

(21c). A solution of methylcyclooctatetraene (198 mg, 1.68 mmol) and tetracyanoethylene (1.28 g, 10.0 mmol) in 10 ml of ethyl acetate was refluxed for 4.5 hr, cooled and processed in the manner outlined earlier. Chromatography of the crude adduct on Florisil and recrystallization from methylene chloride-ether gave 252 mg (61%) of **21c**: mp 203–204.5°; $\delta_{\text{TMS}}^{\text{acetone-d}_6}$ 1.63 (s, 3 H, CH₃), 3.04–3.32 (m, 2 H, cyclobutene sp³ CH), 3.80–4.12 (m, 2 H, bridgehead), 5.63 (s, 1 H, cyclobutene), and 6.32–6.54 (m, 2 H, olefinic).

Anal. Calcd for C₁₅H₁₀N₄: C, 73.15; H, 4.09. Found: C, 73.01; H, 4.12.

The labeled derivative was obtained similarly except for extension of the heating period to 9 hr.

9-Thiabicyclo[4.2.1]nona-2,4,7-triene-1,6-d₂ 9,9-Dioxide (25). To a stirred solution of 9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-dioxide (3.36 g) in 250 ml of anhydrous tetrahydrofuran at –70° under nitrogen was added 40 ml of *n*-butyllithium (2 M) during 15 min. The deep purple solution was stirred for an additional 10 min and treated in one portion with 10 ml of acetic acid-*O-d* (95% *d*₁). The tetrahydrofuran was removed by evaporation under reduced pressure and 20 ml of water was added. Extraction with methylene chloride was followed by washing of the combined

organic layers with water and brine. Drying and evaporation of solvent afforded 2.17 g of **25**.

Cyclooctatetraene-1,4-d₂ (26). A solution containing 1.00 g of **25** in 400 ml of acetone-ether (1:3) was irradiated as before for 2 hr. Removal of the solvent left a yellow oil which was purified by vpc chromatography on column C.⁴⁷ There was obtained 250 mg of **26**; *m/e* calcd 106.0752, found 106.0753.

9,9,10,10-Tetracyano-tricyclo[4.2.2.0^{2,5}]deca-3,7-diene-d₂ (27). A solution containing 53 mg of **26** and 640 mg of tetracyanoethylene in 10 ml of ethyl acetate was refluxed for 8 hr and processed in the usual manner. There was obtained after column chromatography on Florisil 78 mg of **27**, mp 248° (lit. for unlabeled adduct⁴⁸ mp 249°).

Acknowledgment. This research was supported in part with funds provided by the National Science Foundation. The authors are also indebted to Dr. Robert E. Wingard, Jr., for his early pioneering thermolysis experiments which gave impetus to this study.

(48) P. Scheiner and W. R. Vaughan, *J. Org. Chem.*, **26**, 1923 (1961).

Conformational Analysis. CII. Levopimaric Acid and Related Steroidal Dienes^{1,2}

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Abstract: Force field calculations suggest that the conformation of levopimaric acid and configurationally related steroidal dienes such as cholesta-2,4-diene may best be discussed in terms of a conformationally mobile system in which the diene ring can adopt a "levopimaric like" or a "cholesta-2,4-diene like" conformation. The energies of these conformations vary with the number and positioning of substituents, and the resulting equilibria are discussed for a number of model compounds. Previously reported circular dichroism data are discussed in terms of relative populations calculated for these conformers. The effects of substituents appear to be important in determining the amplitudes of the circular dichroism curves.

X-Ray crystallography³ has shown that levopimaric acid (**1a**) exists in a folded conformation in the crystalline state, with the C9–C10 bond in a quasi-axial orientation with respect to the diene ring. Investigation of the optical rotatory dispersion⁴ of levopimaric acid (**1a**) and cholesta-2,4-diene (**2a**) had previously led to the suggestion that levopimaric acid exists in this folded conformation in solution, in contrast to the extended conformation deduced for the configurationally related cholesta-2,4-diene (**2a**), in which the C10–C9 bond is quasi-equatorial. Supporting evidence for the latter conclusion had been obtained from nmr,^{4,5} surface film,⁶ and photochemical⁷ studies.

