond is thought to

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(1) (a) "The Molecular Basis of Optical Activity: Optical Rotatory Dispersion and Circular Dichroism", E. Charney, Ed., Wiley, New York, 1979; (b) "Stereochemistry: Fundamentals and Methods", Vol. 2, H. B. Kagan, Ed., George thieme, Stuttgart, 1977; (c) A. W. Burgstahler, R. C. Barkhurst, and J. K. Gawronski in "Modern Methods of Steroid Analysis", E. Heftmann, Ed., Academic Press: New York, 1973.

(2) (a) A. Moscowitz, E. Charney, U. Weiss, and H. Ziffer, *J. Am. Chem. Soc.*, **83**, 4661 (1961); (b) A. Burgstahler, H. Ziffer, and U. Weiss, *ibid.*, **83**, 4660 (1961).

(3) (a) H. Ziffer and U. Weiss, *J. Org. Chem.*, **27**, 2694 (1962); (b) U. Weiss, H. Ziffer, and E. Charney, *Chem. Ind. (London)*, 1286 (1962); (c) H. Ziffer, E. Charney, and U. Weiss, *J. Am. Chem. Soc.*, **84**, 2961 (1962); (d) K. Mislow and A. Moscowitz, *Tetrahedron Lett.*, 699 (1963); (e) H. Ziffer, T. J. Batterham, U. Weiss, and E. von Rudolff, *Tetrahedron*, **20**, 67 (1964); (f) B. Berkoz, A. D. Cross, M. E. Adame, H. Carpio, and B. Bowers, *J. Org. Chem.*, *28*, 1976 (1963); (g) H. J. C. Jacobs and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **84**, 932 (1965); (h) U. Weiss, H. Ziffer, and E. Charney, *Tetrahedron*, **21**, 3105 (1965).

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(5) (a) E. Charney, J. M. Edwards, U. Weiss, and H. Ziffer, *Tetrahedron*, **28**, 973 (1972); (b) E. Charney, H. Ziffer, and U. Weiss, *ibid.*, **21**, 3121 (1965).

(6) C. Djerassi, R. Reccords, E. Bunnenberg, K. Mislow, and A. Moscowitz, *J. Am. Chem. Soc.*, **84**, 870 (1962).

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(9) A. W. Burgstahler and R. C. Barkhurst, *J. Am. Chem. Soc.*, **92**, 7601 (1970), and references cited therein.

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(13) (a) A. W. Burgstahler, L. O. Weigel, and J. K. Gawronski, *J. Am. Chem. Soc.*, **98**, 3015 (1976); (b) J. Gawronski and K. Gawronska, *J. Chem. Soc., Chem. Commun.*, 346 (1980).

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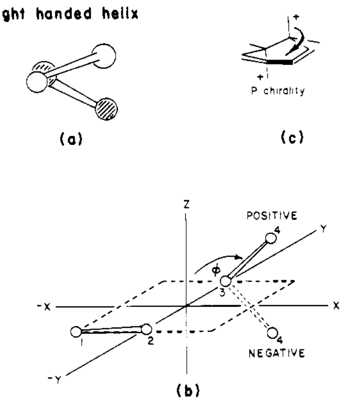
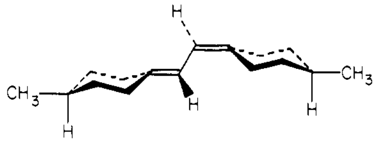


Figure 1. The chirality rules: (a) diene chirality rule; (b) transoid diene rule; (c) allylic axial chirality rule.

form a part of the chromophore responsible for the observed Cotton effect.[13b] In Burgstahler's view[13a] it is the allylic axial group that contributes the sign of the Cotton effect according to its size and polarizability and not the skewed sense of the chromophore. It has also been borne out from sophisticated MO calculations that the contribution from the twist does not outweigh the effects due to substituents.[14-16] Recently a "diene quadrant rule" for cisoid 1,3-dienes[17] and an "amplified sector rule"[18] have been advanced to account for the sign of the Cotton effect.

