DIELECTRIC PROPERTIES, REFRACTIVE INDEX AND FAR INFRARED SPECTRUM OF CHOLESTERYL OLEYL CARBONATE

Dielectric Properties, Refractive Index and Far Infrared Spectrum of Cholesteryl Oleyl Carbonate

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Some dielectric, refractive index and far infrared data on cholesteryl oleyl carbonate (OCC) in the smectic, cholesteric and isotropic liquid phases are reported. The molecular dipole moment is 3.80×10^{-30} C m (1.14 D) and the molecular polarizability ellipsoid nearly spherical. Dielectric relaxation studies show that the enthalpy of activation for molecular reorientation is (70 ± 20) kJ mol^{-1} in the isotropic phase, (44 ± 20) kJ mol^{-1} in the cholesteric phase and (35 ± 20) kJ mol^{-1} in the smectic phase and involves the reorientation of the " lath "-like molecule probably about a lengthwise axis.

A broad absorption is observed at 78 cm^{-1} in the far infrared region in the cholesteric mesophase. This is assigned to a libration of the cholesteric framework about a lengthwise axis. Quantitative aspects suggest that the mean barrier to libration in the mesophase is about 17.3 kJ mol^{-1}.

Recent dielectric [1,2] and far infrared [3] studies have revealed some novel features of the molecular motion and interaction in the crystalline, nematic and isotropic phases of N-(p-methoxybenzylidene)-p-n-butylaniline (MBBA). The observed relaxation time of 76 ps in the isotropic phase originates from molecular rotation about the long molecular axis with an activation energy of 30 kJ mol^{-1}, comparable with the value expected for a rigid molecule of similar size and shape. Comparison of the effective dipole moment in the isotropic and nematic phases shows that molecular aggregation in MBBA is hardly influenced by the phase change. A further absorption [2] (with a relaxation time of 10.1 ps at 300 K) observed in the magnetically aligned nematic phase was assigned to the restricted reorientation of a small dipole component about an axis perpendicular to the long molecular axis and has the relatively large activation energy of (120 ± 20) kJ mol^{-1}. This absorption disappears in the isotropic phase. The far infrared absorption in MBBA is dominated by a strong band at 130 cm^{-1} present in both the nematic and the isotropic phases. The band is sharper and of higher frequency than the Poley [4] absorptions (characteristic of most isotropic liquids). This band arises from torsional oscillations of the molecule about its long axis in an energy well of (14 to 19) kJ mol^{-1}.

The present study investigates (i) molecular reorientation in the smectic, cholesteric and isotropic liquid phases of cholesteryl oleyl carbonate (OCC), to identify the molecular unit involved in the reorientation process and to investigate the effect of phase changes on the molecular motion; and (ii) the far infrared spectrum of the cholesteric phase to establish the molecular origin of the absorption.

EXPERIMENTAL

Cholesteryl oleyl carbonate was used as supplied by Eastman Kodak Ltd. A smectic to cholesteric phase transition occurred at 293 K and a cholesteric to isotropic transition at 309 K. Both transition temperatures are about 2 K higher than the literature values.[5,6]

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The permittivity (ε') and dielectric loss factor (ε'') of OCC were measured over the frequency range 1 kHz to 250 MHz using a General Radio capacitance bridge 1615-A (1 kHz to 100 kHz), a Wayne Kerr B201 bridge (100 kHz to 3 MHz) and a Boonton RX meter type 250 A (0.5 MHz to 250 MHz). A parallel plate capacitor was used at frequencies up to 3 MHz and the application of a magnetic field to the sample produced no detectable change in the dielectric parameters. Above 3 MHz a cylindrical electrode capacitor was used. It was estimated that relative permittivity and loss factor measurements were accurate to $\pm 5 \times 10^{-3}$ or ± 5 %, whichever is the greater. The temperature of the parallel plate capacitor was controlled to better than ± 0.3 K using an air thermostat, while that of the cylindrical cell was controlled to better than ± 0.1 K by a thermostated water jacket.