(1) For paper CI in this series, see D. H. Wertz and N. L. Allinger, *Tetrahedron*, **30**, 1579 (1974).

(2) This work has been supported by a grant from the National Institutes of Health (AM-14042).

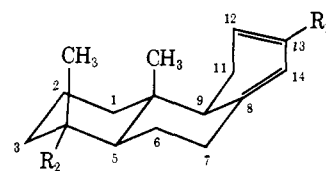
(3) U. Weiss, W. B. Whalley, and I. L. Karle, *Chem. Commun.*, **16** (1972).

(4) A. W. Burgstahler, H. Ziffer, and U. Weiss, *J. Amer. Chem. Soc.*, **83**, 4660 (1961); U. Weiss, H. Ziffer, and E. Charney, *Chem. Ind. (London)*, 1286 (1962); *Tetrahedron*, **21**, 3105 (1965).

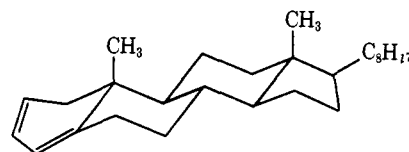
(5) J. C. W. Chien, *J. Amer. Chem. Soc.*, **82**, 4762 (1960); A. W. Burgstahler, J. N. Marx, and D. F. Zinkel, *J. Org. Chem.*, **34**, 1550, 3716 (1969).

(6) U. Weiss and N. Gersheld, *Experientia*, **18**, 355 (1962).

(7) W. H. Schuller, R. N. Moore, J. E. Hawkins, and R. V. Lawrence, *J. Org. Chem.*, **27**, 1178 (1962); W. G. Dauben and R. M. Coates, *J. Amer. Chem. Soc.*, **86**, 2490 (1964).



1a, R₁ = *i*-Pr; R₂ = CO₂H

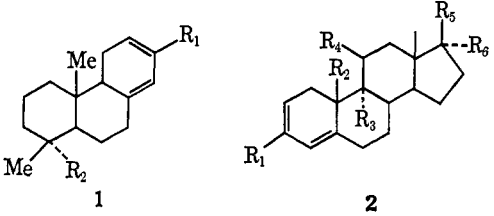


2a

Burgstahler, *et al.*,⁸ have investigated the effect of substituents on the circular dichroism of the $\pi \rightarrow \pi^*$ band at ca. 270 nm of levopimaric acid and configurationally related steroidal 2,4-dienes with varying substitution patterns (see Table I). The sign and magnitude of the Cotton effect showed a marked dependence on the substitution.

The degree to which this dependence reflects conformational changes is not clear *a priori*, and an independent assessment of the effect of substituents on the

(8) A. W. Burgstahler, J. Gawronski, T. F. Niemann, and B. A. Feinberg, *Chem. Commun.*, 121 (1971).

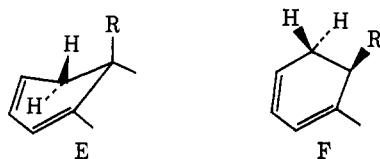
Table I. CD of Levopimaric Acid and Derivatives and Related Steroid 2,4-Dienes^a


	R ₁	R ₂					Δε (ca 270 nm)
1a	<i>i</i> -Pr	CO ₂ H					-12.2
b	<i>i</i> -Pr	CO ₂ H					-11.3
c	H	CMe ₂ OH					-10.9
	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	
2a	H	Me	H	H	C ₈ H ₁₇	H	+12.4
b	Me	Me	H	H	C ₈ H ₁₇	H	+11.1
c	H	Me	H	OH	BMD ^b		+9.4
d	H	Me	H	H	OH	H	+11.7
e	H	Me	H	H	OH	Me	+11.2
f	H	Me	H	OH	OH	Me	+9.5
g	H	Me	Δ9(11)-ene	OH	OH	Me	+7.1
h	H	Me	Me	OH	BMD ^b		+3.9
i	H	H	H	H	OH	H	+2.1

^a Reference 8. ^b BMD = bismethylenedioxy derivative of the hydroxycortisone side chain.

conformation of these systems seemed called for. As we are now able to calculate geometries and conformational energies for molecules containing delocalized systems,⁹ we have carried out molecular mechanics calculations on a number of model systems.

