account for all the lowering of exchange rates. Consequently, activation energies for the monomer and polymer were determined and found to be 16 and 19 kcal/mol, respectively. If this difference of 3 kcal/mol is real, it is more than enough to account for the remaining reductions.

One possibility for an increase in activation energy would be a substantial decrease in effective dielectric constant in the vicinity of the polymeric residues. Model compound studies in 50:50 dioxane–D_2O (dielectric constant of 40), however, have shown only a threefold decrease in the true first-order rate of pD_{min} over that for pure deuterium oxide.[30] Thus, slow exchange in this charged polymer apparently results mostly from steric inhibition of the individual amide groups along the polymer backbone.

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Vibrational Spectra of Liquid Crystals. III. Raman Spectra of Crystal, Cholesteric, and Isotropic Cholesterol Esters, 2800–3100-cm^{-1} Region

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Abstract: The Raman spectra of a series of cholesteric liquid crystals have been recorded in an attempt to elucidate the nature of intermolecular interactions in these phases. While most Raman bands are unaffected by the crystal-liquid crystal and liquid crystal-isotropic liquid phase transitions, certain C–H stretching bands change both frequency and intensity. These bands are assigned using arguments based on model steroids. It is shown that the results are indicative of regions of local order in the cholesteric phase which are similar to those in the crystal.

The nature of the ordering forces in liquid crystals is of current interest. Several techniques, including vibrational spectroscopy, have been employed as a probe of these forces. In this paper we discuss intermolecular effects on the vibrations of cholesteric liquid crystals. Despite several recent reports of vibrational spectra of liquid crystals[1–6] only one spectrum of a cholesteric phase has appeared, that being a brief discussion of the infrared spectrum of cholesteryl propionate.[6]

In previous papers, we have discussed both internal[1] and external[5] modes of vibration of nematic liquid crystals, showing that detailed information about the nematic state and the crystal–nematic transition can be obtained from the spectra. In an attempt to better understand the intermolecular interactions in cholesteric mesophases, the Raman spectra of a number of cholesterol esters have been recorded in crystal, cholesteric, isotropic, and solution phases. The implications of the only significant changes—those occurring in the C–H stretching region—are discussed herein.

The results shed new light on the cholesteric phase by viewing it in terms of the intermolecular interactions of the C–H bonds. Further, the spectra are unique among those recorded for liquid crystals to date in that they show significant differences between liquid-crystal and isotropic phases. In all the previous work, the spectra of these two phases were identical.

Experimental Section

All the cholesterol derivatives used in this study except cholesterol and cholesteryl laurate were purchased from the Vari-Light Corp., Cincinnati, Ohio. The latter two were supplied by Eastman Kodak. Pregnenolone and 19-norprogesterone were National Biochemical Corp., Cleveland, Ohio, products. Ethylestrenol and 19-nortestosterone were obtained from Hoffmann-La Roche. All the chemicals were used without further purification. Reagent grade carbon tetrachloride was used for solution spectra of cholesterol and its derivatives.

The Raman spectra were recorded using a Spex Model 1401 double spectrometer, equipped for photon counting. A Spectra-Physics Model 125 He-Ne laser (632.8 nm) delivered 60 mW at the sample. Spectra were scanned at 5 cm^{-1}/min, with a spectral slit width of approximately 7 cm^{-1}. Samples were illuminated in 1-mm capillaries using the transverse–transverse configuration. The capillary was kept in a heating block which has been described elsewhere.[5] The sequence in which the spectra were recorded was crystal, isotropic liquid, and liquid crystal.

The spectrum of each compound in each phase was run at least three times and the $\Delta\nu$ values of the Raman bands were determined as the average of these measurements. The spectra were reproducible and the uncertainty in the $\Delta\nu$ measurements was estimated as ± 2 cm^{-1}. Although the signal-to-noise ratio was rather poor, all the intensity changes discussed in this paper are for spectra which showed these changes in a highly reproducible fashion. All the compounds whose spectra were studied here have a very large number C–H bonds, and therefore very many C–H stretching bands are expected to appear in the spectra. This consideration precludes the resolution of the observed spectral profile in the C–H

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stretching region into individual components. Thus, no resolution was attempted, and the $\Delta\nu$ values mentioned in this paper refer to the actual positions of the maxima in the recorded spectra. Wherever possible, due attention was given to the possibility of apparent frequency shifts due to changes in relative intensities in the spectra.

