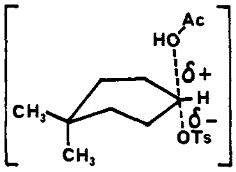
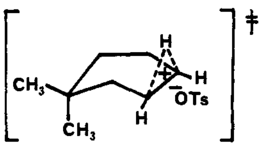
tion states,[12] and may be understood if that for the monocyclic system is characterized by pronounced flattening of the ring about the reaction center, as in half-chair **6**.[18] Nucleophilic solvent participation would thus be facilitated through reduced compression with axial hydrogens at C-3 and C-5, at the expense of new but distributed bond-angle and torsional strains. Such distortion could not be accommodated by the 2-adamantyl framework.

The stereospecificity of substitution with hydride shift from **1** is in accord with hydride migration trans to tightly paired tosylate ion followed by displacement with inversion on the rearranged ion pair or recombined tosylate.[19] Maximum overlap in such rearrangements has been correlated with diaxial orientation of leaving and migrating groups,[20] but such a rule is compromised by the observation of hydride shift to the same extent (according to substitution products) from wholly equatorial 3,3-dimethylcyclohexyl tosylate as from the biconformational[21] 4,4-dimethylcyclohexyl reactant. We propose that hydride shift from the 3,3- and in part from the 4,4-dimethyl reactant may originate from the respective equatorial chair conformations, by ionization to a bridged half-chair transition state, such as **7**.[19]



6



7

The inversion attending acetolysis of tosylate **1** stands in marked contrast to the essentially complete retention observed by Streitwieser and Coverdale[22] for aqueous deamination of cyclohexylamine. Comment is reserved for a full paper.

Acknowledgment. Partial support of this work by National Science Foundation Grant No. GP-20732 is gratefully acknowledged.

(18) Such a structure would explain as well the isotope-effect pattern observed for acetolysis of cyclohexyl tosylate by W. H. Saunders, Jr., and K. T. Finley, *J. Amer. Chem. Soc.*, **87**, 1384 (1965); see also V. J. Shiner, Jr., and J. G. Jewett, *ibid.*, **87**, 1383 (1965), and preceding papers.

(19) Compare ref 1i, j.

(20) See, for example, E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, pp 227–229.

(21) F. R. Jensen, C. H. Bushweller, and B. H. Beck, *J. Amer. Chem. Soc.*, **91**, 344 (1969), have measured the conformational free energy for tosyloxy as 0.515 kcal/mol (eq:ax = 79:21) in carbon disulfide at −80°; see F. R. Jensen and C. H. Bushweller, *Advan. Alicycl. Chem.*, **3**, 139 (1971); see also ref 1a, and E. L. Eliel and R. S. Ro, *J. Amer. Chem. Soc.*, **79**, 5995 (1957).

(22) A. Streitwieser, Jr., and C. E. Coverdale, *ibid.*, **81**, 4275 (1959).

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Cholesteric Liquid-Crystal-Induced Circular Dichroism (LCICD) of Achiral Solutes. A Novel Spectroscopic Technique

Sir:

In our first report[1] of the induced circular dichroism of achiral solutes in cholesteric mesophases the experimentally observed sign of the LCICD bands, for the compounds studied up to that time, was always opposite to the sign of the reflective circular dichroism (CD) of the cholesteric pitch band. This observation seemed rather unusual since in natural and magnetic circular dichroism (MCD) bands of both positive and negative signs are commonly observed in multichromophoric systems.[2]