Whalley, *et al.*,³ discussed the conformation of levopimaric acid and cholesta-2,4-diene and related compounds in terms of a conformationally homo-



geneous system, taking a small Δε value as evidence for a more planar (less chiral) diene system (see below) intermediate between the two extreme conformations.

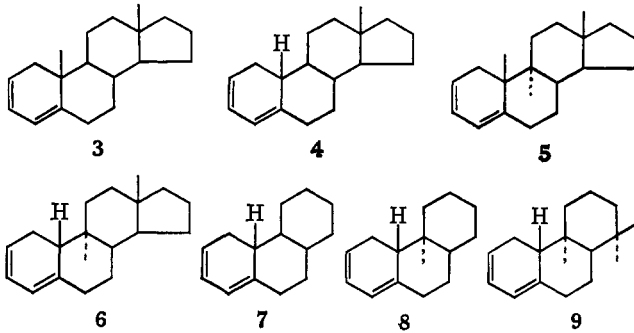
The calculations reported here lead us to suggest that a better approximation to the conformational situation in molecules such as these, in solution, is to treat each diene as a pair of interconverting conformers of type E (extended) and type F (folded).^{4b,8} The observed Cotton effect is then a function of the relative population of the two conformers, the chirality of the diene system in each of the conformers, and substituent effects on the Cotton effect of the diene system in each conformer.

Calculation of Conformational Energies

The calculation method, which has previously been reported,⁹ uses in an iterative cycle a VESCF sequence to calculate bond orders in the conjugated π system and a molecular mechanics minimization of the strain energy of the molecule as a whole, which makes use of the parameters calculated in the VESCF sequence. The steric energy has been calculated for type E and

(9) N. L. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.*, **95**, 3893 (1973).

type F conformers of a number of model systems, and the results are reported in Table II, together with the calculated conformer populations at 298°K.

Table II. Calculated Conformational Properties of the Steroidal 2,4-Diene Derivatives


Model system	Conformer	ΔH°	% conformer population at 298°K
3	E	0.00	99
	F	2.74	1
4	E	0.00	92
	F	1.41	8
5	E	0.00	52
	F	0.06	48
6	E	1.22	11
	F	0.00	89
7	E	0.00	91
	F	1.39	9
8	E	0.84	19
	F	0.00	81
9	E	0.52	30
	F	0.00	70

The fact that minimization of the energies of conformations E and F in each case leads to distinct structures serves to indicate that the molecules exist as equilibrium mixtures with a barrier to interconversion between the two conformers and not a single conformation of intermediate structure.

As the C13 *i*-Pr group was found not to affect the circular dichroism markedly,⁸ calculations were carried out on a C13 H model. The calculations were further simplified by treating the carboxylic acid moiety and the 11β-OH moiety, which the program cannot handle currently, as a methyl group and hydrogen atom, respectively. In the steroid series, the calculations were further simplified by omitting the side-chain structure. These simplifications should not affect the calculated conformer populations or geometries significantly.¹⁰

Results and Discussion

If we take 4 as a starting point, in this case the extended conformation is the more stable by 1.41 kcal/mol (Table II).

The introduction of a β-methyl group at C10 or an α-methyl group at C9 (steroid numbering) will shift the equilibrium between the folded and extended conformers. Our analysis of the interactions involved is largely straightforward and essentially in agreement with the conclusions of earlier workers.^{3,8}

A β methyl at C10, as in 3, leads to the E conformer

(10) N. L. Allinger and G. Lane, *J. Amer. Chem. Soc.*, **96**, 2937 (1974).

being favored by 2.74 kcal/mol. This destabilization of the F conformer relative to the E, comparing **3** to **4**, can be attributed to the unfavorable interactions between the 10 β methyl and the C1 methylene in the F conformation of **3**. This interaction is greatly relieved in the E conformation.