Most of the attention has been paid to 1,3-cisoid dienes[1c,13-17] while transoid dienes have been largely ignored.[5b] Also, very few investigations have been carried out on planar 1,3-dienes[19-21] and planar α,β-unsaturated carbonyl chromophores. We have reported the chiroptical properties of an acyclic transoid 1,3-diene (**1**) of biaxial dissymmetry.[20] We believe that the transoidal four-carbon system, which constitutes the most important part of the chromophore, is planar, requiring that the optical activity arise from some perturbation of the electronic structure by the chiral surroundings (Moscowitz[23]). The low value ($g = \Delta\epsilon\lambda/\epsilon\lambda$) of 10^{-4} for the Kuhn anisotropy factor[22] supports this classification. In Snatzke's[24] classification, this is a chromophore having a chiral second sphere. The molecular dissymmetry of **1** arises from a combination of two chiral olefinic axes. This is the first member of this new class of dissymmetric conjugated dienes—the dicyclohexylideneethane derivatives. This family includes **1** as a special case in which the dissymmetric axes a_1 and a_2 are structurally identical. Since **1** is unique, the interpretation of its CD spectrum is difficult. The fine structure of the $\pi-\pi^*$ CD Cotton effect is analogous to the corresponding UV absorption,[25] and the Cotton effect is intense.



$[\theta]_{259}$ + 14 500; $[\theta]_{249}$ + 22 400; $[\theta]_{241}$ + 20 200; $[\theta]_{234}$ + 7280

(*aR*,*aR*)-(+)-bis(4-methylcyclohexylidene)ethane (**1**)

The various rules described earlier[5b,9,13,18] are found not to be amenable to the analysis of Cotton effects present in **1** as well as to the 10,19-dihydrovitamin D isomers[26] whose 1,3-diene structures have heretofore not been recognized as being chiral chromophores. In order to interpret the chiroptical properties of **1** and related acyclic 1,3-dienes and α,β-unsaturated carbonyl chromophores, we undertook a systematic study of molecules (Figure 2) of known absolute configuration, the syntheses and characterization of which we have reported in the preceding article. The analysis of the long wavelength $\pi-\pi^*$ Cotton effects and the formation of a "planar diene rule" are the subject of this article.

Chiroptical Properties

The lowest energy (longest wavelength) $\pi-\pi^*$ transition of the chromophores exhibited strong UV absorptions in the 250–220-nm spectral region. The UV absorption in the higher energy region is weak and appears only as a shoulder to the main $\pi-\pi^*$ absorption. The nature of these weak transitions are not well understood. In CD, Cotton effects corresponding to the lowest energy $\pi-\pi^*$ transitions and additional Cotton effects on the higher energy (shorter wavelength) side of the spectra were observed. The higher energy Cotton effects had magnitudes ranging from 0 to as high as the main $\pi-\pi^*$ Cotton effects. Therefore one should be careful in selecting the Cotton effect for interpretation. Only the lowest energy $\pi-\pi^*$ Cotton effects have been taken into account for the purpose of interpretation.

In each case the UV and CD spectra were recorded by employing dilute solutions in cyclohexane. Use of a hydrocarbon solvent facilitated the measurement down to 200 nm with the preservation of fine structures in the absorptions. It was found that the use of a polar solvent like methanol did not affect the Cotton effect significantly, indicating a solvent independence for the preferred conformations of these dienes and α,β-unsaturated aldehydes.

Conformation of the Chromophore

In cyclic dienes the chromophore is controlled by ring conformations and it is forced to adopt a skewed conformation so that the overall energy of the molecule is minimized. Sterically hindered 1,2-dialkylidenecycloalkanes are also known to contain skewed chromophores[27] as evidenced by their UV and NMR spectral properties.[27a,b,28] In such molecules the individual double bonds are also twisted and the bond angles and bond lengths deviate[29] from normal values. On the other hand, acyclic dienes have a lesser amount of constraint and they have greater mobility. However, heavily substituted acyclic dienes[30] are known to contain

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(14) (a) J. S. Rosenfield and E. Charney, *J. Am. Chem. Soc.*, **99**, 3209 (1977); (b) E. Charney, C. H. Lee, and J. S. Rosenfield, *ibid.*, **101**, 6802 (1979), and references cited therein.

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(21) (a) O. Korvey, *Recl. Trav. Chim. Pays-Bas*, **94**, 125 (1975); (b) A. DiCorato, *Gazz. Chim. Ital.*, **98**, 810 (1968); (c) G. Giacomelli, L. Lardicci, C. Bertucci, and A. M. Caporusso, *Tetrahedron*, **34**, 2015 (1978).

(22) (a) W. Kuhn, *Trans. Faraday Soc.*, **46**, 293 (1930); (b) S. F. Mason, *Q. Rev., Chem. Soc.*, **17**, 20 (1963).

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(25) (a) I. T. Harrison, B. Lythgoe, and S. Tripett, *J. Chem. Soc.*, 4016 (1955); (b) Dimorth and Johnson, *Chem. Ber.*, **71**, 2658 (1938); (c) H. Booker, L. K.Evans, and A. E. Gilliam, *J. Chem. Soc.*, 1453 (1940); (d) R. Burckhardt, *ibid.*, 10 (1940).

