pentamethylene sulfide are approximately 80, 92, and 100°, respectively.[16] However, all three compounds have essentially the same IP for the b_1 level—**3** (8.43 eV), tetrahydrothiophene (8.40 eV),[17] and pentamethylene sulfide (8.45 eV).[18]

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Cholesteric Liquid Crystal Induced Circular Dichroism (LCICD). VII. LCICD of Achiral Solutes in Lyotropic Cholesteric Mesophases

Sir:

We have reported previously that achiral molecules dissolved in thermotropic cholesteric liquid crystals display extrinsic circular dichroism.[1-4] The sign of the liquid crystal induced circular dichroism (LCICD) was found to be dependent on the chirality of the cholesteric helix,[1] preferred orientation of the solute electric transition dipoles,[2,5] the position of λ_0 of the cholesteric pitch band relative to the wavelength of absorption,[3] and the cholesteric matrix.[3] LCICD intensity, on the other hand, has been observed to be a function of the pitch of the helical cholesteric matrix, temperature, and texture.

The origin of the cholesteric liquid crystal induced circular dichroism is attributed to the following: (a) the helical organization of the solute[5] and (b) the exposure of the solute to the chiral organization of liquid crystal molecules.

Recently Sackmann[5,6] and Holzwarth[7,8] have been able to predict the LCICD behavior for both solutes and the cholesteric matrix, respectively. This was done by extending the theory of electromagnetic radiation in nonabsorbing cholesteric liquid crystals to the absorbing case by adding a frequency-dependent complex contribution to the spiralling dielectric tensor of the liquid crystal. In these studies LCICD is attributed to the helical arrangement of molecules in the cholesteric liquid crystal (mechanism a). LCICD has been found experimentally to be proportional to the linear dichroism consistent with theory.[5,6,8] Contribution from mechanism b to LCICD which does not require a helical ordering of the solute but electronic and/or magnetic interactions between solute and matrix molecules[9] has not been clearly established.

Certain synthetic polypeptides, *e.g.*, poly(γ-benzyl-L-glutamate) (PBLG), are known to exist in an α-helical conformation in a variety of solvents.[10] In these systems extrinsic circular dichroism has been observed within the electronic transitions of certain dyes,[11,12] such as Acridine Orange, complexed to isotropically oriented polypeptide molecules in an α-helical conformation. Concentrated solutions of these polypeptides, in helix supporting solvents, readily form birefringent lyotropic cholesteric liquid crystalline mesophases, where the helical polypeptide is analogous to the cholesteryl derivative in thermotropic cholesteric systems.[13,14]

In this communication we wish to report that achiral molecules, such as anthracene and pyrene, which do not exhibit induced circular dichroism in dilute or concentrated isotropic solutions of PBLG, do indeed exhibit LCICD in the anisotropic birefringent lyotropic cholesteric mesophases formed by PBLG in helix supporting solvents such as chloroform, methylene chloride, and dioxane.

LCICD has been observed for a number of achiral molecules dissolved in birefringent concentrated solutions of PBLG in helix supporting solvents. We believe this induced effect to be quite general and independent of the chemical structure of the solute in contrast to rigid requirements for solutes that complex to isotropically oriented helical polypeptides.[11,12] The extrinsic CD of the achiral solute is associated with the formation of the birefringent cholesteric mesophase and disappears when the α-helical molecules of PBLG become randomly orientated by means of small changes in concentrated PBLG while the relative concentration of achiral solute, *e.g.*, anthracene, to PBLG is held constant. In other words, the extrinsic CD of anthracene in PBLG–dioxane mixtures is associated only with the lyotropic cholesteric mesophase.