In the F conformers, the C1 hydrogens adopt a staggered relationship with respect to the 10 β bond. The interactions between the 10 β substituent, whether hydrogen or methyl, and the 1 β hydrogen are about the same in both the extended and folded conformers. However, a strong repulsive interaction is introduced between the 1 α -H and the 10 β moiety in the F conformers, which is more severe in the 10 β -methyl compounds (*e.g.*, **3**) than in the 10 β -H compounds (*e.g.*, **4**). The unfavorable interactions between the 11 α H and 1 β H in the E conformer are replaced by an unfavorable interaction of similar magnitude between the 11 α H and the 1 α H in the F conformer and do not contribute appreciably to the conformational energy difference.

If both a 10 β -methyl group and a 9 α -methyl group are present as in **5**, the E conformer is favored by only 0.06 kcal/mol. For the 10 β -H,9 α -methyl compound (**6**), the F conformer is now favored by 1.22 kcal/mol. The substitution of a 9 α methyl for a 9 α H destabilizes the E conformer relative to the F by a very similar amount in the presence and absence of a 10 β -methyl group. Thus the change in the relative energy of the F and E conformers is 2.68 kcal/mol between **3** and **5** and 2.63 kcal/mol between **4** and **6**. In other words, additivity of these methyl group interactions is a good approximation in the steroidal compounds.

The destabilizing effect on the E conformer of the 9 α methyl, compared to a 9 α H, is due largely to the unfavorable interaction between the 1 α H and the adjacent 9 α -methyl proton in the E conformer. This interaction is relieved in the F conformer. However, unfavorable interactions are introduced between C2 and C4 and the adjacent 9 α -methyl protons, in contrast to the attractive force at one time postulated to exist between the 9 α -methyl and the diene system.^{4a}

More subtle effects come to light in comparing the steroids with the "resin acid" series. The effect of a 9 α -methyl group in destabilizing the E conformer relative to the F (**7** and **8**) is notably smaller than in the steroid case, and the substitution of a 14 α methyl for a 14 α H decreases the effect still further. These changes can be related to buttressing effects.

Comparing the least substituted "resin acid" structure (**7**) with the simplest steroid structure (**4**), the D ring in the latter bends the 14 α H back toward the center of the C ring where it interacts unfavorably with the 9 α H. This interaction is almost independent of the A ring conformation here, and the E conformer is favored over the F by 1.39 kcal/mol in **7** and 1.41 kcal/mol in **4**.

When a 9 α methyl is substituted for the 9 α hydrogen, as in **8**, the F conformer is preferred by 0.84 kcal/mol, compared to 1.22 kcal/mol in the steroid **6**. The difference can be related to the greater flexibility of the "resin acid" structures. In the highly substituted steroid **5**, in which flexibility would be expected to be very small, the E conformer is greatly destabilized by a 2.63-kcal/mol repulsion between the 9 α methyl and 1-methylene. This repulsion is much less serious in the

E conformer of the "resin acid" structure **8** (0.55 kcal/mol). In the steroids, the D ring forces the 14 α H back into the 9 α methyl, which is in turn forced hard against the C1 methylene. If the D ring is missing, as in **8**, the 14 α hydrogen can lean out away from the C ring and the 9 α methyl can lean away from C1 so the repulsion is less serious.

By this line of reasoning, the introduction of a 14 α -methyl group as in **9** should further destabilize the E conformation. However, calculations show the opposite trend. The F conformer is favored by 0.84 kcal/mol in **8** but only 0.52 kcal/mol in **9**.

The expected increase of the 9 α -methyl/C1 methylene repulsion in the E conformer on substitution of a 14 α methyl for a 14 α H is in fact calculated. The repulsion between the nearest hydrogen on the 9 α methyl and the 1 α hydrogen is 0.47 kcal/mol in **8** and increases to 0.58 kcal/mol in **9**. The geminal dimethyl at C14 does destabilize the conformation in the way supposed, but this is overridden by some other effect.