Refractive indices for both the ordinary and the extra-ordinary ray were measured using an Abbé refractometer modified as described by Waters and Sarada [6]; permittivity values in dilute cyclohexane solutions were measured on a WTW dipolmeter and an effective molecular dipole moment calculated using the Guggenheim equation.[7]

The far infrared spectra (5 to 200 cm^{-1}) were taken with an N.P.L./Grubb Parsons Michelson " cube " interferometer [8] using amplitude modulation of the radiation reaching a quartz-windowed Golay SP 16 pneumatic detector from a Philips high pressure broad band source. At room temperature a variable path liquid cell (R.I.I.C. VC-10) with TPX [poly-(4-methylpent-1-ene)] windows was used. Any refractive index changes were eliminated by working with a ratio of path lengths rather than sample to background.[9] Fourier transformation of this ratio gave the power coefficient α (neper cm^{-1}) at different wavenumbers ($\tilde{\nu}$). A resolution of 4 cm^{-1} was used throughout. The runs at liquid nitrogen temperature were made using an evacuable cryostated cell with polypropylene windows and Teflon spacers. No attempt was made to align the mesophase by pretreatment of the TPX windows, since the maximum path length used for measurement of the cholesteric phase was 0.75 mm, small enough to incorporate surface alignment.

RESULTS AND DISCUSSION

REFRACTIVE INDEX MEASUREMENTS

When OCC is aligned on the refractometer prism with the optic axis perpendicular to the prism face then light entering the sample at grazing angle travels perpendicular to the optic axis. A polarizer inserted in the refractometer eyepiece allows the measurement of the refractive index of both the ordinary (n_0) and the extra-ordinary (n_e) ray.[6] The former is related to the mean polarizability perpendicular to the optic axis; the latter to the polarizability parallel to the optic axis. The refractive indices
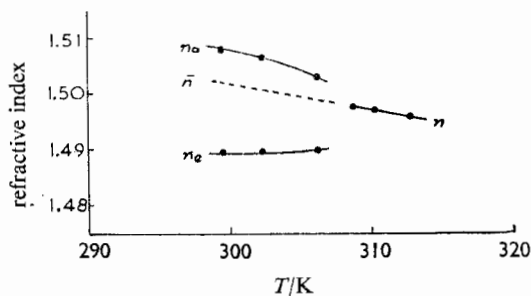

FIG. 1.—Variation of the refractive index of OCC with temperature in the cholesteric and isotropic liquid phases (n_0 and n_e are the refractive indices of the ordinary and the extraordinary rays, $\bar{n}$ the mean refractive index and n the refractive index in the isotropic phase).

are shown in fig. 1, together with the refractive index of the isotropic liquid. It should be noted that the calculated mean refractive index $[\bar{n} = \frac{1}{3}(2n_0^2 + n_e^2)^{\frac{1}{2}}]$ in the cholesteric phase extrapolates smoothly to the refractive index of the isotropic phase. The

molecular polarizability of OCC calculated from the refractive index of the isotropic phase is 9.32×10^{-39} C m V^{-1} (83.7×10^{-24} cm^3), while the mean molecular polarizability perpendicular to the optic axis [10] is 9.5×10^{-39} C m V^{-1} (85.4×10^{-24} cm^3) and is 9.1×10^{-39} C m V^{-1} (81.6×10^{-24} cm^3) parallel to the optic axis. The polarizability anisotropy in OCC is not very different from that of other molecules which do not form a cholesteric phase. The molecular polarizability ellipsoid is nearly spherical and the contribution of the anisotropy of the polarizability to the forces responsible for the formation of the cholesteric phase must be correspondingly small.

DIPOLE MOMENT MEASUREMENTS

The permittivity increment for OCC in cyclohexane solutions is linear with respect to concentration up to the highest concentration measured (0.085 mol dm^{-3}). This establishes that the solute has a constant effective dipole moment per molecule and implies the absence of molecular association over this concentration range. The derived dipole moment is 3.80×10^{-30} C m (1.14 D) and is higher than the value previously observed for other molecules containing the carbonate group [e.g. dimethyl carbonate : $\mu = 2.9 \times 10^{-30}$ C m (0.87 D) [11].]