(26) (a) A. Mourino and W. H. Okamura, *J. Org. Chem.*, **43**, 1653 (1978); (b) W. H. Okamura, M. L. Hammond, A. Rego, A. W. Norman, and R. M. Wing, *ibid.*, **42**, 2284 (1977). (c) The Cotton effects for the compounds described in ref 26a and 26b can be found in the following article.

(27) (a) D. J. Pasto and J. K. Borchardt, *J. Am. Chem. Soc.*, **96**, 6220, 6937, 6944 (1974); (b) K. B. Alberman, R. N. Haszeldine, and F. B. Kipping, *J. Chem. Soc.*, 3287 (1952); (c) F. B. Kipping and J. J. Wren. *ibid.*, 3246 (1957); (d) L. W. Jelenski and E. F. Kiefer, *J. Am. Chem. Soc.*, **98**, 281, 283 (1976).

(28) (a) W. F. Forbes, R. Chilton, and A. Balasubramaniam, *J. Org. Chem.*, **29**, 3527 (1964); (b) J. E. Starr and R. H. Eastmann, *ibid.*, **31**, 1393 (1966); (c) D. J. Pasto, A. F. T. Chen, and G. Binsch, *J. Am. Chem. Soc.*, **95**, 1553 (1973); (d) E. F. Kiefer, T. J. Levek, and T. T. Bopp, *ibid.*, **94**, 4751 (1972).

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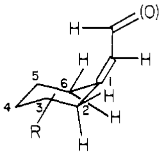
skewed s-trans and s-cis conformations.

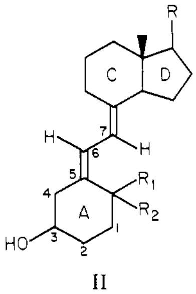
The conformation of butadiene has been studied extensively,[31] and its trans planar conformer (97%) has been estimated to be 2.6 kcals/mol more stable than the next higher energy conformer, which is a planar or a skewed *s*-cis conformer. According to a molecular mechanics calculation,[32] *trans*- and *cis*-1-methyl substitution does not destabilize the planar *s*-trans conformer, which is still, respectively, 2.1 and 2.5 kcal/mol more stable than a skewed *s*-cis conformer. Cycloalkylidene substitution can be regarded as methyl substitution on butadiene because the methylenes other than the two that are linked to the butadiene terminal carbon(s) are tied back. Structure I, a generalized structure of the molecules studied, is shown below. Therefore



I

cyclohexylidenepropenes would also be expected to have transoidal planar chromophores.

Similar in structure to **1** and the generalized structure I are the vitamin D and dihydrotachysterol isomers (II). The con-



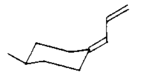
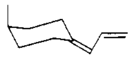
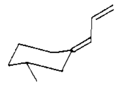
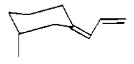
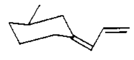
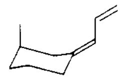
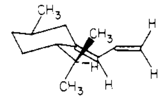
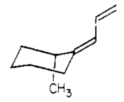
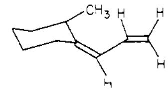
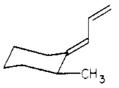
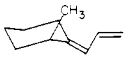
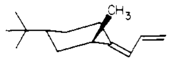
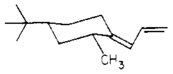
II

$R_1,R_2 = H, CH_3; R_1 + R_2 = CH_2$
$R = C_9H_{19}, C_9H_{17}, C_8H_{17}$

formations of the vitamin D have been extensively studied by use of ^1H and ^{13}C NMR techniques.[26,33] It has been concluded that ring A exists in two chair conformations. It has also been noted that the diene chromophore is planar as is evident by the intense UV spectra[34] observed.

Molecular models of **1** and structure I suggest that there is no $A^{1,3}$-strain interaction[35] between the C_2 and C_6 allylic equatorial hydrogens and the vinyl hydrogen. However, such $A^{1,3}$ interactions can be envisioned when the C_6 allylic equatorial hydrogen (I) is replaced by a methyl group. Under this circumstance, the six-membered ring assumes a more favorable conformation in which the methyl group is now in an axial orientation.[26] The diene chromophore remains unaltered as shown by its UV spectrum, which is still characteristic of a transoidal planar diene.