This overriding effect appears to be the destabilization of the F conformer of **9** by a "reflex effect."¹¹ The syn-diaxial methyl interaction tends to spread apart the 9 α and 14 α methyls in **9**, and the resulting reflex effect forces together the 10 β hydrogen and the 8 β hydrogen. This might be expected to affect both the E and F conformers. However, investigation of the calculated structures of the F conformers of these compounds reveals a rather subtle feature. The repulsion between the 11 α H and 1 α H (and perhaps also the 10 β -R/C1-methylene interactions) in the F conformers results in opening of the C1-C10-C9 angle and a rotation of the 10 β -R group into the B ring. Hence the reflex effect of the 14 α -methyl/9 α -methyl repulsion in **9** would be expected to have a greater destabilizing effect on the F conformer, in which the 10 β -H/8 β -H interaction is intrinsically more severe (see diagrams). According to the calculations, the 10 β -H/8 β -H interaction is already severe in the F conformer of **8** (0.65 kcal) and is increased to 0.82 kcal/mol in the F conformer of **9** by the reflex effect of the syn-diaxial methyls.

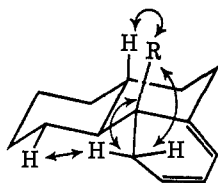
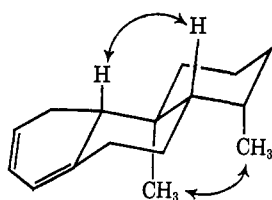
The reflex relationship also results in more severe interactions on the α face of the molecule in the F conformers. The distance between the 9 α -methyl carbon and the 14 α hydrogen is 3.00 Å in the E conformer of **8** and is reduced to 2.89 Å in the F conformer, despite the fact that the interaction between the 9 α methyl and 1 α H in the E conformer is relieved in the F conformer, and the 9 α methyl and 14 α H might be expected to splay apart. The effect is greater in the more crowded structure **9**. In the extended conformation of **9**, the distance between the syn-diaxial carbons is 3.60 Å, while in the folded conformation it is 3.45 Å.

These unanticipated reflex effects which become important with the geminal dimethyl substituent outweigh what appeared at first sight to be the dominant effect, and they seem to account for the difference calculated between the equilibria in **8** and in **9**.

Conformations and Cotton Effect Data

Accepting that the conformational energies are reasonable in terms of our physical model, the problem

(11) E. L. Eliel, N. L. Allinger, G. A. Morrison, and S. J. Angyal, "Conformational Analysis," Wiley-Interscience, New York, N. Y., 1965.

rotation of 10 β substituent into B ring of F conformers

reflex effect in 9

of reconciling the observed Cotton effects with conformer populations remains. It is calculated that the levopimaric acid model (8) would adopt the F conformation to the extent of 70% at 298°K (see Table II). The diene torsional angle calculated is -12.3° which compares with the values of -9.1 and -11.8° reported for the dimeric molecules in the crystalline state. The $[M]_{315}$ of a solution of levopimaric acid in isooctane was reported⁴ to show a slight decrease between $+6$ and $+82^\circ$. The corresponding calculated conformer populations for the model system are 71.1% F, 28.9% E and 66.9% F, 33.1% E. This trend is in the right sense.¹² Androsta-2,4-diene (3) as a model for cholesta-2,4-diene (2a) is calculated to adopt the extended E conformation deduced from ORD⁴ to the extent of 99% at 298°K.

The opposing signs of the Cotton effects observed for levopimaric acid (1a) and its derivatives (1b, 1c), on one hand, and cholesta-2,4-diene (2a), on the other, are in accord with the predictions of the diene chirality rule¹³ for the dominant conformer in each model system. The quantitative relationship between the Cotton effect data and the calculated structures and conformer populations is less clear.

Hug and Wagniere¹⁴ have recently calculated the rotatory strengths of the two long wavelength $\pi \rightarrow \pi^*$ bands of a butadiene system at different dihedral angles, using a CNDO-CI procedure. Their results suggest that the rotatory strength rises approximately linearly with increasing diene dihedral angle, for small angles. Using the data in the paper and the suggested relationships linking rotatory strength and $\Delta\epsilon$ ¹⁴ and assuming a linear relationship with the diene dihedral angle, the values of $\Delta\epsilon$ have been calculated for the equilibrium mixtures (Table III). In each case for which circular dichroism data are available, the sign of the observed Cotton effect is predicted correctly. This is the limit of accuracy usually demanded of theories of the Cotton effect.