DIELECTRIC RELAXATION MEASUREMENTS

The dielectric relaxation behaviour of OCC was measured in the smectic, cholesteric and isotropic liquid phases over the frequency range 1 kHz to 250 MHz and the dielectric absorption (ε'') as a function of frequency (f) analysed using the Fuoss–Kirkwood equation [12]

$$\cosh^{-1}\left(\frac{\varepsilon''_m}{\varepsilon''}\right) = \beta \ln\left(\frac{f_m}{f}\right) \tag{1}$$

where the subscript m refers to the properties at maximum absorption and β is an empirical parameter describing the half-width of the absorption ($0 < \beta \leqslant 1$; $\beta = 1$ for a Debye absorption contour). The results are summarized in table 1, where τ is

TABLE 1.—THE DIELECTRIC RELAXATION PARAMETERS FOR OCC (SEE TEXT FOR KEY TO SYMBOLS)

phase	T/K	$10^3 \varepsilon''_m$	$10^8 \tau$/s	β	ε_0	ε_∞	$10^{30} \mu$/C m
smectic	275	29	48.0	0.63	2.46	2.34	2.27
	276	28	33.0	0.82	2.44	2.34	2.00
	283	27	27.0	0.38			
	293	20	13.0	0.70	2.39	2.33	1.90
cholesteric	296	23	2.1	0.43	2.44	2.33	2.56
	303	24	1.6	0.46	2.40	2.30	2.56
	308	27	1.1	0.50	2.41	2.31	2.63
isotropic	310	24	1.1	0.41	2.41	2.29	2.77
	313	24	0.8	0.41	2.41	2.29	2.80
	319	28	0.5	0.44	2.41	2.28	2.97

the relaxation time $[(2\pi f_m)^{-1}]$, ε_0 the low frequency permittivity, ε_∞ the permittivity at frequencies just beyond the relaxation process and μ is the dipole component involved in the relaxation as calculated from the absorption intensity using the Onsager equation.[13]

The relaxation time of cholestenone (a molecule of similar shape but smaller volume than OCC) in decalin solution is 0.07×10^{-8} s.[14] Comparison of this relaxation time

with that of OCC in the isotropic phase suggests that the observed relaxation process involves the reorientation of the whole molecule. However, the dipole moment involved in this relaxation is smaller than that deduced from the low frequency measurements in solution (see section on dipole moment measurements). This implies the presence of a second relaxation at frequencies above 250 MHz. Such an absorption occurs in the far infrared region in the cholesteric phase of OCC (see section on far infrared measurements) and the intensity (equivalent to a dipole moment of 1.5×10^{-30} C m) is sufficient to account for the difference observed between the dipole moment as measured in dilute solution and that involved in the relaxation process.
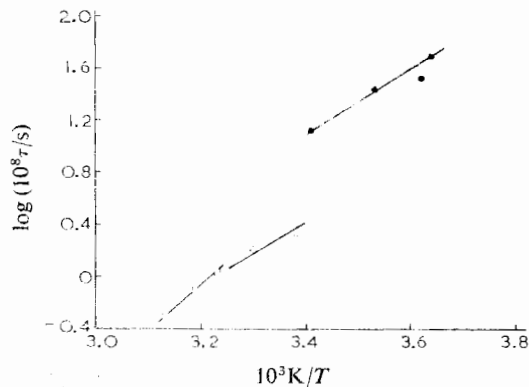

FIG. 2.—Temperature variation of the relaxation time (τ) of OCC : $\square$, isotropic phase ; $\bigcirc$, cholesteric phase ; $\bullet$, smectic phase.

The temperature variation of the relaxation time in the isotropic liquid phase and in the cholesteric and smectic phases is illustrated in fig. 2. The enthalpy of activation for the relaxation process in the isotropic phase is (70 ± 20) kJ mol^{-1}, in the
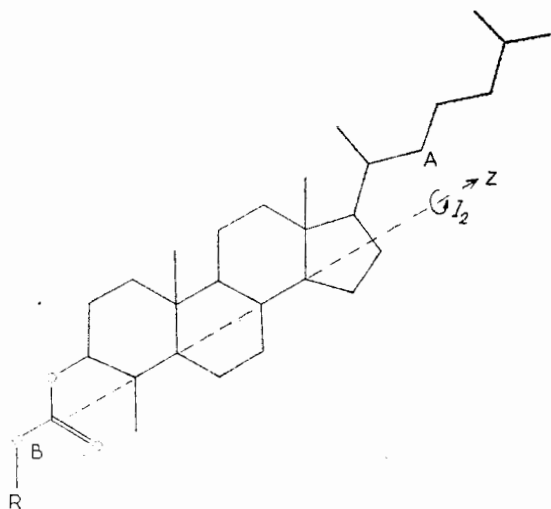