The observed LCICD for anthracene in the lyotropic cholesteric mesophase formed by PBLG in dioxane is distinctly different from that observed in thermotropic cholesteryl mesophases composed of cholesteryl derivatives.[3] Figure 1 presents the LCICD and electronic spectra of anthracene dissolved in thermotropic and lyotropic cholesteric mesophases. The LCICD spectrum of anthracene between 300 and 400 nm in PBLG–dioxane (18:82 wt %) shows CD bands of a single sign which follow its absorption spectrum quite closely. The CD for the pitch band and anthracene absorption bands are both of negative sign. The chirality of the cholesteric helix in dioxane is then left-handed, *i.e.* of opposite chirality to the helicity of the polypeptide.[15,16] The

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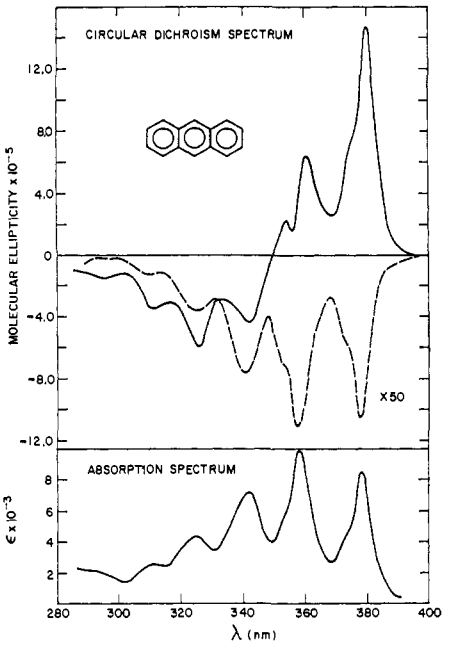

Figure 1. Circular dichroism and absorption spectrum of anthracene in (–) a thermotropic cholesteric mesophase composed of 60/40 (wt %) cholesteryl chloride–cholesteryl nonanoate (pitch $\simeq$ 9 μ); (---) a lyotropic cholesteric mesophase composed of PBLG–dioxane (18:82 wt %) (mol wt PBLG = 125,00, pitch $\simeq$ 18 μ).

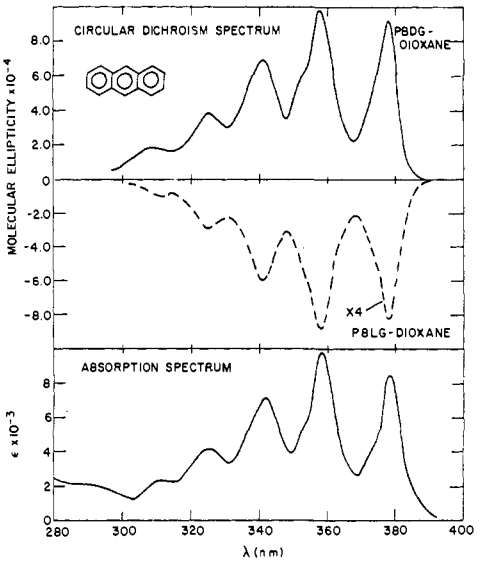

Figure 2. Circular dichroism and absorption spectrum of anthracene in (---) a lyotropic cholesteric mesophase composed of PBLG–dioxane (18:82 wt %) (mol wt PBLG = 125,000, pitch $\simeq$ 18 μ); (–) a lyotropic cholesteric mesophase composed of PBDG–dioxane (20:80 wt %) (mol wt PBDG = 120,000, pitch $\simeq$ 21 μ).

chirality of the cholesteric helix in chloroform, however, is opposite to that in dioxane and methylene chloride, *i.e.* right-handed. The LCICD spectrum of anthracene in a thermotropic cholesteric mesophase composed of cholesteryl chloride–cholesteryl nonanoate (60:40 wt %) (right-handed helix) shows CD bands of both positive and negative signs between 300 and 400 nm whose relative intensity does not follow its absorption spectrum. The LCICD spectrum of anthracene in the thermotropic cholesteric mesophase is consistent with its previously determined order parameter[17,18] in similar systems as well as the polarization of the transitions in question, while, on the other hand, the LCICD spectrum of anthracene in the PBLG–dioxane cholesteric mesophase is not consistent with its linear dichroism spectrum.

