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Vibrational Spectroscopy of Liquid Crystals: IV. Infrared and Far Infrared Spectra of the MBBA and EBBA Liquid Crystals

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Vibrational Spectroscopy of Liquid Crystals

IV. Infrared and Far Infrared Spectra of the MBBA and EBBA Liquid Crystals

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Infrared spectra have been recorded for N(*p*-methoxy) benzylidene- (*p*-*n*-butyl) aniline (MBBA) and its ethoxy analog in the crystalline, mesomorphic and isotropic phases. From the spectra obtained for a homeotropic layer in the nematic phase and for an isotropic layer, assignments of the bands are given which are supported by a previous normal coordinate analysis for benzylidene-aniline. Far infrared spectra have also been investigated for these compounds. The observed bands mostly consist of internal vibrations except the presence of a 120 cm^{-1} band assigned to a librational mode about the long axis of the molecule.

INTRODUCTION

N. Kirov and P. Simova[1,2] investigated the half-width temperature dependance of various infrared bands of different liquid crystals. They determined the potential barriers of the molecules around the long and short axes in the

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different phases. They found that not all bands broadened with temperature and that only those with projection value of the first derivative of the molecule dipole moment along the axes of the observer coordinate system would change. Same features are also observed when applying an a.c. electric field to a homeotropic layer and a homogenous one.[3] In order to correlate the typical behavior of each band with the type of vibration involved it is necessary to possess precise Raman and infrared data for the studied substances as well as correct assignments. In this paper we report infrared and far infrared spectra of MBBA and EBBA with particular emphasis on assignments supported by a normal coordinate analysis and dichroism measurements.

INFRARED SPECTRA OF MBBA AND EBBA

Infrared and Infrared/Raman spectra of MBBA were previously reported and tentative assignments were given.[4–6] We present here infrared spectra of MBBA recorded for the sample as a liquid film (isotropic layer) and for a homeotropic layer in the nematic phase. In the latter case, the directors are perpendicular to the plates. The Perkin–Elmer Model 180 spectrophotometer of the Organic Spectrochemistry Section at the National Research Council of Canada was used for recording the spectra. The wavenumber scale was calibrated over the range 500–300 cm^{-1} with a 1.1.1 mixture of indene/camphor/cyclohexanone and with HCl vapor in the lower wavenumber range. The spectral slit width was 2 cm^{-1} at 500 cm^{-1} and 3 cm^{-1} at 200 cm^{-1}. The technique is that described by H. Kelker *et al.*[7] This method is based on the measurements of the absorption of unpolarized light by a homeotropic layer and by an isotropic one. The so called dichroic ratio of longitudinally and transversally polarized bands leads to values of the degree of order as well as a support of assignments previously given on the basis of Raman data and a straightforward normal coordinate analysis of benzylidene-aniline.[8,9] Table I gives the infrared frequencies observed for MBBA in the liquid state and for its ethoxy analog EBBA in the nematic phase as well as assignments supported by the polarization of the absorption bands with particular emphasis on the modes corresponding to the rings for which the numbering is that given in Ref. 8. Figures 1 and 2 show typical spectra recorded for MBBA (isotropic) and EBBA (nematic). As previously found[10] these results show that, in the region below 1700 cm^{-1}, the degree of coupling is of great importance and none of the modes arise from a single type of molecular vibration.

If, in the normal coordinate analysis, we consider a mode for which from the potential energy distribution there is a component greater than 50% to be a characteristic group frequency, of the 96 normal modes, only 8 satisfy