FIG. 3.—Two dimensional projection of OCC. Z is the approximate direction about which the framework between A and B is taken to librate. R is the oleyl chain assumed to exist in the wholly *trans* configuration.

cholesteric phase is (44 ± 20) kJ mol^{-1}, and in the smectic phase is (35 ± 20) kJ mol^{-1}. The large uncertainty in these enthalpies arises chiefly from the very limited temperature range over which measurements are possible. It is significant that the relaxation times observed in the isotropic and cholesteric phases are very similar despite the difference in viscosity between the two phases. The molecular shape approximates to a lath (see fig. 3) and molecular reorientation occurs about the long axis of the molecule. Such a reorientation involves only minor displacements in the molecular environment and should not be greatly affected by the phase changes. An analogous situation occurs in rotator phase solids [15, 16] where the activation energy for molecular reorientation is sometimes lower in the solid rotator phase than it is in the liquid phase due to the increased irregularity of the molecular environment in the liquid. A similar situation exists for the " lath "-like OCC.

<div align="center">FAR INFRARED MEASUREMENTS</div>

CHOLESTERIC PHASE AND SOLUTION

Far infrared measurements were made on the pure cholesteric phase and on solutions of OCC in cyclohexane, carbon tetrachloride and cyclo-octane. In all these systems the broad band at 78 cm^{-1} persisted and behaved typically as a Poley absorption whose intensity is proportional to the number density of OCC molecules present. Some representative measurements are given in table 2 and in fig. 4. The absorption
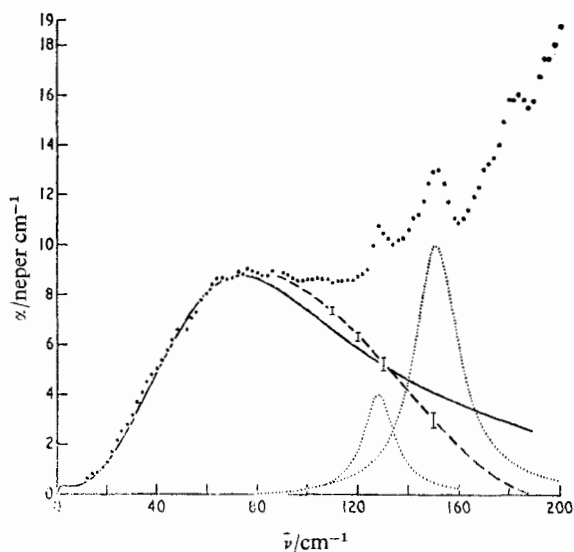
FIG. 4.—Mean of several determinations of the absorption of OCC at 298 K : - - - - -, idealized line shape [17] (broadened by collision) of the 128 and 151 cm^{-1} absorption bands ; – – –, resolved high frequency part of the 78 cm^{-1} band ; ———, calculated band shape.[24]

values $[\alpha(\tilde{\nu})/\text{neper cm}^{-1}]$ are uncertain to about ± 4 % : this uncertainty increases at $\tilde{\nu} > 140$ cm^{-1} or so due to beam-splitter characteristics [8] and due to the sharp bands centred at (128 ± 2) cm^{-1}, (183 ± 3) cm^{-1} and about 200 cm^{-1}. These sharp bands are obviously of intramolecular origin and any quantitative inferences made from the bandshape of the 78 cm^{-1} absorption depends on the method used to resolve these overlapping bands. The best attempt at resolution is based on the representation

of the two intramolecular mode features at 128 and 151 cm^{-1} in terms of a contour calculated by Brot [17]

$$\frac{\alpha c}{4\pi} = \frac{Ne^2}{m} \frac{2\omega^2/\tau_1}{(\omega^2 - \omega_0^2)^2 + 4\omega^2/\tau_1^2}. \tag{2}$$

This is similar to the van Vleck–Weisskopf function but appears more realistic in the present instance. In eqn (2), τ_1, is the mean time between adiabatic collisions perturbing an ensemble of harmonic vibrators; ω_0 is the angular velocity associated with $\tilde{\nu}_0 = 128$ or 151 cm^{-1}, m the mass and e the electronic charge. Subtraction on this basis was adjusted to leave the 78 cm^{-1} feature as an approximately symmetric absorption (fig. 4).