The variation in LCICD of anthracene between the two cholesteric systems is tentatively attributed to the difference in ability of the mesophases to physically order the solute and not the minor variation in pitch between the two cholesteric mesophases. In the thermotropic system the preferred conformation of the anthracene is such that it aligns its long axis parallel to the long axis of the liquid crystal molecules.[18] In the lyotropic system, however, alignment of the long and short axis of anthracene perpendicular to the long axis of the PBLG α helix seems to be equally preferred, *i.e.* a more random ordering of solute. This conclusion is consistent with the relative sizes of the solute anthracene ($\sim$10 Å) and PBLG molecules ($\sim$850 Å for mol wt 125,000).[19] The ordering of solute molecules by the liquid crystal would be most efficient for solutes of comparable size and shape to the liquid crystal molecules.

Enantiomeric lyotropic cholesteric mesophases are produced by PBLG and PBDG in dioxane solvent as indicated by the LCICD spectra for anthracene in Figure 2. The chirality of the cholesteric helix in the lyotropic mesophase can be established by determining the sign of the CD in the region of the reflective wavelength of the cholesteric pitch band.[15] Once a correlation between the sign of the CD for the pitch and a LCICD band has been made the chirality of the cholesteric helix may be determined simply from the sign of LCICD.[4] The chirality of the cholesteric helix formed by PBLG and PBDG in dioxane (shown in Figure 2) is left- and right-handed, respectively. The difference in LCICD intensity of anthracene in the PBLG and PBDG cholesteric mesophase is attributed to the variation in pitch between the two systems.

Molecular ellipticity values for anthracene in PBLG of differing molecular weights, *i.e.*, 46,000 and 125,000, were *identical* within experimental error for samples of virtually *identical* pitch. The lower molecular weight sample relaxed from the Grandjean to the focal conic texture in 1–2 hr while the higher molecular weight samples took 24–30 hr.

LCICD has also been observed within the electronic transitions of the polypeptide itself. Rotational strengths for the polypeptide absorption bands are approximately 10^2–10^3 larger in the cholesteric mesophase than in isotropic solution. The ^1L_b electronic transition of the benzyl group in PBLG shows large positive CD in a left-handed helical cholesteric mesophase.

Circular dichroism (CD) and absorption spectra were run at room temperature ($T \sim 22°$) on a Cary 61 CD spectropolarimeter and a Cary 15 spectrophotometer, respectively. Spectroscopy was performed on thin films of the liquid crystal between 1 in. $\times$ $^1/_8$ in. quartz disks using 1-mil Mylar spacers, and the optical cells containing the lyotropic cholesteric mesophases were sealed with an epoxy cement to prevent solvent evaporation. The absorption and CD measurements obey Beer's law providing the change in concentration of solute does not produce a change in pitch of the mesophase. The polypeptides used in this study were

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purchased from Miles Laboratories, Inc., Elkhart, Ind. 46514. Solute concentrations in the cholesteric mesophases were normally between 10^{-2} and 10^{-3} *M*.

In summary, LCICD of noncomplexing achiral molecules has been observed in lyotropic cholesteric mesophases composed of PBLG and PBDG in a variety of helix supporting solvents. LCICD of anthracene in lyotropic cholesteric mesophases is distinctly different from that found in thermotropic cholesteric mesophases which is tentatively attributed to a variation in the ability of the two cholesteric mesophase types to order anthracene single molecules or possibly the intervention of the previously suggested mechanism b.

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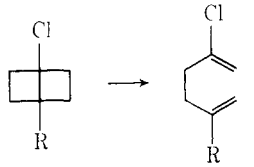
Ring Opening of Bicyclo[2.2.0]hexanes. Effect of Alkyl Group Substitution upon Interpretation of Radical Stabilization Energies

Sir:

Without exception, the substitution of an alkyl group for a hydrogen atom in a series of aliphatic hydrocarbons will decrease the α-bond strength.[1] This decrease is made up of a contribution from increased steric (gauche) interactions in the parent molecule and an increased stability of the radical formed in the series tertiary > secondary > primary.[2] The picture is not so clear for cyclic hydrocarbons, as in several cases alkyl substitution increases the activation energy for α-bond scission.[2] Within the approximations of the biradical mechanism, O'Neal and Benson[2] have shown that radical stabilization energies derived from cyclic compounds are in reasonable agreement with those derived from acyclic compounds.[3] To explain a large increase found in the activation energy for the ring opening of 1,1,3,3-tetramethylcyclobutane, Cocks and Frey[4] introduced a further variable into the mechanism, that of steric interactions in the ring opening of cyclobutanes. Our studies on the bicyclo[2.2.0]hexane system have now reached a stage where we can conclude that our results are not in agreement with the above postulates. These results are presented in their present form due to the possible effect on the large volume of work which incorporates the above assumptions.