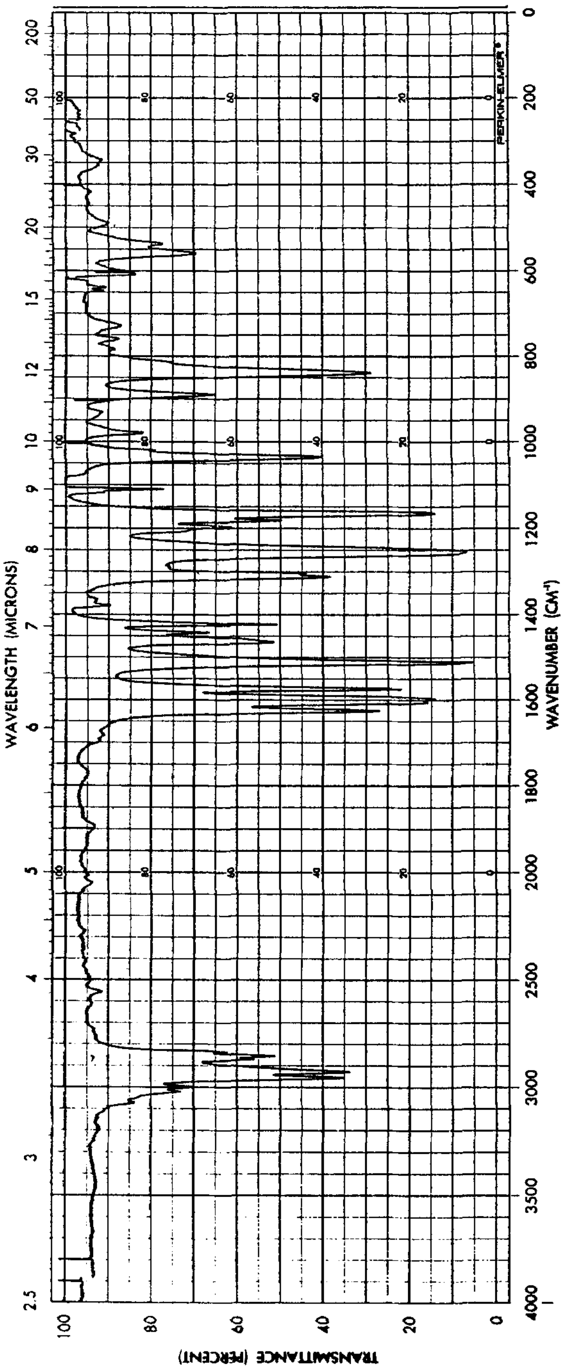


FIGURE 1 Infrared spectrum of isotropic MBBA.