However, if the calculated torsional angles and conformer populations are taken to be essentially correct, it may be seen that the observed results cannot be ac-

(12) An experimental free energy difference of the order of 0.50 kcal/mol between the two levopimaric acid conformers is reported from low-temperature CD studies according to a private communication from Professor A. W. Burgstahler.

(13) A. Moscowitz, E. Charney, U. Weiss, and H. Ziffer, *J. Amer. Chem. Soc.*, **83**, 4661 (1961); E. Charney, *Tetrahedron*, **21**, 3127 (1965).

(14) W. Hug and G. Wagniere, *Helv. Chim. Acta*, **54**, 633 (1971).

Table III. Calculated and Experimental CD of Chiral Dienes

Compd	Conformer	% population ^a	Diene ^{a,b} dihedral angle	$\Delta\epsilon$ (calcd) ^c	$\Delta\epsilon$ (exptl) ^b	$\delta\Delta\epsilon^d$
1c	E	30	+7.6	-3.8	-10.9	-7.1
	F	70	-12.3			
2a	E	99	+11.6	+7.0	+12.4	+5.4
	F	1	-11.2			
2i	E	92	+7.9	+3.6	+2.1	-1.5
	F	8	-12.8			
2h	E	52	+11.2	+0.5	+3.9	+3.4
	F	48	-10.5			

^a Calculated value for model system. ^b Signed according to the chiral sense. ^c Calculated assuming a linear $\Delta\epsilon/\omega$ relationship from the results of Hug and Wagniere (ref 14). ^d Difference between experimental and calculated values. ^e See footnote b of Table I.

commodated quantitatively, even by adjusting the magnitude of the linear term. The discrepancies may be due to inaccuracies and approximations in the calculations. Factors other than the nonplanarity of the diene system may also influence the sign and magnitude of the Cotton effect of a diene chromophore. These factors may include twisting of the olefinic bonds,¹⁵ dynamic effects,¹⁶ and substituent effects. We will limit our discussion to the last of these.

In view of the predictive success of the diene chirality approach in accounting for the correct sign of the Cotton effects in each case, we will discuss substituent effects in terms of the difference between the observed $\Delta\epsilon$ and that calculated from the diene chirality¹⁴ ($\delta\Delta\epsilon$, Table III). If this difference is attributed to substituent effects, then in the three cases in which a clear conformational preference is predicted (1c, 2a, 2i) the substituent effect must be strongly positive (2a), weakly negative (2i), and strongly negative (1c).

For the 10 β -H compound (2i) the calculated $\Delta\epsilon$ from the chirality of the diene chromophore agrees well with the observed $\Delta\epsilon$. The substitution of a 10 β -methyl group for a 10 β -H (2a, 2i) appears to result in a strong positive substituent effect in the E conformer, over and above the effect of the altered dihedral angle of the diene chromophore. For the levopimaric acid derivative (1c), a strong negative substituent effect is observed for the F conformer. This may be due to the altered angular relationship of the B ring to the diene system or the unusual proximity of the 9 α methyl to the diene chromophore.

Questions of the existence and mode of substituent

(15) C. C. Levin and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 3446 (1972).

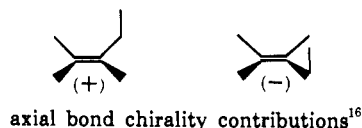
Table IV. Axial Allylic Bond Chirality¹⁶

Compd	Conformer	% population	—Axial allylic bond contributions—				Net ^a effect $\delta\Delta\epsilon^b$
			Positive		Negative		
1c	E	30	C-C	C-H 10 β H 1 α H	C-C	C-H 6 β H	-C-H -7.1
	F	70	C6-C7		C10-C9	1 β H	
2a	E	99	10 β Me	1 α H		6 β H	+C-C +5.4
	F	1	C6-C7		C10-C9	1 β H	
2i	E	92		10 β H 1 α H		6 β H	+C-H -1.5
	F	8	C6-C7		C10-C9	1 β H	
2h ^d	E	52	10 β Me	1 α H		6 β H	c +3.4
	F	48	C6-C7		C10-C9	1 β H	

^a Allowing for conformer population. ^b From Table III. ^c Indeterminate effect. ^d See footnote *b* of Table I.

effects in dienes,^{18,15-17} conjugated ketones,^{16,18} α -diones,¹⁹⁻²¹ and isolated olefins²²⁻²⁶ are the subject of current controversy. The substituent effects postulated here do not appear to be accounted for by any one set of self-consistent rules.

