porphyrin. More detailed investigations into the identity of the piperidine radical and the scope of these reactions are in progress and will be reported in the future.

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Cotton Effect Behavior of Skewed 1,3-Cyclohexadienes. Evidence for Dominance of Homoannular Allylic Chirality Contributions

Sir:

According to the widely accepted diene chirality rule,[1] the inherent dissymmetry or skew sense of a nonplanar conjugated diene controls the long-wavelength (lowest-energy) $\pi \rightarrow \pi^*$ transition Cotton effect (positive for a right-handed diene helicity; negative for a left-handed one). Although apparently successful in explaining many cases, the rule does not adequately correlate rotational strength with skewness,[2] nor does it allow for effects of substituents.[3] Likewise, it cannot be applied without modification[4] to heteroannular cisoid dienes,[5] nor does it predict the nonconforming behavior of a number of substituted cyclohexadienes of unambiguous chirality, including several steroidal 19-nor-5(10),6-dienes[6] and various C-16 epimeric pentacyclic steroidal ring-E dienes.[7]

Here, as an extension of the allylic chirality concept[8] (see signs and arrows in drawings below) previously applied to heteroannular,[5] allylic oxygenated,[3b] and planar[9] dienes, we present evidence that the long-wavelength Cotton effects of skewed 1,3-cyclohexadienes *are determined primarily by chirality contributions of the homoannular allylic axial substituents or bonds according to their size or polarizability and not by the helicity or amount of twist of the chromophore.* Such a predominant role for homoannular allylic chirality is probably related to the electronic features of the 5,6 σ-bond that produce the characteristic bathochromic shifts in the uv absorption maxima of 1,3-cyclohexadienes.

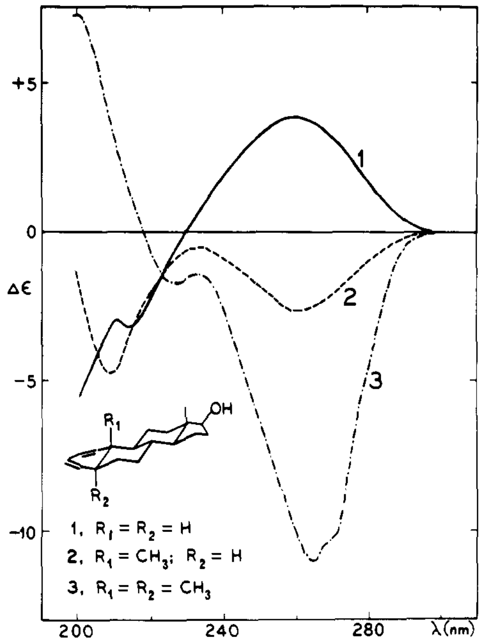
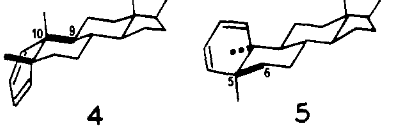


Figure 1. CD curves of 5α-estra-1,3-dien-17β-ol (**1**), 5α-androsta-1,3-dien-17β-ol (**2**), and 5α-methylandrosta-1,3-dien-17β-ol (**3**); measurements were made in hexane in a 1.0-cm cell with a Cary 6001 CD accessory unit on a Cary 60 recording spectropolarimeter.

P chirality M chirality
(enantiomeric 1,3-cyclohexadienes)

As seen in Figure 1, the 260-nm region Cotton effects of steroidal 5α 1,3-dienes show a direct dependence on the axial substituents at C-5 and C-10. The 5α-methyl diene **3**[10] exhibits a much more intense CD band ($\Delta\epsilon_{264}$ −11.1) than either the parent 5α diene **2**[3a,11] ($\Delta\epsilon_{260}$ −2.7) or the 19-nor 5α diene **1**[11] ($\Delta\epsilon_{260}$ +3.8), even though all three compounds probably have nearly the same C-2–C-3 diene torsional angle of ca. −17°.[12] These widely divergent Cotton effects indicate a significant difference in the chirality contributions by methyl and hydrogen, perhaps because of the greater anisotropic polarizability of an allylic C–alkyl bond compared to that of an allylic C–H bond.[13]

In the A/B cis steroid series even greater chirality effects are observed for allylic axial substituents larger or more polarizable than a methyl group. From their ORD amplitudes[10] dienes **4** and **5** can be estimated[14] to have $\Delta\epsilon_{264}$ +27.6 and +14.7, respectively. Both compounds have comparable P-diene chirality, but in the former the bulky C-9 tertiary allylic axial substituent at C-10 evidently makes an especially strong positive chirality contribution. In the latter



4 **5**
(allylic axial bonds intensified)

the smaller C-6 secondary allylic axial group at C-5 exerts a weaker positive effect.