Results and Discussion

The cholesteric liquid crystals exhibit unique optical properties. They are uniaxial, optically negative, and optically active with very high optical rotatory powers. In white light, they appear to reflect bright, iridescent colors, the precise wavelength of which is very sensitive to temperature in some cases.

Oseen[7] and deVries[8] have explained these optical properties using a model which involves a helical structure for the cholesteric state. The cholesterol ring framework is essentially planar, with the two methyl groups at positions 18 and 19, the side chain at position 20, and the hydroxyl (in the case of cholesterol) projecting out of the plane. In the liquid-crystalline phase, the cholesteryl esters lie on a number of birefringent planes. Each plane or layer contains its own optic axis, which is displaced by a small angle relative to the optic axes of the neighboring planes. The directions of the optic axes of the successive planes describe a helix, the pitch of the helix corresponding to the wavelegnth of the strongly scattered iridescent color. For a liquid crystal which scatters green light when illuminated by a white light source, the pitch is thus about 500 nm.

None of the Raman spectra of steroids in the C–H stretching region reported in this work has been discussed in the earlier literature. In selecting compounds for study, attention has been focused on the short-chain esters and cholesteryl chloride. The already large number of vibrations in these molecules are further overlapped by the additional bands in the longer aliphatic chain esters. Such additional bands make observations of subtle changes in a particular band more difficult. In this paper, only cholesteryl chloride, acetate, and propionate are discussed in detail, with brief mention of cholesteryl nonanoate, cholesteryl laurate, and mixtures of these two esters with cholesteryl chloride.

To our knowledge, the only liquid-crystalline cholesterol derivatives whose structures have been determined by X-ray crystallographic methods are cholesteryl chloride and bromide.[9] Here the structure consists of molecular layers with two molecules per unit cell. From the data, it is estimated that the thickness of a layer is about 0.4 nm. Since the liquid crystal also contains a layer structure, it is likely that the layer thickness in the liquid crystal is also of the same order. Such a thickness implies that there should be considerable interaction between those parts of the molecule which project out of the molecular plane.

The infrared spectrum of cholesteryl propionate has been reported recently, with changes noted as the crystal–cholesteric transition took place.[6] No detailed discussion of the origin of these changes was given, nor were any changes found at the cholesteric–isotropic liquid transition.

The complete Raman spectra of cholesteryl chloride, cholesteryl laurate, and a cholesteric mixture containing the laurate and the chloride have been recorded in the crystal (c), cholesteric (ch), and isotropic (l) phases. In all these spectra the details in the region below 1800 cm^{-1} were essentially unchanged at the phase transitions. This was not true in previous experiments with nematic liquid crystals, for which several authors have reported major changes in the spectra, especially at the c–n transition.

Two important conclusions can be drawn from the insensitivity of the vibrational spectra of cholesteric compounds to the phase transitions. (1) The crystal forces which are responsible for extensive splitting of bands in nematogenic crystals are not as strong in the cholesteryl ester crystals. (2) The modes below 1800 cm^{-1} are mostly skeletal vibrations, and the absence of any significant change in these bands means that there are probably no conformational changes involving the carbon skeleton occurring at the phase transitions.

Whereas in the spectra below 1800 cm^{-1} there are no significant changes at the c–ch and ch–l transitions, differences do appear in the spectra in the C–H stretching region (2800–3000 cm^{-1}). The present paper deals with the spectral changes in this region. All the liquid crystals studied here have Raman lines at approximately 2830, 2850, 2870, 2900, 2930, and 2960 cm^{-1}. As will be described in detail below, these lines change in positions and intensities during phase transitions.