Burgstahler, *et al.*,^{16,19} have shown that in a number of cases in which the observed Cotton effect cannot be reconciled with the diene chirality rule,^{13,15,17} the observations can be rationalized in terms of an empirical axial allylic bond chirality rule. The sign of the contribution of an axial allylic bond is shown in the diagram. The axial allylic bond contributions to the chirality of the dienes under consideration are listed in Table IV. For convenience these are separated into C-H bond contributions and C-C bond contributions.



Our conclusions about the allylic bond chirality effect for the folded levopimaric acid conformer are somewhat different from those of Burgstahler, *et al.*⁸ From our calculations, the C6-C7 bond is quasi-axial with a calculated 4-5-6-7 dihedral angle of 109°, whereas the 4-5-6-6H dihedral angle is calculated to be only 14°, and the C6-6 β H bond is essentially equatorial. Thus the allylic bond chirality contributions may be only weakly negative in this case.¹⁹

Chirality rules framed in terms of axial allylic bond contributions imply some type of specific orbital interaction between the allylic bond and the chromophore,^{18,22} although one suggested rule for olefins is framed in terms of allylic bond polarization.²³ This should be contrasted with symmetry rules involving

any proximate substituent, such as the olefin octant rule,²⁴ which imply a static dissymmetric perturbing field model.²⁷ A semiquantitative estimate of the effect of an alkyl substituent in the latter case can be made by considering the proximity of the substituent to the chromophore and to the nodal planes of the symmetry rule. The data presented by Burgstahler and Barkhurst¹⁶ do not appear to be amenable to this type of analysis.

If an allylic bond chirality rule is to be applied in a quasi-quantitative manner, some idea of the relative importance of the factors involved is required. The formulation of the rule in terms of axial bonds suggests that the dihedral angle subtended with the diene system is one factor. Another possible factor is the nature of the moieties connected by the allylic bond.^{18,23,25,28} Models invoking specific interactions with axial allylic bonds have tended to treat axial allylic C-H bonds as important.^{16,22} In the absence of a quantitative theory, it should be noted that whatever the relative weighting attached to axial allylic C-H bonds compared to axial allylic C-C bonds, the axial allylic bond chirality approach fails to account satisfactorily for the data presented here (Table IV).

If we attribute essentially all of the effect to axial allylic C-C bonds, this allows the results for 1a and 2i to be reconciled and also accounts for the data originally presented by Burgstahler and Barkhurst.¹⁶ The strong negative effect in 1c is now anomalous, but an alternative source of this effect may be postulated.

In the model structure 9, the homoallylic 9 α methyl is close enough to the α face of the diene chromophore in the folded conformer to be involved in a repulsive interaction with C2 and C4 (above). Thus a specific interaction with this moiety may be responsible for the strong negative effect observed in 1c.

A general contribution by axial homoallylic bonds has been suggested by Gawronski and Kielczewski.²⁵ The anomalous diene Cotton effects discussed by Burgstahler and Barkhurst¹⁶ cannot be reconciled with such an effect, and the data discussed by Gawronski and Kielczewski²⁵ are at any rate open to another interpretation.²⁶ However, if the postulated effect of a 9 α -methyl group arises from a specific interaction as suggested here, such interactions would not be expected

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in more planar structures. Calculations suggest that through-space orbital interactions²⁹ may play an important role in determining the spectroscopic properties of molecules.