Similar chirality contributions also account for the Cotton effects of other cyclohexadienes. For example, ORD and CD data for over 30 steroidal 5,7-dienes,[1,15] including a 19-nor-5,7-diene with an otherwise anomalous positive 280-nm Cotton effect,[15] show a direct dependence on chirality contributions of the substituents at C-9 and C-10 according to the amount of their axial character[16] and steric bulk (or polarizability).[17]

In the case of the conformationally rigid diene **1** and the other exceptions already cited,[6,7,15] the reversed sign of the long-wavelength Cotton effect suggests an inverse (or "dissignate" [18]) chirality contribution by allylic axial hydrogen. However, such a chirality effect does not appear to be very strong and, under some circumstances, can evidently be outweighed by normal (or "consignate" [18]) ring-chirality contributions corresponding to the helicity of the diene. This is indicated by the CD data of the following, conformationally flexible dienes, in which at least one of the two homoannular allylic axial hydrogens is secondary: estra-2,4-dien-17β-ol ($\Delta\epsilon_{260}$ + 2.1[2a]), palustric acid (abieta-8,13-dien-18-oic acid) ($\Delta\epsilon_{260}$ + 1.1[5b,19]), 3β-acetoxy-17α-ethyl-17^2-cyano-17^2,21-cyclo-D-homo-5α-pregna-17a,21-diene ($\Delta\epsilon_{304}$ +6.2[7]), and α-phellandrene [(−)-*p*-mentha-1,5-diene] ($\Delta\epsilon_{260-265}$ +5.5 at −186 °C[20]).

Obviously, further investigation of this problem is required. Nevertheless, the present findings clearly demonstrate that allylic chirality contributions play a key role in the Cotton effects of skewed 1,3-cyclohexadienes.

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Diffusion in Mixed Solvents. 3. The Heat of Mixing Parameter and the Soret Coefficient[1]

Sir:

Diffusion processes[2-12] and intermolecular interactions[13-16] in binary solvents are of strong fundamental interest to scientists in several disciplines. Reactions are performed in mixed solvents to facilitate solvation. Biological reactions and fluid flow processes always take place in complex solvents which are at least binary.[10,14] Diffusion processes and intermolecular interactions in the mixed solvent system are responsible for reported anomalous peaks and valleys in the entropies and enthalpies of activation for numerous reactions[7,10] and fluorescence phenomena.[10,11] Anomalies in several sets of solvated electron reaction rate constants,[3] ground[6,8] and triplet[2] states electron transfer reaction rate constants, and diffusion coefficient data[9] for entire solvent mixture ranges are due to the intermolecular interactions in the binary solvent.[2,15,16] The heat of mixing parameter (HMP) plots reported earlier,[2,15,16] which strongly implicate thermal diffusion[17] as being important to the explanation of these processes, successfully correlates the above mentioned anomalies. Further, the HMP theory as conceptually outlined[15] appears to be supported by recent magnetic relaxation results for protein–water interactions.[14]

Presented here is new evidence which demonstrates that for aqueous glycerol solutions, the Soret coefficient of glycerol,[17] $\sigma_1 = D_1^{T}/D_1$ (where D_1^{T} and D_1 are the thermal and self-diffusion coefficients of glycerol, respectively, in aqueous solution), is an integral part of the HMP, defined as $(-\partial\Delta H^{M}/\partial n_2)/X_2$ for this system, where X_2 is the mole fraction of water.[2,15,16] Figure 1A shows that the HMP plot for the self-diffusion coefficients of glycerol[18] is linear for $0 < X_1 < 0.44$; further, it nearly superimposes on similar plots for the data for two different reactions[6,8,19] in aqueous glycerol solvent. Figure 1B demonstrates that both the HMP and the diffusion parameter, DP, $(k\eta\epsilon/(k\eta\epsilon)_2$ where k represents the diffusion coefficient or second-order reaction rate constant, plotted against $\partial \ln a_1/\partial \ln c_1$ exhibit curves which appear