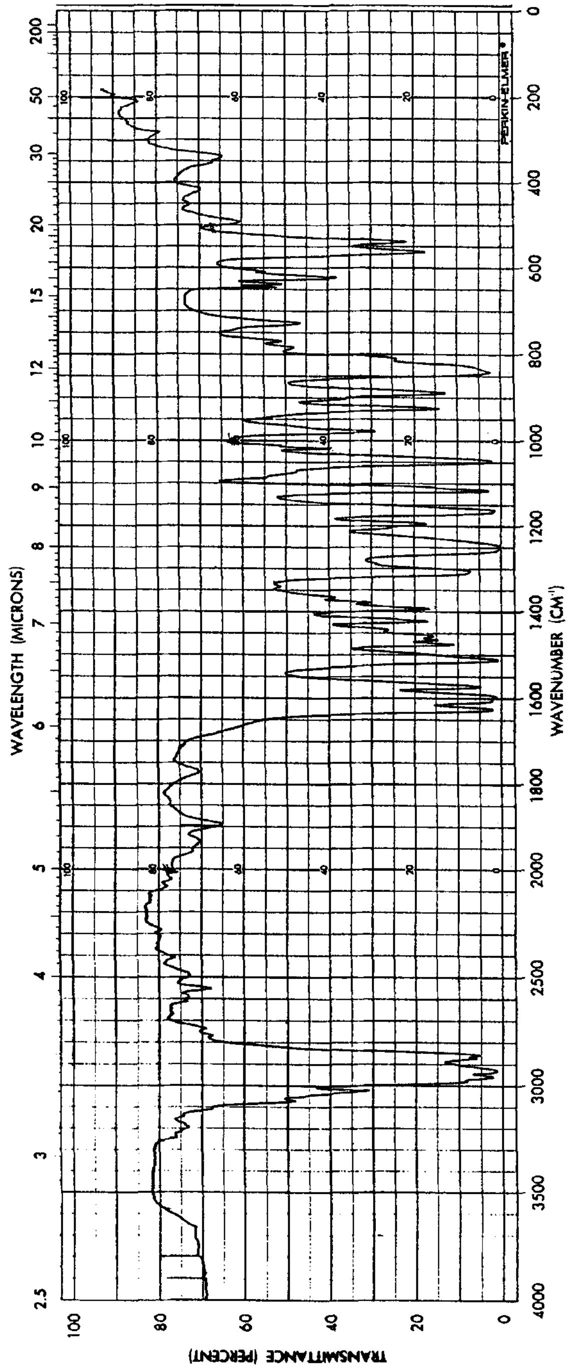


FIGURE 2 Infrared spectrum of nematic EBBA.

TABLE I

Infrared frequencies of MBBA and EBBA and their assignments

MBBA (liquid film)	EBBA (nematic)	Assignment
cm^{-1}	cm^{-1}	
	210 m	
	280 m	
340 w	340 s	
	350 sh	
	415 m	
420 w		
	450 w	
490 m	490 m	
536 m	540 s	$S_6(A_1)$ 25% $\parallel$
560 m	562 s	
610 m	610 w	
	622 s	$S_6(A_1)$ 40%
638 m	638 m	
646 m	645 m	
730 m	730 s	$S_{17}(B_2)$ 40%
	745 sh	
760 m		
	770 m	
784 w	785 m	
	810 m	
815 sh		
	830 sh	
840 s	840 s	$S_{10}(B_2)$ 70% $\perp$
890 s	890 s	$S_{10}(B_2)$ + CC skeletal stretching $\parallel$
	900 sh	
	925 s	
930 m		
980 s	980 s	$S_5(B_2)$ 40% and $S_{17}(B_2)$ 60% $\perp$
	1010 sh	
1020 m	1020 s	$S_2(A_1)$ 60% and $S_{13}(A_1)$ $\parallel$
1035 vs	1050 vs	
	1070 sh	
	1085 sh	
1110 s	1110 sh	$S_{19}(B_1)$ 37% and $S_{10}(B_2)$ $\perp$
1118 sh	1118 vs	
1165 vs	1165 vs	$S_8(A_1)$ and $S_9(A_1)$ 67% $\parallel$
1180 s		
1196 s	1195 s	ϕ—C stretching
1205 sh	1205 sh	
1254 vs	1250 vs	$S_9(A_1)$ 20% and $S_{13}(A_1)$ $\parallel$
	1290 sh	
1305 m		
1310 s	1310 s	$S_{14}(B_1)$ 50% and $S_9(A_1)$ 15% + CH_2 twist and rock $\parallel$
	1340 vw	
1365 v	1368 w	CH_3 symmetric deformation
1380 m	1380 m	
	1395 d	

TABLE I (*Continued*)

MBBA (liquid film)	EBBA (nematic)	Assignment
cm^{-1}	cm^{-1}	
1420 s	1422 s	$S_{19}(A_1)$ 26% and $S_9(A_1)$ 15% $\parallel$
1440 s	1440 m	CH_3, CH_2 deformation
1455 sh	1455 m	
1463 s	1465 m	
	1475 m	
	1500 sh	
1512 vs	1510 vs	$S_{20}(A_1)$ 50% and $S_{19}(A_1)$ 32% $\parallel$
1572 vs	1572 vs	$S_8(A_1)$, $S_7(A_1)$ and $S_9(A_1)$ $\parallel$
1598 vs	1595 vs	$S_8(A_1)$ 64%, $S_7(A_1)$ and $S_9(A_1)$ $\parallel$
1605 vs	1605 vs	
1625 vs	1625 vs	C=N stretching and ϕ—N stretching $S_8(A_1)$ $\parallel$
2835 m		
2855 s	2860 s	CH_2 asym. stretching
2875 m	2875 s	CH_3 sym. stretching
2925 vs	2930 vs	CH_2 asym. stretching $\perp$
2955 vs	2960 vs	CH_2 asym. stretching $\perp$
	2980 sh	CH_3 asym. stretching
3000 m		
3020 m	3020 sh	$S_6(A_1) + S_{18}(A_1)$ $\parallel$
	3040 sh	
3070 m	3070 m	

