

proach of the catalyst, $\text{HCo}(\text{CO})_4$, from the α side of the 2,3-ene, and as a consequence it would react preferentially on the β side, leading to one product. Once hydrogenolysis of the allylic anomeric acetate occurs, the steric hindrance of the C-1 acetate is lost, and approach of the catalyst can occur from both sides, thus leading to both the *D-gluco* and the *D-altro* branched-chained anhydroalditols III.

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The Nuclear Magnetic Resonance Spectra of Enantiomers in Optically Active Liquid Crystals

Sir:

Pirkle and Beare¹ have reported the observation of distinct nmr spectra for the *d* and *l* enantiomers of a suitable compound when dissolved in an optically active solvent. The difference of the spectra can be interpreted as resulting from a difference in the chemical shifts of the two enantiomers: the disparity of their geometry in relation to the solvent environment results in unequal solvent effects.

In a recent communication,² we have noted that a similar differentiation will be expected for enantiomers dissolved in an optically active liquid crystal. Here the major differentiating factor would be the degree of orientation of the solute molecules. We believe the situation can be described as follows. It is well known that nematic liquid crystals become macroscopically oriented in a magnetic field, and this orientation is transferred to dissolved molecules. As a result of this orientation, the direct nuclear dipole-dipole interactions are no longer zero and, in fact, become the dominant interaction in the interpretation of the nmr spectrum.³ The basic idea of the experiment is to use a liquid-crystal solvent that exhibits not only orientation anisotropy but a screw sense as well. This can be achieved by using an optically active liquid crystal. In such a solvent the degree of orientation of optically active solute molecules will differ for the *d* and the *l* geometry. Thus the nuclear dipole-dipole interactions will be different, and distinct spectra for the two enantiomers will result.

In this note we report observations confirming this expectation. The actual situation, however, is not quite so straightforward. It was shown in ref 2 that, when an asymmetric center is introduced in a molecular species which gives a nematic phase, the screw sense of the molecules prevents parallel stacking, and a helical (that is cholesteric) structure, rather than a nematic one, results. No high-resolution nmr spectra can be obtained in such a phase. The way out is the use of a

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(2) E. Sackmann, S. Meiboom, and L. C. Snyder, *ibid.*, **89**, 5981 (1967).

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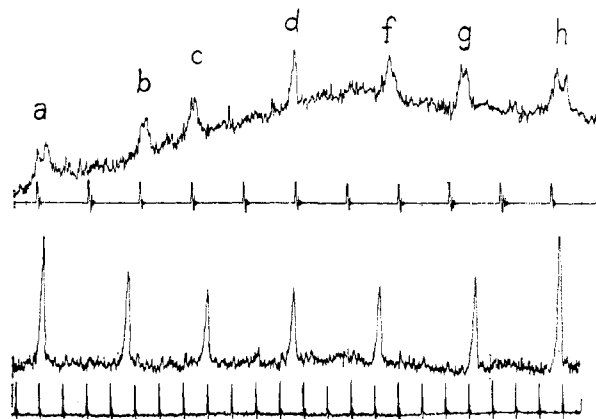
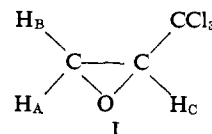


Figure 1. The upper trace gives the 60-MHz nmr spectrum at 40° of a mixture of 0.01 g of racemic 3,3,3-trichloropropylene oxide, 0.53 g of cholesteryl chloride, and 0.28 g of cholesteryl myristate. The very broad background is due to the solvent. The lower trace gives the spectrum of 0.01 g of racemic 3,3,3-trichloropropylene oxide in 0.1 g of *p,p'*-di-*n*-hexyloxyazoxybenzene at 90°. The trace below each spectrum gives frequency markers, spaced 106 Hz apart.

“compensated” mixture of cholesteryl chloride and a cholesteryl ester, described in ref 2. The crucial point is that, although such a mixture can be so adjusted that the solvent molecules will stack parallel to each other on the average, compensation relative to the solute molecules will not in general be complete. In other words, the solute molecules will be in a helical local environment, even if no macroscopic helicity is present.

The observed nmr spectra of racemic 3,3,3-trichloropropylene oxide (I) are displayed in Figure 1. The



upper spectrum was obtained in a 1.9:1 by weight mixture of cholesteryl chloride and cholesteryl myristate. The lower spectrum was obtained in nematic *p,p'*-di-*n*-hexyloxyazoxybenzene. We interpret the doubling of lines in the upper spectrum to be due to slightly different spectra of *d* and *l* molecules of the racemic solute. When the solvent is optically inactive as in the lower spectrum, no doubling occurs. The observed line positions are given in Table I.

Table I. Experimental Line Positions in Hertz for the Spectra in Figure 1

Solvent	a	b	c	d	f	g	h
Cholesteryl mixtures	-529	-325	-225	-20	176	325	524
Hexyloxy-azoxybenzene	-548	-335	-233	-20	185	335	543
	-1207	-815	-447	-54	344	791	1189

An analysis⁴ and computer simulations⁵ of the observed spectra have been made. We are able to obtain a close fit of the spectrum observed in the optically active solvent only if we attribute the lines in row 1 of

(4) L. C. Snyder, *J. Chem. Phys.*, **43**, 4041 (1965).