1-Chloro-4-methylbicyclo[2.2.0]hexane (**1**, R = CH_3) was prepared from 1-chloro-4-hydroxymethylbicyclo[2.2.0]hexane[5] (**1**, R = CH_2OH) by hydride displacement of the mesylate (**1**, R = CH_2OMs; recrystallized from hexane; mp 47°) with $LiAlH_4$. 1-Chloro-4-ethylbicyclo[2.2.0]hexane (**1**, R = CH_2CH_3) was obtained by photochemical (Hanovia 450 W, Pyrex filter, MeOH) Arndt–Eistert homologation of the acid[5] (**1**, R = CO_2H) followed by $LiAlH_4$ reduction of the ester (**1**, R = $CH_2CO_2CH_3$) to the alcohol (**1**, R = CH_2CH_2OH), mesylate (mp 55°) formation, and hydride displacement with $LiAlH_4$.



1 2

The rate of ring opening of these two alkyl derivatives (**1**, R = CH_3 and C_2H_5) to the dienes (**2**, R = CH_3 and C_2H_5) was measured both in the gas phase and in solution (over the temperature range 136.5–238.6°) as previously described.[6,7] Least-squares calculations on the results gave the following Arrhenius equations for the 4-methyl derivative: $\log (k_g/\text{sec}^{-1}) = (13.86 \pm 0.03) - (36.90 \pm 0.07)/\theta$; $\log (k_a/\text{sec}^{-1}) = (13.55 \pm 0.31) - (35.50 \pm 0.13)/\theta$; $\log (k_b/\text{sec}^{-1}) = (13.64 \pm 0.30) - (35.68 \pm 0.13)/\theta$. The following equations were derived for the 4-ethyl derivative: $\log (k_a/\text{sec}^{-1}) = (13.68 \pm 0.29) - (36.19 \pm 0.13)/\theta$ and $\log (k_b/\text{sec}^{-1}) = (13.55 \pm 0.15) - (35.87 \pm 0.06)/\theta$, where $\theta = 2.303RT$ kcal/mol, error limits are least-squares deviations, and the subscripts g, a, and b refer to the gas phase, tetrachloroethylene, and *o*-dichlorobenzene as solvent, respectively. These may be compared to activation energies for 1-chlorobicyclo[2.2.0]hexane (**1**, R = H) of 35.42, 34.50, and 34.60 kcal/mol and Arrhenius log *A* values of 13.49, 13.21, and 13.25 in the gas phase, tetrachloroethylene, and *o*-dichlorobenzene as solvent, respectively.[8]

Both gas and liquid phase results are consistent with a small but significant increase of 1.2 ± 0.5 kcal/mol in the activation energy when the bridgehead hydrogen atom is replaced by a methyl group; there is an additional small increase in the activation energy on substituting an ethyl group for the bridgehead hydrogen atom.

We have previously obtained excellent group additivity in the following 1,4-disubstituted bicyclo[2.2.0]hexane series: H,H, H,Cl, Cl,Cl, and Cl,H, Cl,CO_2CH_3, CO_2CH_3,CO_2CH_3—this assumed no 1,4 interactions in the transition complex.[9] From the absence of any interactions between the pairs Cl,CO_2CH_3 and CO_2CH_3,CO_2CH_3 it may be concluded that likewise there will be no 1,4 interaction between the smaller Cl,CH_3 and Cl,C_2H_5 groups. The increase in activation energy on alkyl substitution must be an intrinsic property of the alkyl group and not a result of steric interaction.[10]

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