In order to assign these lines to the various functional groups in the molecule, the solid-state Raman spectra of a few selected model steroids were recorded in the C–H stretching region. These spectra are reproduced in Figure 1. As can be seen from the figure, the spectrum of the ethylestrenol (Figure 1e), a compound containing no angular methyl groups attached to the steroid ring skeleton, has no Raman line in the 2890–2910-cm^{-1} region. 19-Norprogesterone and 19-nortestosterone, each having only one angular methyl group, have only weak bands at 2910 cm^{-1}. All other compounds examined in this study have bands of medium intensity in this region. Examination of normal aliphatic hydrocarbons shows no Raman line at 2910 cm^{-1}; however, Fox and Martin[10] have assigned a band observed at 2910 cm^{-1} in the infrared spectra of branched and unsaturated hydrocarbons to a methyl. stretching vibration. On the basis of these empirical arguments, we assign the Raman lines in the 2910-cm^{-1} region to angular methyl group stretching.

The C–H stretching frequencies of saturated aliphatic hydrocarbons have been pretty well established.[11] The CH_3 group frequencies are 2962 ± 10 (antisymmetric) and 2872 ± 10 cm^{-1} (symmetric). The CH_2 group frequencies are 2926 ± 10 (antisymmetric) and 2853 ± 10 cm^{-1} (symmetric), and the C–H (tertiary) frequency is at 2890 ± 10 cm^{-1}. The $=C-H$ stretching frequency is above 3000 cm^{-1}.[12]

From the above discussion, the following general assignments for cholesterol and its esters are reasonable: 2830, 2850, and 2930 cm^{-1} arise from ring CH_2 vibrations; 2860, 2900, and 2950 cm^{-1} are CH_3 group vibrations; of the latter, the 2900-cm^{-1} band can be assigned more or less definitely to a ring CH_3 group vibration. This does not definitely rule out the possi-

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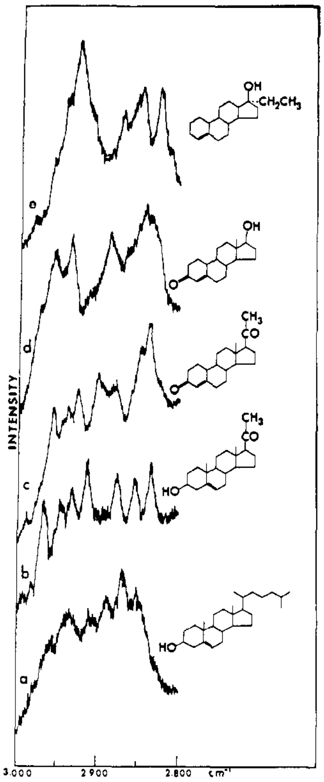

Figure 1. Raman spectra of (a) cholesterol, (b) pregnenolone, (c) 19-nortestosterone, (d) 19-norprogesterone, and (e) ethylestrenol.

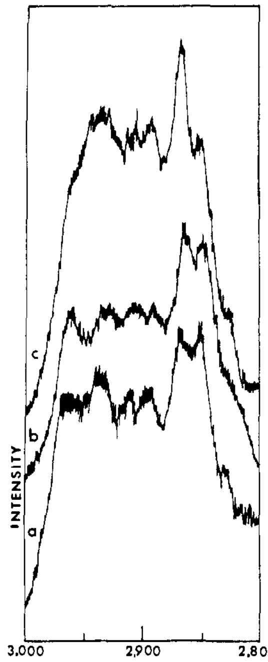

Figure 2. Raman spectra of cholesteryl chloride in the C–H stretching region: (a) solid at 25°, (b) liquid crystal at 57°, and (c) isotropic liquid at 130°.

bility that 2860- and 2950-cm^{-1} vibrations are also due to ring methyl vibrations.

The spectra of all the cholesteryl esters were recorded in CCl_4 solution. These spectra are almost identical with those in the isotropic state, when one takes into account the difference in temperature. The CCl_4 spectra also show that as the length of the aliphatic ester

Table I. Raman Spectra of Cholesteryl Chloride, Acetate, and Propionate[a]