TABLE 2.—PROPERTIES OF THE 78 cm^{-1} BAND OF CHOLESTERYL OLEYL CARBONATE IN CYCLO-HEXANE

T/K	phase	w/w %	$\tilde{\nu}_{max}$/cm^{-1}	α_{max}/neper cm^{-1}	$\Delta\tilde{\nu}$/cm^{-1}
298	cholesteric	100	78±2	8.8±0.2	96
298	isotropic	34.23	70±2	2.5±0.1	90
111	supercooled	100	100		

The resolved broad band at 78 cm^{-1} is interpreted in terms of libration (torsional oscillation) of the rigid part of the molecular framework about an axis whose approximate orientation [18] is illustrated in fig. 3. The reasons for this arise chiefly from comparison with the similar libration found in MBBA [3] and are given below.

(i) An intramolecular origin is unlikely because of the great width ($\Delta\tilde{\nu}$) of the absorption, and because of the slight shift in $\tilde{\nu}_{max}$ to 70 cm^{-1} in a 34.23 wt. % cyclohexane solution.

(ii) Similar broad absorption bands have been observed in the rotator [19] and isotropic [4, 8, 20] phases of dipolar molecules in this region. These have all been attributed to an intermolecular origin. Experimental results and theoretical appraisals [21, 22] agree that this absorption is part of the molecular rotational mode, i.e. a high frequency adjunct to the microwave (Debye) relaxation absorption. Thus the total intensity from about 0.1 to 200 cm^{-1} has been accepted for discussion in terms of the permittivity dispersion amplitude [23]

$$A_2 = \frac{1}{2\pi} \int_0^\infty \frac{\alpha(\tilde{\nu})n}{\tilde{\nu}^2} \, d\tilde{\nu} = \frac{\pi}{2}(\varepsilon_0 - n_{ir}^2). \tag{3}$$

As mentioned earlier the discrepancy between the dipole moment as measured in dilute solution and from the dielectric relaxation intensity is removed when due consideration is made for this far infrared absorption.

(iii) Comparison with the previously reported results for MBBA [3] leads to the expectation that the absorption in OCC should occur at lower wavenumbers than found in MBBA since $\tilde{\nu}_{max}$ is inversely [24] proportional to the square root of the relevant component of the inertia tensor. Also, the integrated intensity per molecule of the absorption band is, by Gordon's sum rule,[25] proportional to the squares of the relevant dipole components and inversely to the sum of the inertia tensor components. Hence, the intensity would be expected to be smaller in OCC than in MBBA since the former is heavier and has a smaller dipole moment. Both these predictions regarding the frequency of maximum absorption and the absorption intensity are experimentally confirmed.

A systematic study [26] of the moments of inertia associated with various units in the molecule of OCC show that the only plausible librating unit consistent with an

acceptable barrier to libration ($V = 17.3$ kJ mol^{-1}, see below) is that of the cholesteric ring framework, with the oleyl chain near the all-*trans* position of minimum internal energy. This simple model can only be justified *a posteriori*, but implies that the swivelling motion between the " frictionless joints " A and B (see fig. 3) and about an axis Z will be hindered only by the fields of the nearest neighbours. Whole molecule rotational motion about axes perpendicular to Z will be severely hindered by the presence of alkyl chains. Using this model the principal moment of inertia about the long axis of the cholesteric unit is estimated to be 117×10^{-39} g cm^2.