Abbreviations used: s: strong; vs: very strong; m: medium; w: weak; vw: very weak; sh: shoulder.

this requirement in the region below 1700 cm^{-1}. Such an observation necessitates caution in structural interpretations when characteristic group frequencies are used. Concerning the 890 cm^{-1} band, it exhibits a parallel dichroism. From the potential energy distribution with respect to the eigenvectors, it is shown that there is a contribution of the S_{10} mode (symmetry B_2) of the benzenic rings to that band. These two observations are not compatible. A reasonable assumption is to assign this band to the CC skeletal stretching of the butyl part of the molecule. The same conclusions are found for the 1310 cm^{-1} band which is assigned to the CH_2 twisting and rocking modes.

Such conclusions are of great importance when correlations have to be made between the type of vibration and the behavior of vibrational bands under the influence of applied external magnetic or electric fields.[11]

FAR INFRARED SPECTRUM OF EBBA IN THE POLYCRYSTALLINE STATE

Far infrared spectra, a typical example of which is shown in Figure 3, have been recorded for EBBA at room temperature in the range 500–30 cm^{-1}.

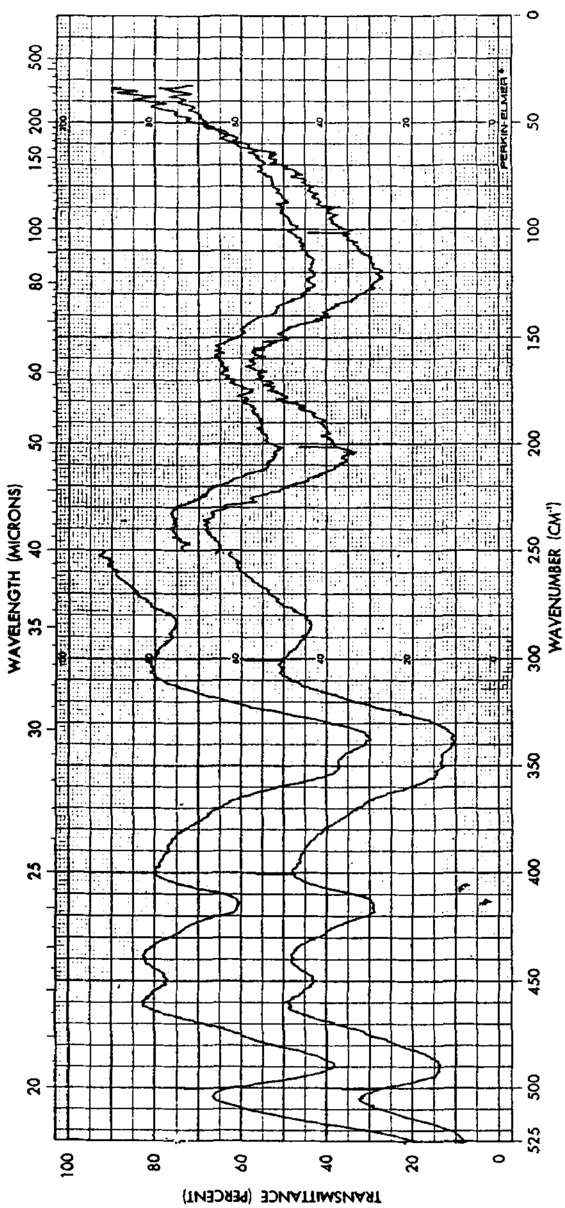


FIGURE 3 Far infrared spectrum of polycrystalline EBBA.