Compound	Phase	Temp, °C	$\Delta\nu$, cm^{-1}, and relative intensity								
Cholesteryl chloride	Solid	25		2828 (w)	2850 (s)	2861 (s)	2891 (m)	2905 (m)	2930 (m, b)		2960 (m, b)
	Liquid crystal	57		2829 (w)	2850 (s)	2862 (s)	2893 (m, b)	2905 (m, b)	2930 (m, b)		2960 (m, b)
	Liquid	130		2830 (w)	2952 (m)	2870 (vs)	2894 (m, b)	2908 (m, b)	2935 (s, b)	2952 (m, b, sh)	2965 (w)
Cholesteryl acetate	Solid	25	2822 (m)	2830 (w)	2849 (m, sh)	2862 (s, b)	2895 (m)	2906 (s)	2938 (s)		2961 (m, b)
	Liquid crystal	105	2823 (w)	2831 (w)	2853 (m, b, sh)	2869 (s)	?	2905 (s)	2939 (s)		2960 (m, b)
	Liquid	125		2828 (w)	2853 (m)	2870 (s)	2899 (m, b)	?	2934 (s, b)	2949 (s, sh)	2960 (m, sh)
Cholesteryl propionate	Solid	25	2821 (m)	2828 (w, sh)	2853 (m, sh)	2863 (vs)	?	2904 (s)	2935 (s)	2945 (s, S)	2965 (m) 2972 (m)
	Liquid crystal	88		2832 (w, b)	2852 (m)	2869 (s)	2895 (m, b)	2907 (m, b)	2937 (s, vb)	2954 (m, sh)	
	Liquid	103		2830 (w, sh)	2852 (m, sh)	2871 (s)	2895 (m, b)	2905 (m, b)	2938 (s, b)	2955 (m, sh)	2960 (w, sh)

[a] s = strong, m = medium, w = weak, sh = shoulder, S = sharp, b = broad; ? = frequency shift could not be determined accurately.

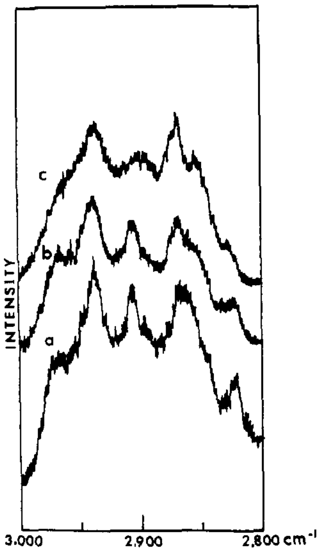

Figure 3. Raman spectra of cholesteryl acetate: (a) solid at 25°, (b) liquid crystal at 105°, and (c) isotropic liquid at 125°.

chain increases, the band at approximately 2850 cm^{-1} increases regularly in intensity. Thus, the scattering in this region is clearly attributable in part to CH_2 stretching from the side chains.

Figure 2 shows the Raman spectra of cholesteryl chloride in the crystal, cholesteric, and isotropic liquid states. A summary of the data is included in Table I. One notes that the five distinct maxima of the crystal are all present in the liquid crystal, but their relative intensities are changed. In the isotropic phase, further changes take place. The line which was at 2861 cm^{-1} in the solid has now shifted to 2870 cm^{-1} and is the strongest line in the spectrum. The lines at 2891 and 2905 cm^{-1} in the solid have shifted to slightly higher frequencies, while those at 2930 and 2960 cm^{-1} appear to have coalesced into one strong broad band, with a maximum at 2935 cm^{-1} and a shoulder at 2952 cm^{-1}. Although in this spectrum no inflection can be discerned at 2960 cm^{-1}, when the polarization of the incident beam is rotated through 90°, the strongest line in the spectrum is at 2960 cm^{-1}, indicating a component at this frequency. In the isotropic state all the Raman lines in the C–H stretching region are partially polarized, with the 2965-cm^{-1} line being the most depolarized. While this is consistent with the C_1 symmetry for the chloride, it is of no help at all in the assignment of these bands. In all work on the vibrational spectra of liquid crystals, these spectra represent the first case of important spectral changes being observed at the liquid crystal to isotropic liquid transition.

The spectrum of the liquid crystal shown in Figure 2 was recorded at 57°. As the temperature is raised in the liquid-crystalline phase, the band at 2862 cm^{-1} gradually increases in intensity relative to the 2850-cm^{-1} band. The remainder of the C–H spectrum does not show much temperature dependence in this phase. In the isotropic liquid phase, the ratio of the intensities of the 2870- to 2850-cm^{-1} bands is insensitive to temperature changes.