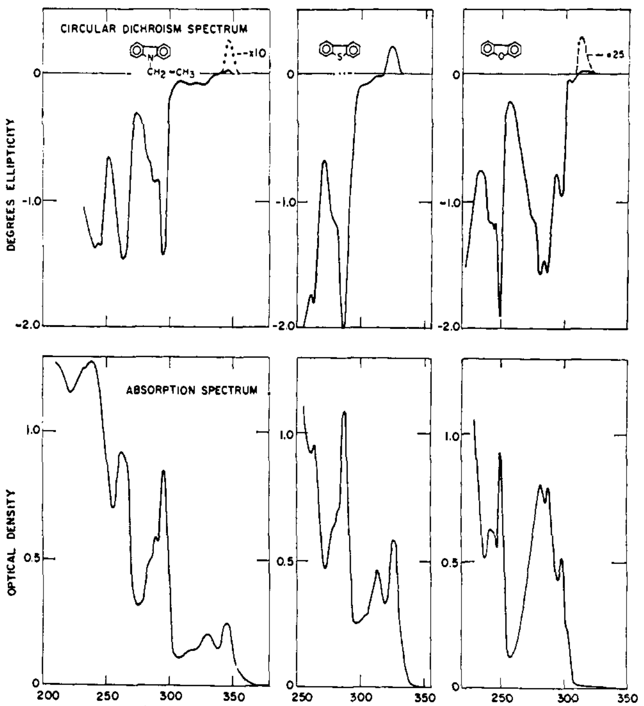
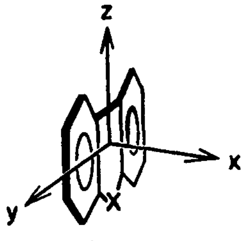


Figure 1. Cholesteric liquid-crystal-induced circular dichroism (LCICD) and absorption spectrum of *N*-ethylcarbazole, dibenzofuran, and dibenzothiophene (1.0 wt %) in 60/40 (wt%) cholesteryl chloride (CC)–cholesteryl nonanoate (CN) (right-handed helix) as ~5-μ film between 1 × 1/8 in. quartz disks.

This communication presents the LCICD spectra of *N*-ethylcarbazole (I), dibenzothiophene (II), and dibenzofuran (III), which are known to possess $\pi \rightarrow \pi^*$ electronic transition moments, at wavelengths >200 nm, polarized along different molecular axes[3–5] as shown below, and indicates their spectroscopic significance.



Electronic Transition	Polarization (axis)
1 ($^1L_b \leftarrow {}^1A$)	*z*
2 ($^1L_a \leftarrow {}^1A$)	*y*
3 ($^1B_a \leftarrow {}^1A$)	*y*

Compd	X
I	NC_2H_5
II	S
III	O

The LCICD and absorption spectra of compounds I–III dissolved in a right-handed helicoidal cholesteric mesophase are presented in Figure 1, where a positive

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(1) F. D. Saeva and J. J. Wysocki, *J. Amer. Chem. Soc.*, **93**, 5928 (1971).

(2) A. Moscowitz, *Proc. Roy. Soc., Ser. A*, **297**, 16 (1967).

(3) A. Bree and R. Zwarich, *J. Chem. Phys.*, **49**, 3355 (1968).

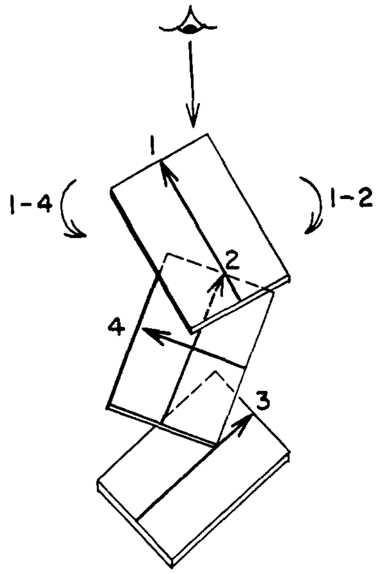
(4) H. Schutt and H. Zimmermann, *Ber. Bunsenges. Phys. Chem.*, **67**, 54 (1963).

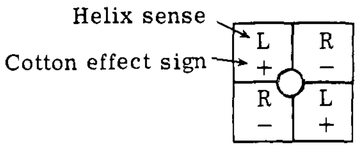
(5) C. A. Pinkham and S. C. Wait, Jr., *J. Mol. Spectrosc.*, **27**, 326 (1968).