Table I. Geometries and Conformational Energies[a]

		C_1-C_2-C_3-C_4 dihedral angles	$\Delta H°$, kcals/mol	% conformer population at 25 °C
2a		179.90	0	95
2b		179.93	1.78	5
6a		179.87	0	89
6b		179.71	1.24	11
8a		179.89	0	87
8b		179.76	1.14	13
10		179.51		
12a		179.71	0	99
12b		179.76	3.14	1
14a		179.70	0	68
14b		180.0	0.45	32
16		179.95		
20		179.92		

[a] These data were obtained at the facilities provided in the laboratory of Professor N. L. Allinger, University of Georgia, Athens, Georgia. We acknowledge and thank Professor Allinger for all his help.

Additional evidence for the transoidal planar chromophore come from IR and NMR data. In the IR spectra of the α,β-unsaturated aldehydes, the C=C stretching (1625 cm^{-1}) band is much weaker than the C=O stretching (1670 cm^{-1}) band. This is characteristic of a transoid geometry of the chromophore.[36] In ^1H NMR of the α,β-unsaturated aldehydes and the dienes, the allylic equatorial proton having a cis relationship (I) with the C=O or the CH=CH_2 double bond is deshielded[37] to a considerable extent (δ 3.33 and 2.78). The deshielding indicates the coplanarity of the C=O or the CH=CH_2 double bond with the allylic equatorial hydrogen, which would be expected to be in the plane of the exocyclic double bond. All the data are consistent with a planar conformation of the chromophore.

Calculation of Conformation Energies

Although some knowledge about the conformation of the chromophore has been extracted, an independent assessment was

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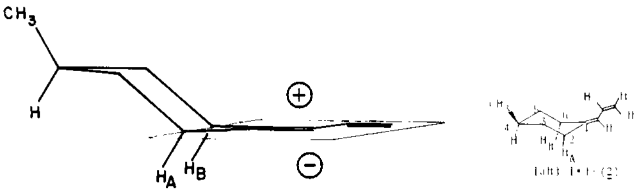

Figure 2. "Planar diele rule" as applied to (aR)-(+)-**2**.

desirable. Allinger's force-field calculation[38] was performed on some of the dienes (see Table I), and the geometries and energies of the lowest energy conformer and the next higher energy conformer have been calculated. The calculation method uses in an iterative cycle a VESCF sequence to calculate bond orders in the conjugated π-system. Then it carries out a molecular mechanics minimization of the strain energy of the molecule as a whole making use of the parameters calculated in the VESCF sequence. Thus, Allinger's MMPI and MMP2 programs were both tested on our molecules. We found that MMP2 calculations provided us with better results, which are reported in Table I. The data indicate that all the diene chromophores are transoidal and planar. The most stable conformers predicted by the calculation are in agreement with our ^1H and ^{13}C NMR data.

"Planar Diene Rule" Hypothesis

We will consider (aR)-(+)-(4-methylcyclohexylidene)propene (**2**) for the discussion (Figure 2). Applying the allylic axial chirality rule[13] for the allylic axial hydrogens H_A and H_B and allylic axial methylenes C_3 and C_5 causes some confusion. For example, should two of the allylic axial bonds cancel the other two? This would lead to the prediction of a zero Cotton effect. Should H_A reinforce H_B and C_3 reinforce C_5? This cannot be, since the molecule is axially dissymmetric.

For chiral acyclic planar 1,3-dienes, the "planar diene rule" states that, after the 1,3-diene chromophore and all the atoms directly attached to it are placed in a single plane, oriented as shown in the diagram (Figure 2), atoms or groups of atoms falling above the plane will make a positive contribution and those falling below will make a negative contribution to the Cotton effect for the long wavelength $\pi-\pi^*$ transition.

The "planar diene rule" should also be applicable to chiral transoidal planar α,β-unsaturated aldehydes for their long wavelength $\pi-\pi^*$ transition.

As applied to (4-methylcyclohexylidene)propene (or (4-methylcyclohexylidene)acetaldehyde) the chromophore is placed in a plane *as shown* (when the molecule is viewed from C_4–C_1, the double bond attached to the six-membered ring is on the right-hand side of the other double bond). One notes that the plane not only contains the four carbon atoms of the diene but also carbon atoms 2 and 6 of the cyclohexane ring and their attached equatorial hydrogen atoms. Molecular mechanics calculation of the geometry of **2** places these two equatorial hydrogens exactly in the plane. Moreover, the plane bisects the angle made by the axial allylic hydrogen atoms (H_A and H_B) attached to carbon atoms 2 and 6 and the allylic carbon atoms 3 and 5 of the ring. Those atoms or groups of atoms lying in the plane will make very little, if any, contributions to the long wavelength $\pi-\pi^*$ Cotton effect. The other atoms or group of atoms that are closer to the chromophore[24] will determine the sign of the long wavelength $\pi-\pi^*$ Cotton effect.