(5) The spectrum simulation programs were written by R. L. Korne-gay.

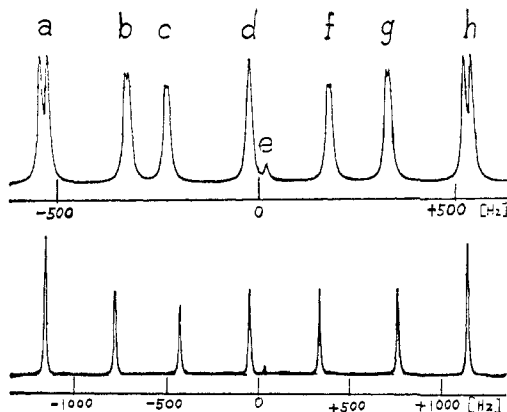


Figure 2. Computer simulated spectra corresponding to those given in Figure 1. The parameters used are given in Table II.

Table I to one enantiomer, and the lines in row 2 to the other. The spin-Hamiltonian parameters⁴ which fit the observed spectra are listed in Table II. In addition

Table II. Parameters of Spin Hamiltonian in Hertz

Solvent	Chemical shifts		—Dipolar interactions—		
	δ_B	δ_C	D_{AB}	D_{AC}	D_{BC}
Cholesteryl mixture	+0.8	-27.5	-505.0	+347.5	-14.0
Hexyloxy-azoxybenzene	-16.0	-57.0	+1218.5	-707.0	+27.5
Pure trichloro-propylene oxide	-7.3	-48.0	0	0	0

the following indirect coupling constants were used: $J_{AB} = +4.6$, $J_{AC} = +3.6$, and $J_{BC} = +2.1$ Hz. The computer simulations are given in Figure 2. We also give in Table II the parameters for pure 3,3,3-trichloro-propylene oxide. One may note in Table II that the chemical shifts in the isotropic pure solute are between those found for the two nematic solvents. This is consistent with our finding² that one of these solvents orients benzene parallel to the magnetic field, and the other perpendicular to it.⁶

A few isolated observations confirming the above interpretation follow. (1) Nonoptically active solute molecules, such as benzene, give only single, sharp lines in the compensated solvent. (2) We have observed line doubling also for racemic 2,3-epoxypropanal. (3) The same doubling of lines for compound I was found in compensated mixtures of cholesteryl chloride and a number of different cholesteryl esters.

(6) It should be pointed out that the anisotropy in the chemical shift in Table II should not be interpreted as a property of the solute molecule only. Shifts due to the susceptibility of the solvent must be considered too, and the customary assumption of a spherical cavity in which the solute molecule fits is quite unrealistic in the anisotropic solvents.

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Saturation and Removal of Electron Trapping Sites in Hydrocarbon Glasses¹

Sir:

The nature of the trapping sites at which electrons are stabilized in γ -irradiated organic glasses at 77°K is still highly speculative,^{2,3} although the electrons may be observed by their infrared⁴ and esr absorption spectra⁵ and by electrical conductivity⁶ and luminescence⁷ during warm-up of trapping matrices.

This communication reports evidence that, in each of three glassy hydrocarbons (methylcyclohexane (MCH), 3-methylpentane (3MP), and 3-methyloctane (3MO)), increasing γ dose causes the electron concentration to increase, pass through a maximum, and then decrease. The effect in MCH is illustrated in Figure 1. It is

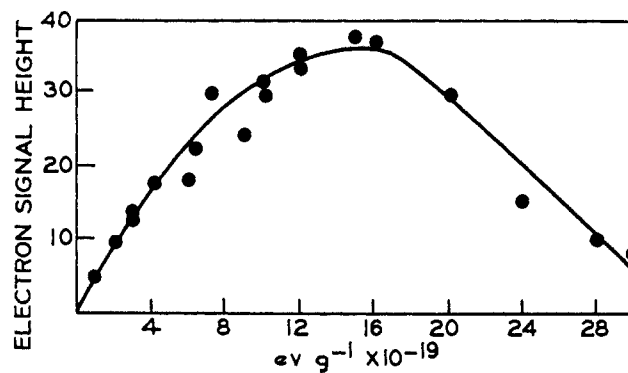


Figure 1. Height of esr e^- singlet as function of γ dose in MCH (later portions of curve would be slightly higher if corrected for Suprasil and radical background).

contrary to the expectation that the concentration should reach a steady state at which the rate of thermal and "radiation-catalyzed"⁸ neutralization of ion pairs is equal to their constant rate of production. It seems to indicate that (1) the matrix contains only a limited number of trapping sites; (2) electrons trapped in these sites are vulnerable to reaction with some product of the irradiation; and (3) when such reaction occurs, the site is either removed or remains occupied in such a way that it cannot trap another electron.

Reactions which might conceivably occur between trapped electrons and species produced by the ionizing radiation are: (1) $R + e_t^- \rightarrow R^-$; (2) $H^+ + e_t^- \rightarrow H$; (3) $RH^+ + e_t^- \rightarrow RH$; (4) $e^- + e_t^- \rightarrow (e^-)_2$; (5) $H + e^- \rightarrow H^-$.

Reaction 5 seems best able to account for the experimental observations. Trapped H atoms have been

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