The remaining result on which the calculations shed some light is the smaller positive $\Delta\epsilon$ observed for the 2,4,9(11)-triene (**2g**) in comparison to the analogous 2,4-diene (**2e**) (+7.1; cf. +11.2). Both are essentially completely in the E conformation, according to the calculations on the model systems, and the calculated diene dihedral angle is in fact slightly greater for the triene. The position and intensity of the uv absorption maximum of the long wavelength $\pi \rightarrow \pi^*$ band of the triene (**2g**) do not suggest any great degree of conjugation between the diene system and the homoallylic double bond (**2g**, λ 267 nm, ϵ 5670; **2e**, λ 265 nm, ϵ 6400). The calculated VESCF bond order between the C5 π orbital and the C9 π orbital when the 9(11) double bond is included in the π system is 0.03 (distance 2.529 Å) as against a bond order of 0.31 between the C3 and C4 π orbitals. The dihedral angle between the 9-11 and 5-4 bonds is calculated to be -17.1° for the model system. This is in the opposite sense to the chirality of the 2,4-diene system in this conformer. It seems reasonable that an interaction of this type should affect the vectorial rotational strength more than it affects the scalar oscillator strength. (This also holds true for the axial allylic bond effect.) The small $\Delta\epsilon$ observed

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for the 2,4,9(11)-triene (**2g**) should thus be attributed to a specific electronic interaction rather than to a conformational change.

An alternative analysis of this observation might be made in terms of an allylic bond polarization rule.²³ However, such a rule as presently formulated would require that a $\Delta 9(11)$ double bond and a 10β -methyl group have a substituent effect of the same sign, contrary to observation.

Perhaps the most important insight provided by the calculations is that very different conformational situations can give rise to very similar Cotton effects. Thus according to our calculations, the small $\Delta\epsilon$ observed for the 10β -H, 9α -H compound **2i** arises from an essentially conformationally homogeneous system and is attributable to the near planarity of the diene and the absence of substituent effects. However, the small $\Delta\epsilon$ observed for the $9\alpha,10\beta$ -dimethyl compound **2h** arises from the canceling Cotton effects of two conformers present in a near 1:1 ratio, which would each individually be expected to show a strong Cotton effect.

A more exact definition of the conformational properties of such flexible systems (and hence of the veracity of the calculated conformational preferences) must await further experimental data or advances in the quantitative theory of the Cotton effect. The value of force field calculations in providing insights into such complex conformational problems does seem clear, particularly in view of the difficulties in interpreting measurements of the Cotton effect.

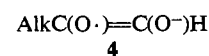
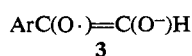
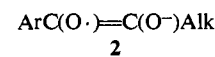
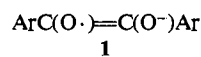
Aliphatic Semidiones. XXII. Acyclic Dialkyl-1,2-semidiones¹

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Abstract: Mixtures of cis and trans isomers have been detected by esr spectroscopy for the symmetrical semidiones $\text{RC}(\text{O}\cdot)=\text{C}(\text{O}^-)\text{R}$ where $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, (\text{CH}_3)_2\text{CHCH}_2, (\text{CH}_3)_3\text{CCH}_2,$ and $(\text{CH}_3)_2\text{CH}$ and for the series $\text{RC}(\text{O}\cdot)=\text{C}(\text{O}^-)\text{CH}_3$ where $\text{R} = \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, (\text{CH}_3)_3\text{CCH}_2, (\text{CH}_3)_2\text{CH},$ and $(\text{CH}_3)_3\text{C}$. Symmetrical semidiones with $\text{R} = (\text{CH}_3\text{CH}_2)_2\text{CH}, (\text{CH}_3\text{CH}_2\text{CH}_2)_2,$ and $(\text{CH}_3)_3\text{C}$ showed only a single (trans) isomer. When both cis and trans isomers were detectable the cis isomers were favored by the presence of smaller gegenions and solvents of lower polarity. Lowering the temperature seemed to have little effect on the conformation of alkyl groups such as $(\text{CH}_3)_2\text{CH}$ or CH_3CH_2 in the semidiones. Lower temperatures favored the trans isomers over the cis isomers and caused the semidiones to disproportionate into the diketone and enediol dianion.

Diarylsemidiones (**1**),⁴⁻⁷ alkylarylsemidiones (**2**),^{8,9} monoarylglyoxal radical anions (**3**),⁹⁻¹³ and monoalkylglyoxal radical^{10,13,14} anions (**4**) have been de-



scribed. Semidiones **1** and **2** prefer to exist in a trans

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