The mechanism by which a C–H or a C–C bond interacts with a diene chromophore is not clearly understood; Lightner et al.[16] offer some predictive guides regarding allylic axial hydrogen and methyl group in 1,3-cisoid dienes. Some authors have interpreted chiroptical properties in terms of a dominant contribution from a C–H bond[17] while others have argued that a C–C bond contribution is dominant.[13] Most molecular orbital calculations[14-16] have predicted that a C–C bond is more significant than a C–H bond, but a firm conclusion with regard to relative importance has yet to be established. In view of the above mentioned difficulties, we will adopt the view, which is consistent with earlier work,[13,39] that a C–H bond will have a smaller dissignate effect than a C–C bond.

On examination of the groups that fall in the (+) or (−) space, one notes that the allylic axial methylenes C_3 and C_5 fall in the (+) space, allylic axial hydrogens H_A and H_B fall in the (−) space, and C_4 falls in the (+) space. The signs assigned to the spaces above and below the plane are now consistent with the observed positive Cotton effect of (aR)-(+)-(4-methylcyclohexylidene)propene (**2**) and the hypothesis that a C–C bond is more dominant than a C–H bond (a ring $CH_2 > CH_3 > H$).

Results and Discussion

The most stable conformer of (aR)-(+)-(4-methylcyclohexylidene)propene (**2**), which is 1.78 kcal/mol more stable than the next higher energy conformer (Table I), exhibited a positive Cotton effect of molecular amplitude, $[\theta]$ +12 300 at the center peak of the absorption (Table II). The chiral groups surrounding the chromophore in (aR,aR)-(+)-bis(4-methylcyclohexylidene)ethane (**1**) are just twice that in **2**. Conformationally **1** should parallel **2**. We therefore reasoned that the intensity of the CD should be additive and that of **1** should be twice that of **2** and with the same sign, as is observed.[20] The results obtained from **1** and **2** were used to assign the (+) and (−) signs to the space above and below the chromophore plane.

Since the molecule **2** exists in a conformational equilibrium, the higher energy conformer **2b**, according to the "planar diene rule", should make an opposing contribution to the Cotton effect. If we remove this conformational population by the introduction of a conformation-anchoring group the intensity of the Cotton effect would be expected to go up. Thus, (aR)-(+)-(4-*tert*-butylcyclohexylidene)propene (**4**) ($[\theta]$ +16 900), which is conformationally homogeneous, exhibited a Cotton effect (Table II) stronger than that of **2** ($[\theta]$ +12 300).

$(E,3R)$-(−)-(3-Methylcyclohexylidene)propene (**6**) also has two conformers that must be taken into account: **6a** and **6b**. Conformer **6a** has been estimated to be more stable than **6b** by 1.24 kcal/mol, placing the **6a**:**6b** ratio at 89:11. On examination of **6a** we find the C_3 $CHCH_3$ group, C_4, and C_5 in the (+) space. The predicted Cotton effect is therefore positive. Conformer **6b** on the other hand reveals the C_3 $CHCH_3$ group, C_4, and C_5 in the (−) space, and the contribution will be negative. Since **6a** represents the major population the net Cotton effect is predicted as positive. This is what was observed (Table II) ($[\theta]$ +8860).

The conformational equilibrium in $(Z,3R)$-(−)-(3-methylcyclohexylidene)propene (**8**) is similar to its geometrical isomer discussed above, **8a** being 1.14 kcal/mol more stable than **8b**. In the analysis of **8a** we note that the C_4 and C_5 methylene and the C_3 equatorial methyl groups fall in the (−) space, whereas in **8b** the same groups fall in the (+) space. The net contributions to the Cotton effect in **8** should therefore be negative. The observed Cotton effect (Table II) ($[\theta]$ −17 800) confirms this prediction. The actual magnitude of conformer **8a** would be expected to be even stronger than the observed one. The Cotton effects in **6** and **8** offer some predictive values for the 10,19-dihydrovitamin D isomers.