Cotton effect (CE) is found for the first electronic transition ($^1L_b \leftarrow {}^1A$) in compounds I–III and negative CE's for all other bands >220 nm. The relative intensities of the LCICD bands in compounds I–III follow the ordinary absorption except for the $^1L_b \leftarrow {}^1A$ transition which has mixed polarization character resulting in a reduction of CD band intensity due to overlapping positive and negative transitions within the CD bands.[6,7]

LCICD appears to arise from (a) the solute being exposed to a helical arrangement of solvent molecules, as well as (b) a helicoidal arrangement of solute molecules. The relative importance of the above two mechanisms seems to vary with solute concentration and symmetry, as well as the characteristics of the liquid-crystalline solvent. The details of the physical origin of LCICD will be the subject of a future publication.[8]

Since the organizations of planar solute molecules in liquid-crystalline mesophases are known to orient their long axis parallel to the alignment of the liquid-crystal molecules,[9] an attempt was made to rationalize the change in LCICD sign with the solute transition moment polarization. The following diagram describes the situation for dilute solutions of solutes in cholesteric mesophase (mechanism a) where each block represents a single isolated molecule (arrows indicate molecular axes) in three nematic-like layers in the cholesteric helix. If the molecule in the center, for example, is a solute with perpendicular electronic transition moments, as in compounds I–III, one can readily see that the longitudinally polarized transition moment is in an environment of opposite chirality (right-handed helix) from that seen by the transversely polarized moment (left-handed helix). With the above experimental observations in mind a general rule for relating the sign of solute LCICD bands to the polarization of their electronic transition moments is proposed. Looking down the transition moment axis of the chromophore of interest (normal to the cholesteric helical axis), the chirality of the perturbing helical environment (*vide infra*) is noted.





If the transition moment is exposed to a right-handed helical disposition of molecules in the cholesteric helix (upper right and lower left quadrants), a negative LCICD band is observed. Conversely, a positive LCICD band is observed when the transition moment is exposed to a left-handed helical structure (upper left and lower right quadrants). The above rule is designed for solutes in cholesteric mesophases composed of cholesteryl derivatives and may change as the components of the cholesteric mesophase are varied (*e.g.*, from steroidal to nonsteroidal).

In summary, LCICD is a novel technique for investigating the circular dichroism of achiral and chiral molecules. The sign of the LCICD bands has been found to provide spectroscopic information about solutes in cholesteric mesophases, and a quadrant rule for predicting electronic transition polarizations from the sign of the LCICD band has been formulated. More detailed studies attempting to compare LCICD to natural and MCD are currently underway.

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[6] O. E. Weigang, Jr., *J. Chem. Phys.*, 43, 3609 (1965).

[7] J. Horwitz, F. H. Strickland, and C. Billups, *J. Amer. Chem. Soc.*, 91, 184 (1969).

[8] F. D. Saeva, to be submitted for publication.

[9] G. P. Ceasar and H. B. Gray, *J. Amer. Chem. Soc.*, 91, 191 (1969), and reference cited therein.

Photocyclizations of Pharmacodynamic Amines. VII. Photorearrangements and Roentgen-Ray Analyses of Novel Tyramine Dimers[1]

Sir:

When *N*-chloroacetyltyrosine was irradiated by uv light the phenolic chromophore disappeared rapidly.[2] Previous attempts to isolate the photocyclization products were unsuccessful.[3] We have now been able to isolate dimers from the photolysis of six homologous *N*-chloroacetyltyramines (Ia–e) and to elucidate the structure of these novel cage compounds by Roentgen-ray analysis. These dimers are remarkable because they result from ortho and para ring closures of reactive dienones (or exciplexes) which, rather than adding solvent, undergo a series of $[_{\pi}4 + {}_{\pi}2]$ and $[_{\pi}2 + {}_{\pi}2]$ cycloadditions and, in the end, an unexpected bond switching process or possibly a cycloreversion $({}_{\sigma}2_a + {}_{\sigma}2_a)$.[4]

When a 10 m*M* solution of Ia in 10% aqueous ethanol was irradiated for 1.5 hr with a 100-W high-pressure

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[1] Preceding paper in this series: O. Yonemitsu, H. Nakai, Y. Okuno, S. Naruto, K. Hemmi, and B. Witkop, *Photochem. Photobiol.*, 15, 509 (1972).

[2] O. Yonemitsu, B. Witkop, and I. L. Karle, *J. Amer. Chem. Soc.*, 89, 1039 (1967).

[3] O. Yonemitsu, T. Tokuyama, M. Chaykovsky, and B. Witkop, *ibid.*, 90, 776 (1968).

[4] R. B. Woodward and R. Hoffmann, The Conservation of Orbita Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1971, pp 65–100.