The experimental band shape can now be fitted by a theoretical contour generated by the libration of a central unit in energy walls of half angular aperture ξ formed by the presence of Z nearest neighbours. Perturbation of this simple harmonic motion is assumed to arise from weak collisions (separated by an interval τ_i) and by stronger ones (separated by τ_r) which cause a jump (over a time τ_j) into a neighbouring well. The spectral consequences of such a model have been evaluated by Lassier and Brot.[21] Assuming a dependence of the form $V(\theta) \propto \sin^2 \theta$ (where θ is the angle through which a molecule has rotated from its initial position) and denoting $1/\tau'$ as the total width due to thermal motion and the uncertainty principle Larkin [24] has developed an algorithm for calculating the theoretical band shape $\alpha(\tilde{v})$ using only two arbitrary parameters τ' and V. Therefrom, besides $\alpha(\tilde{v})$, the parameters τ_i, τ_j and τ_r can be computed, and are not independent variables.

In MBBA with a hexagonal arrangement of six nearest neighbours ξ is 30° and apparent barriers to libration of 14 and 19 kJ mol^{-1} are calculated. There is no comparable X-ray data for OCC which enables one to determine the number of nearest neighbours, but again taking ξ as 30°, the theoretical band shape generated using the data in table 3 is shown in fig. 3. The relatively large V reflects the effect of the large $I(z)$ with the libration taking place within a narrow well whose shape and depth has been shown in the previous study on MBBA [3] to be dominated by the repulsive part of the intermolecular potential.

TABLE 3.—DYNAMICAL PARAMETERS ESTIMATED FOR OCC AT 298 K FROM THE BROT–LARKIN MODEL

$V/$ kJ mol^{-1}	$\tau'/$ps	$\xi/$rad	$\tau_r/$ps	$\tilde{v}_{max}$(obs.)/ cm^{-1}	$\tilde{v}_{max}$(calc.)/ cm^{-1}	$\tau_i/$ps	$\tau_j/$ps	narrowing factor
17.3	0.10	0.52	737	78	74	0.49	0.68	0.48

From this over simplified model for the constrained motion in the cholesteric phase the experimental absorption in the frequency region 2 to 180 cm^{-1} is reproduced quite well. The value of V used as input is physically meaningful in comparison with other systems. The " true " situation in the cholesteric phase is undoubtedly complex and the above analysis merely probes the situation on the scale of one or two molecular diameters.

ISOTROPIC PHASE

The behaviour of the 78 cm^{-1} band on dilution to 34.23 wt. % in cyclohexane (table 2) is similar to that of MBBA. There is, however, a slight shift of 8 cm^{-1} to lower frequencies. Such observations may be consistent with the following molecular behaviour.

(i) The libration in solution is still constrained largely to that about the long axis and the frequency shift indicates that the barrier to this motion has decreased slightly.

(ii) As evidenced from Kerr effect studies [26] in solutions of MBBA in benzene and in carbon tetrachloride molecular interaction between MBBA molecules occurs

at concentrations down to about 50 wt. % in both solvents. Prior to these observations it was assumed that the mesophase disappeared at the clarifying point (about 5 % solvent). Molecular interaction would be consistent with the small shift in the far infrared librational bands observed in MBBA and here.
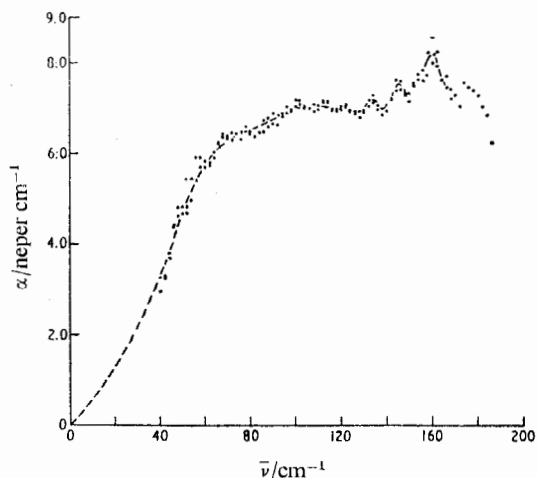

Fig. 5.—The absorption of OCC at 111 K. Mean of three runs with different samples.

AMORPHOUS PHASE AT 111 K

The frequency dependence of α (fig. 5) is broadly similar to that of the cholesteric phase. The molecules are apparently constrained to librate against a higher barrier because the maximum absorption now occurs at about 100 cm^{-1} although not well resolved from the overlapping absorptions peaking at 134, 146, 160 and 175 cm^{-1}.

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