$(E,2S,5R)$-(−)-(2-Isopropyl-5-methylcyclohexylidene)propene (**10**) is a conformationally static system bearing at C_5 the same absolute configuration as that in **8**. This compound was studied to examine the effect of an isopropyl group in the allylic equatorial position. Disregarding the contribution from the isopropyl group, the Cotton effect predicted of this molecule would be negative and stronger than $[\theta]$ −17 800, the observed Cotton effect of **8**. On steric grounds, the isopropyl group was expected to show some effect on the planarity of the diene chromophore. However, the UV characteristics are indicative of a planar chromophore. The molecular mechanics calculation (Table I) also supports this finding. The C_8–isopropyl bond is bent 19° out of the plane and into the (+) space. The isopropyl group adopts a conformation

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Table II. π-π* UV and CD Data for the (Cyclohexylidene)propenes

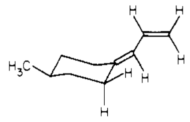
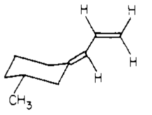
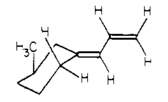
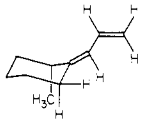
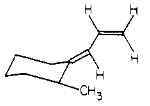
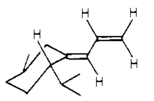
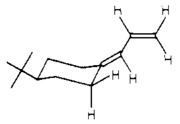
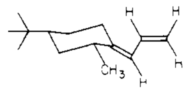
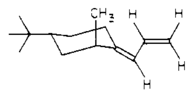
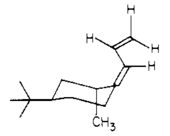
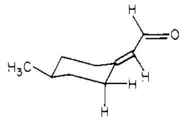
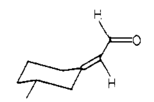
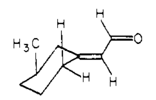
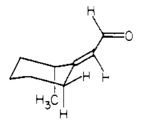
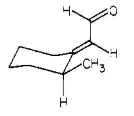
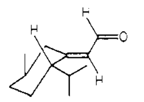
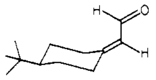
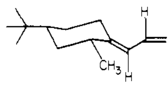
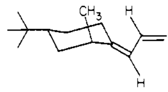
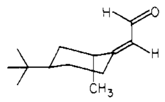
compound	UV λ_{max}, nm	CD, [θ]
 (*aR*)-(+)-2	246 (ε 16 400) 237.5 (ε 24 300) 231 (ε 22 000)	+12 300
 (*E*,3*R*)-(-)-6	246.5 (ε 20 100) 238 (ε 30 300) 231 (ε 27 600)	+8 860
 (*Z*,3*R*)-(-)-8	246 (ε 20 800) 238 (ε 31 300) 231 (ε 28 600)	-17 800
 (*Z*,2*S*)-(+)-12	246 (ε 19 100) 238 (ε 28 700) 231 (ε 26 200)	+13 100
 (*E*,2*S*)-(+)-14	247 (ε 17 000) 239 (ε 25 700) 232 (ε 23 400)	+14 200
 (*E*,2*S*,5*R*)-(-)-10	248 (ε 18 700) 239 (ε 28 200) 233 (ε 25 800)	-9 100
 (*aR*)-(+)-4	246 (ε 20 900) 238 (ε 31 900) 231 (ε 29 000)	+16 900
 (*E*,2*R*,4*R*)-(-)-20	247 (ε 18 300) 239 (ε 26 300) 232 (ε 24 200)	-15 600
 (*E*,2*S*,4*R*)-(+)-16	246 (ε 17 400) 239 (ε 26 300) 232 (ε 24 300)	-5 530
 (*Z*,2*S*,4*R*)-(+)-18	246 (ε 18 700) 239 (ε 26 900) 232 (ε 24 700)	+10 000

Table III. π-π* UV and CD Data for the (Cyclohexylidene)acetaldehydes

compound	UV λ_{max}, nm	CD, [θ]
 (*aR*)-(-)-3	230 (ε 19 500)	+6 870
 (*E*,3*R*)-(-)-7	231 (ε 16 700)	+2 690
 (*Z*,3*R*)-(-)-9	232 (ε 17 800)	-15 000
 (*Z*,2*S*)-(+)-13	231 (ε 13 200)	+16 300
 (*E*,2*S*)-(-)-15	232 (ε 17 800)	+11 800
 (*E*,2*S*,5*R*) (-)-11	236 (ε 12 500)	-8 920
 (*aR*)-(-)-5	231 (ε 15 600)	+8 750
 (*E*,2*R*,4*R*)-(+)-21	232 (ε 17 900)	-11 100
 (*E*,2*S*,4*R*)-(+)-17	233 (ε 15 100)	-7 140
 (*Z*,2*S*,4*R*)-(+)-19	232 (ε 18 200)	+11 500

in which the isopropyl hydrogen and one of the methyl groups have a gauche relationship with the closest vinyl hydrogen and the other methyl group lies almost in the plane. The dissymmetric conformation of the isopropyl group is also borne out by the 2–3 ppm ^{13}C NMR chemical shift difference between the two methyl groups. In molecular mechanics, the steric energy of the system was found to go up if one rotates the isopropyl group from its minimum energy orientation. Qualitatively speaking, part of the isopropyl group is found in the (+) space, and this may be a factor in reducing the magnitude of the negative Cotton effect. The observed Cotton effect is negative, [θ] -9100 (Table II).