This change, as well as the change in intensity of the 2960-cm^{-1} band during the ch–l transition, suggests the possibility that crystalline splitting of the modes due to two molecules per unit cell in the crystal may be maintained in the liquid crystal of cholesteryl chloride, at least at low temperatures. Alternatively, the changes observed may be due only to changes in the environments of the ring hydrogens. The latter would give rise to a similar spectroscopic effect, assuming that the environment is more isotropic in the liquid than in the liquid crystal. As mentioned previously, the changes do not arise from conformational changes, which would be reflected in the low-frequency spectra.

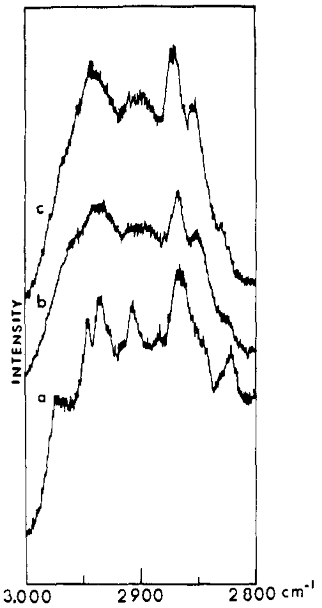

Figure 4. Raman spectra of cholesteryl propionate: (a) solid at 25°, (b) liquid crystal at 88°, and (c) isotropic liquid at 103°.

The Raman spectra of cholesteryl acetate in the solid, cholesteric, and isotropic phases are shown in Figure 3. The relevant frequencies are given in Table I. The Raman spectrum of the solid has prominent lines at 2822 (with shoulder at 2830), 2862 (with shoulder at 2849), 2906 (with shoulder at 2895), 2938, and 2961 cm^{-1}. In the liquid crystal, the shoulder at 2849 cm^{-1} has become prominent and the shoulder 2895 cm^{-1} has either become weaker or shifted to higher frequency. In the isotropic liquid spectrum, the 2862-cm^{-1} line of the solid has shifted to 2870 cm^{-1}, while the 2853-cm^{-1} line has become very distinct. The 2961-cm^{-1} line in the solid seems to have lost intensity and shifted to lower frequency. The polarization data again show a small residual band at 2960 cm^{-1}. The 2822-cm^{-1} band of the solid becomes weaker in the liquid crystal and disappears in the liquid spectrum. The acetate liquid-crystal spectrum looks, on the whole, intermediate between the solid and liquid spectra.

The spectral changes at the phase transitions discussed above are similar to those in the chloride, and these changes can be traced to the crystalline environment of the methyl and methylene groups on the steroid framework. As the lattice parameters and forces are undoubtedly different in this case, however, it is not surprising that the band envelopes at the high- and low-frequency ends of the spectrum are different in details.

The data for cholesteryl propionate are entered in Table I and shown in Figure 4. The overall spectral changes taking place when cholesteryl propionate undergoes phase transitions are very similar to those

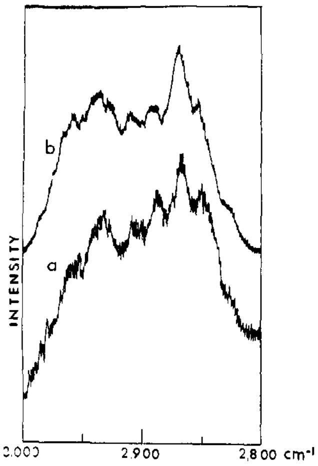

Figure 5. Raman spectra of cholesterol: (a) solid at 25° and (b) concentrated solution in CCl_4.

occurring in the acetate. In both the acetate and the propionate, the Raman lines in the liquid phase are sharper than those in the liquid-crystal phase. This sharpening is not apparent in the chloride spectra. This may reflect weaker intermolecular forces in the esters in which the strong, rigid, C–Cl dipole is not present.

It is possible that the changes observed in the spectra of cholesteryl esters are simply changes in the cholesterol framework itself. To examine this problem, the spectrum of cholesterol has been observed in solid and CCl_4 solution. Figure 5 shows these spectra. They are clearly identical, except for a minor solution effect which shifts all the frequencies slightly.

It is surprising to observe changes of this magnitude in C–H stretching frequencies. In general, these bands in infrared and Raman spectra are very insensitive to environmental changes. For example, in the spectra of nematic liquid crystals,[1] where very significant changes were observed in all spectra, no changes in the C–H stretching region were ever found. The reason for this insensitivity is generally believed to be the localized nature of C–H stretching vibrations. They have little or no interaction with other internal coordinates of the molecule and, because of the nonpolar nature of the bonds, exhibit very little coupling between modes in the crystalline unit cell.

Nonetheless, a molecular model of the cholesterol framework, particularly one in which the hydrogens are represented by van der Waals radii, reveals the importance of certain of the C–H bonds as the most far-reaching probes of the intermolecular environment. Particularly noticeable in this regard are the methyl groups at positions 18 and 19 and on the hydrocarbon side chain, several ring hydrogens, and the ester side chain, if any.

The observation of changes in the spectra of cholesteryl chloride and acetate indicates that the ester side chain does not play an important role in the changes reported herein. Indeed, the changes are more difficult to observe in the higher esters, as the additional bands from this side chain overlap the other C–H stretches.

The changes observed in the Raman spectra fall into two broad categories: (1) a difference in relative intensities, of bands, with the actual number of bands appearing to remain constant and (2) disappearance of bands from the spectrum. For case 2, one can generalize that there are always fewer bands in the higher temperature phase.

The intensities of Raman lines are sensitive probes of local symmetry, other factors being constant. Although the molecules considered have a formal C_1 symmetry, higher symmetry undoubtedly exists at certain points. It is common, for example, for the vibrations of a freely rotating methyl group in a molecule of low symmetry to still retain selection rules approximating C_{3v} symmetry. If specific interactions restrict the methyl group so that the hydrogens see an anisotropic environment, however, then there may be a change in the relative intensities of weakly allowed and strongly allowed bands when compared with idealized selection rules.

In the spectra of the above three compounds, we find changes in the spectrum between 2890 and 2910 cm^{-1}. The spectra indicate that the vibrations of the methyl groups are different in each phase, probably due to variations in the rotational freedom of these groups. This internal rotation will change the average symmetry of the methyl group and give rise to different relative intensities for bands arising from the methyl C–H stretches.

As discussed above, the increase in intensity of the 2860-cm^{-1} band in the spectrum of the chloride is not sudden, but takes place gradually as the temperature is raised in the liquid-crystalline phase. This change is the only one observed in this study which appears to vary with temperature (and hence pitch) in the liquid-crystalline phase. If the pitch changes as the temperature is raised, we expect the symmetry and environment of certain sites to stay approximately constant while others change radically, depending upon their location with respect to the screw axis in the locally ordered region. It is thus not surprising that such variations within the liquid-crystalline phase are observed for one band but not for others, although we had expected to see more such variations in other systems. This and the results for mixed-ester systems discussed below lead one to conclude that the Raman spectrum is not particularly sensitive to pitch.

Cholesteryl chloride, acetate, and propionate present several new aspects of vibrational spectra of liquid crystals. For the first time we see changes in the internal vibrations of the molecules making up the liquid crystal when the liquid crystal to isotropic liquid phase transition takes place. These changes, occurring as they do in the C–H stretches, seem to be probes of their nearest-neighbor molecules. When the environment is not averaged in the time scale of the vibrations, crystalline effects seem to persist in the liquid crystal. The spectra are indicative of regions of local order, even in the absence of orienting fields, in cholesteric liquid crystals.

The Raman spectra of the higher esters of cholesterol are very similar to one another. The spectrum of the crystal, cholesteric, and isotropic cholesteryl nonanoate, a typical representative of these esters, is shown in Figure 6. None of the higher esters shows the Raman line at approximately 2823 cm^{-1} found in the acetate and the propionate. The spectra of the three esters studied here, the butyrate, the nonanoate, and the laurate, do change at the c–ch and ch–l, transitions, but the changes are not as distinct as those in the case of the chloride,

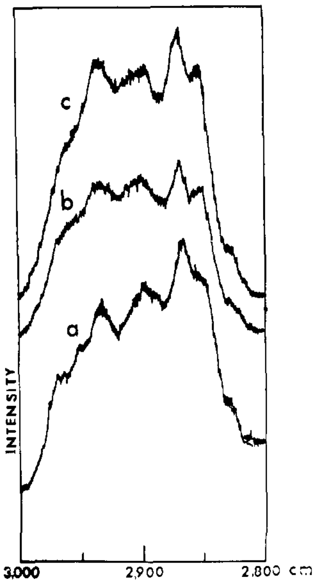

Figure 6. Raman spectra of cholesteryl nonanoate: (a) solid at 25°, (b) liquid crystal at 90°, and (c) isotropic liquid at 106°.