(*Z*,2*S*)-(+)-(2-Methylcyclohexylidene)propene (**12**) is an interesting example. It can exist in two possible conformations in which the C_2 methyl is either equatorial or axial. In the "planar diene rule" analysis of the equatorial methyl conformer (ring C_3, C_4, and C_5 in (-) space and two axial hydrogens on C_2 and C_6 in (+) space) the predicted sign is negative and for the axial methyl conformer it is positive. Because of the $A^{1,3}$ interaction found in the equatorial methyl conformation the equilibrium would be expected to lie largely toward the axial methyl conformation.[26] The ^1H NMR data strongly support this conclusion. The complex one-proton multiplet at 3.10 ppm must be due to the deshielded C_2 equatorial proton.[37] In other systems in which the C_2 methyl is absent, this signal occurs at 2.65 ppm as a broad doublet with J = 12–13 Hz. The 0.45 ppm further downfield shift for the proton in **12** is consistent with the additional deshielding effect of the methyl group. Similar deductions have been obtained for the conformations of the A rings in dihydrovitamin D, DHV_2-II, and DHV_2-IV isomers.[26] In each case, an A-ring chair conformer with the C_{10} methyl (steroid numbers) in axial orientation was the preferred one and was found to be present to the extent of 95%. Molecular mechanics calculation also predicts the axial methyl chain conformer of **12** to be most stable, and it places it 3.14 kcal/mol below that of the equatorial methyl chair conformer. The UV characteristics (intensity and λ maximum) in **12** are the same as those found in the previous examples. The observed Cotton effect (Table II) is positive ($[\theta]$ +13 000), thus in agreement with the prediction using the "planar diene rule" (ring C_3, C_4, and C_5 in (+) space and C_2 axial methyl and C_6 axial hydrogen in (−) space).

(*E*,2*S*)-(+)-(2-Methylcyclohexylidene)propene (**14**) is another interesting example that bears a C_2 methyl group. There is no $A^{1,3}$ interaction in this molecule, and therefore the methyl group takes on an equatorial conformation. A similar system, the A ring of dihydrovitamin D (DHV$_2$-III), is also known to have an equatorial methyl chair conformation.[26] The molecular mechanics calculation places the equatorial methyl conformer **14a** at 0.45 kcal/mol below that of the axial methyl conformer **14b**. It constitutes an equilibrium population of 68% of **14a** and 32% of **14b**. Analysis of the space contributions leads to the following conclusion: In conformer **14a**, the C_2 equatorial methyl group lies approximately in the nodal plane A, and it will therefore make no contribution. The C_3, C_4, and C_5 ring methylenes lie in the (+) space, and this contribution from **14a** to the net Cotton effect is clearly positive. In conformer **14b**, the C_2 axial methyl lies in the (+) space and it subtends an angle of 74° with the plane of the chromophore, whereas the C_3 and C_5 methylenes lie in the (−) space and subtends an angle of 54° with the same plane. One would expect a methylene and a methyl to be consignate.[40] Since they are in opposing sectors, their relative importance needs to be known in order to predict the contribution from **14b**. On the other hand, the observed positive Cotton effect (Table II) of **14** does not lend itself to settle the question of this relative importance because of the conformational equilibrium (**14a**, **14b**) involved. Therefore it was decided to investigate a conformationally homogeneous system in which the C_2 methyl group is fixed in an axial orientation.

(*E*,2*S*,4*R*)-(+)-(2-Methyl-4-*tert*-butylcyclohexylidene)propene (**16**) is suitable for such an investigation. The C_2 axial methyl lies in the (+) space and bears an angle of 70° with the chromophore plane. The C_3 and C_5 methylenes lie in the (−) space and bears an angle of 57° with the plane. From the observed weak negative Cotton effect[41] of $[\theta]$ −5530 (Table II) as against the strong Cotton effect, $[\theta]$ −16 870, of (*aR*)-(+)-**4**, we conclude that the effect from the C_3 and C_5 methylenes is stronger than the C_2 axial methyl. This is so in spite of the fact that the C_2 methyl bears a larger angle with the chromophore. Hence, ring $CH_2 > CH_3 > H$.