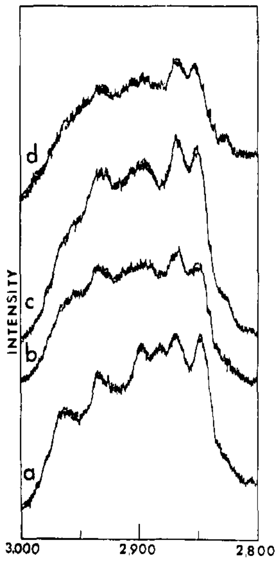

Figure 7. Raman spectra of 75% cholesteryl laurate–25% cholesteryl chloride mixture: (a) solid at 25°, (b) liquid crystal at 75°, and (c) isotropic liquid at 110°; (d) Raman spectrum of liquid crystalline 60% cholesteryl laurate and 40% cholesteryl chloride mixture at 75°.

acetate, or propionate. Principal changes occur in the 2890–2910-cm^{-1} region as well as in the band at approximately 2960 cm^{-1}. These regions are associated with CH_3 stretching vibrations.

Raman spectra were also recorded for two mixed systems, cholesteryl chloride-cholesteryl nonanoate and cholesteryl chloride–cholesteryl laurate. Spectra of one of these systems, containing 75% laurate and 25% chloride, are shown in Figure 7.

Another aspect of local order is revealed by the spectra of the chloride–nonanoate system. Adams, *et al.*,[13] have discussed this system, raising questions as to the nature of the helical regions when two components are present. In this regard, it is interesting to compare the spectra of the mixed esters with artificial spectra constructed from those of the pure components.

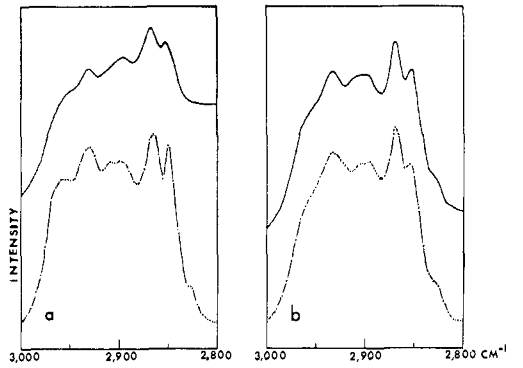

Figure 8. Raman spectra of a 60% cholesteryl nonanoate and 40% cholesteryl chloride mixture: (a) liquid crystal and (b) isotropic liquid. Solid lines are actual recorded spectra and the broken lines are spectra computed from normalized weighted spectra of the individual components in the corresponding phases.

Since Raman intensities are directly proportional to concentration, the individual spectra were normalized and weighted by concentration in the mixture, then added. A "constructed" spectrum is thus obtained, as shown for the cholesteric and isotropic phases in Figure 8. The constructed spectra are compared with smoothed actual spectra of the mixtures. This procedure is justified since there is very little background in this spectral region. (Actually, the spectra reproduced in Figures 1–7 were run at 500 counts/sec and the noise was no greater than 30–40 counts/sec.) Thus there are no large differences due to differences in the Rayleigh scattering losses in the liquid-crystalline and isotropic phases. In the case of the isotropic liquid, there is an excellent match between the actual and constructed spectra, whereas in the liquid-crystalline case differences occur, principally in the regions where changes in the spectra discussed above were noted. This result is good evidence for the fact that the locally ordered regions in mixed-liquid crystals are completely homogeneous in character, having a different environment, pitch, etc., from that of either of the pure components.

The two mixed systems are known to be sensitive to temperature, shear, organic vapors, and chemical composition. These changes are believed to be due to changes in the pitch of the helix. The mixtures exhibit bright iridescent colors which are quite temperature sensitive. With this in mind, we recorded the Raman spectra of the chloride–laurate and chloride–nonanoate mixtures at different temperatures in the liquid-crystalline phase. The resulting Raman spectra appear to be essentially the same at all temperatures.