If one examines the above result from the view point of a C–H bond vs. a C–CH_3 bond, one can conclude that an allylic axial hydrogen makes a more important contribution[17] than an allylic axial methyl.[13,16] Such an interpretation does not, however, include the effect of the C_3 and C_5 methylenes, which cannot be ignored. Therefore it is only a convenience to arbitrarily set the contribution of a C–H bond at 0 as it has been done in the original octant rule.[39]

From the above observation regarding the relative importance of a methylene vs. a methyl, we can predict that the Cotton effect in conformer **14b** is weak negative. This, coupled with the minor population of **14b**, allows us to state that the Cotton effect of **14** is essentially a contribution from conformer **14a**, which the "planar diene rule" predicts to be positive. The observed Cotton effect (Table II) is in agreement with the prediction.

It is sufficient to mention that the data (Table II) from (*Z*,2*S*,4*R*)-(+)-(2-methyl-4-*tert*-butylcyclohexylidene)propene (**18**), positive Cotton effect ($[\theta]$ +10 010), and (*E*,2*R*,4*R*)-(+)-(2-methyl-4-*tert*-butylcyclohexylidene)propene (**20**), negative Cotton effect ($[\theta]$ −15 570), reinforce the findings from molecules **12** and **14**, respectively.

Turning our attention to the α,β-unsaturated aldehydes **3**, **5**, **7**, **9**, **11**, **13**, **15**, **17**, **19**, and **21**, we observe that they have conformations analogous to their corresponding dienes. The Cotton effects for their lowest energy $\pi-\pi^*$ transition centered at 231–232 nm are of the same sign as their dienes. The observed Cotton effects are presented in Table III, and as with the dienes we find that all the α,β-unsaturated aldehydes obey the "planar diene rule" in sign.[42]

Acknowledgment. This work was supported by a grant from the National Science Foundation. We thank Professor A. Burgstahler for a number of helpful discussions. We also appreciate the generosity of Professor N. L. Allinger in making his facility available to us. We wish to especially acknowledge the contribution of Professor J. Brewster, whose critical insight helped us to formulate the "planar diene rule".

Registry No. (*aR*)-(+)-**2**, 85048-15-3; (*aR*)-(−)-**3**, 85048-14-2; (*aR*)-(+)-**4**, 85048-22-2; (*aR*)-(−)-**5**, 85048-21-1; (*E*,3*R*)-(−)-**6**, 85048-28-8; (*E*,3*R*)-(−)-**7**, 85048-27-7; (*Z*,3*R*)-(−)-**8**, 85048-32-4; (*Z*,3*R*)-(−)-**9**, 85048-31-3; (*E*,2*S*,5*R*)-(−)-**10**, 85048-62-0; (*E*,2*S*,5*R*)-(−)-11, 85048-61-9; (*Z*,2*S*)-(+)-**12**, 85048-40-4; (*Z*,2*S*)-(+)-13, 85048-39-1; (*E*,2*S*)-(+)-**14**, 85048-43-7; (*E*,2*S*)-(−)-**15**, 85048-42-6; (*E*,2*S*,4*R*)-(+)-**16**, 85066-66-6; (*E*,2*S*,4*R*)-(+)-**17**, 85048-51-7; (*Z*,2*S*,4*R*)-(+)-**18**, 85048-49-3; (*Z*,2*S*,4*R*)-(+)-**19**, 85048-48-2; (*E*,2*R*,4*R*)-(−)-**20**, 85048-55-1; (*E*,2*R*,4*R*)-(+)-**21**, 85048-54-0.

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(40) The term "consignate" refers to the sign contribution of groups in the same sector.

(41) In **16** the long wavelength $\pi-\pi^*$ negative Cotton effect centered at 239 nm was found to overlap a strong negative Cotton effect centered at 218 nm. From the appearance of the spectrum, we can confidently say that the negative sign of the $\pi-\pi^*$ Cotton effect and intensity at 239 nm were not affected by the 218 nm band. Corroborating the negative $\pi-\pi^*$ Cotton effect is also the result obtained from α,β-unsaturated aldehyde **17**.

(42) On the basis of the symmetry rules for optical rotation, Schellman predicted that for *trans*-dienes and other π-electron systems belonging to the point group C_{2h}, the Cotton effects would be predicted by a simple planar rule (J. Schellman, *J. Chem. Phys.*, **44**, 55 (1966)).