The pitch of the helix in the chloride–nonanoate and chloride–laurate systems is supposed to be dependent on the mole per cent of chloride present.[13] The helical pitch goes through a minimum, and for the laurate–chloride system the minimum occurs at approximately 39 mol % chloride. The Raman spectrum of a mixture containing 40% chloride is shown in Figure 7d. It can be seen that there are but minor differences between this spectrum and that of the mixture containing 25% chloride (Figure 7b). These differences may be due to the different amounts of each component present in the mixture.

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Conclusion

The changes in the relative intensities of the Raman lines in the C–H stretching region in going from the crystal to liquid crystal to isotropic phases are indicative of pseudocrystalline intermolecular interactions in the liquid-crystalline phase. Regions of local order, relatively unperturbed during the time of a vibration, exist in the liquid crystal even when no external fields are aligning the mesophase. It is interesting to note that the hydrocarbon side chain, with the possible exception of the methyl group, does not reflect the changes in local symmetry at the phase transitions. Although this side chain is purported to play a major role in the structure of cholesteric phases, it may be in a "liquid" state even in the liquid-crystalline phase.

The results for mixed cholesteric liquid crystals support the idea that the phases are completely homogeneous, with intermolecular forces different from those in either pure component.

Further work on these and other systems is in progress.

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Electron Paramagnetic Resonance Studies of Ketyl Ion Pairs in Ethereal and Polar Solvents[1]

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Abstract: Detailed studies on the structures of ion pairs of ketyls in ethereal solvents (THF and DME) and mixtures of DME and DMF are reported. Temperature dependence of the alkali metal splittings in ethereal solvents and its connection to the ion pair structure are considered in detail. The effects of the addition of DMF on the structures of ion pairs were investigated. The addition of small amounts of DMF produces DMF-solvated ion pairs. Detailed thermodynamic and kinetic studies of the solvent-exchange processes have been made in DME–DMF mixtures. The lifetimes of DMF-solvated species are determined at low temperatures. In solutions containing large fractions of DMF, dissociation–association equilibria take place. Estimates of equilibrium constants and association and dissociation rate constants were made from epr spectra. It is shown that ketyls never exist as solvent-separated ion pairs under the conditions employed here. The factors which determine the ion pair structures are discussed.

The structural and kinetic properties of ion pairs of radical ions and carbanions have been the subjects of current interest, and a number of detailed investigations have been made in recent years.[2] From spectroscopic[2–4] (epr, nmr, visible, uv) and conductometric studies,[5] some detailed models of ion pair structures were proposed. Ion paris of hydrocarbon radical ions[3b,c,5] and carbanions[3a] in ethereal solvents have been investigated most thoroughly so far. It now seems to be well established that different structures of ion pairs, such as contact (tight) and solvent-separated (loose) ion pairs,[6] exist in many hydrocarbon anion systems. On the other hand, ion pairs made of other than aromatic hydrocarbons are much less studied and there still remain a number of questions to be answered concerning the properties of ion pairs. For example, it is not well known whether or not the same model of ion pair can be applied generally to many different types of systems, including the ion pairs made of radical anions with more localized charge densities such as ketyls. The cause of temperature dependence of alkali metal splittings in the epr spectra of radical ions such as ketyls is not well understood. The factors which determine the structures of ion pairs are not completely understood.

In radical ions, such as ketyls, the negative charges are more localized on the carbonyl groups. Thus the electrostatic interaction between positive and negative ions is expected to be much stronger than in hydrocarbon ion pairs. Therefore, contact ion pair structures are expected to prevail in such ion pairs. In fact, epr data indicate contact ion pair structures for ketyls in ethereal solutions.[7] Then the following questions may arise. (1) What is the cause of the large temperature dependence of alkali metal splittings in such systems, if the ion pairs are contact pairs and there exist no dynamic equilibria between contact and solvent-separated pairs? Is the process producing the

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[6] The term "contact ion pair" may not be very accurate here, since the separation between positive and negative ions is larger than expected from the ionic radii of the two ions because of solvation. Contact ion pair is used to represent tight ion pairs in which no solvent is present between the two ions.

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