TABLE II

Far infrared frequencies of EBBA and their assignments

cm^{-1}		Assignment
490	strong	N=C—C deformation 15% ϕ—C deformation 14%
450	medium	CCN deformation 30% and O—C wagging 18%
416	strong	S_{16} (20%), S_{17} (23%), S_4 (21%) and ϕ—C wagging 26%
350 336	broad, strong	S_{16} (60%) and S_{17} (40%)
284	medium	S_{16} (22%) CC torsion (15%) and C—N torsion (14%)
204 190	broad, strong	C—N and C—C torsion, ϕ—C and N=C—C bendings
120	broad	libration about the long axis

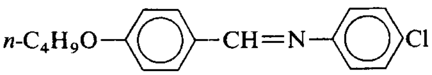
Most of the observed bands, given in Table II, consist of internal vibrations. A strong feature centred at 120 cm^{-1} is assigned to a hindered rotation about the long axis of the molecule. This band persists in the nematic and isotropic phases. Such a band was also observed in the Raman spectrum of crystalline MBBA[12] and in the infrared spectrum of MBBA.[13] This frequency 120 cm^{-1} is much higher than the Poley absorptions characteristic of most isotropic polar liquids (70 cm^{-1}) due to the librational oscillation of one polar molecule within the cage of its neighbours. This difference was described by Mansel Davies *et al.*[14] as due to the deeper and narrower energy wells provided by an hexagonal environment of parallel molecules in which the lathlike molecule librates.[15] They found a considerable barrier to rotation about the long axis (14–19 kJ mole^{-1}) which exists in the nematic phase and even in the isotropic liquid phase.

An alternative explanation to the presence of this band was given by J. A. Janik *et al.*[6] who suggested that the bands at 94, 102, 117 and 137 cm^{-1} in the infrared spectrum recorded at 149 K for stable MBBA were due to libration modes of C_6H_4 rings with respect to an in plane axis and to the 6 fold axis. They also estimated a libration frequency with respect to the long axis for various models of approximately 11–16 cm^{-1} which seems to be too low. P. Simova and N. Kirov[2] investigated the anisotropy of rotational diffusion in the nematic and isotropic liquid phases for a number of mesomorphogenics including MBBA and EBBA.

From the half-width temperature dependence of some infrared bands they obtained the preorientation barriers $U_{or}^{\parallel}$, $U_{or}^{\perp}$ around the long axis and around an axis perpendicular to it respectively. These authors found that the activation for hindered rotation of the molecules around the short axis is about 3–4 times bigger than the one around the long axis. From the preorientation potential barriers $U_{or}^{\parallel}$ and $U_{or}^{\perp}$ obtained for MBBA, and the principal moments of inertia and under the assumption that the 120 cm^{-1} band corresponds effectively to the libration around the long axis, the libration frequency around the short axis is expected at 38 cm^{-1}. There is effectively a band at 38 cm^{-1} in the Raman spectrum recorded at 100 K.[10] Unfortunately the considerable broadening of the Rayleigh wing before the crystal–mesophase transition makes impossible a temperature dependence study of the very low frequency bands.

Recently a Raman study of solid phases of MBBA was reported by J. Le Brumant *et al.*[16] These authors confirmed the existence of two crystallographic phases (stable and metastable) from the low frequencies Raman data. From their study, we can conclude that the Raman spectra recorded by one of us[10] is that of the form III, the nature of which is not elucidated. J. Le Brumant *et al.* found several bands in the very low frequency range (40–5 cm^{-1}). It would be useful to investigate the nature of the bands at 16–27 cm^{-1} in order to confirm the presence of the rotatory lattice modes perpendicular to the long axis.

B. J. Bulkin *et al.*[13,17] investigated the 135 cm^{-1} observed in the infrared spectrum of MBBA. From a study of solutions in CCl_4, they conclude that this mode is of intermolecular origin. We have also recorded the low frequency Raman spectra of:



which exhibits several smectic phases.[18] Eighteen bands have been observed in the range below 150 cm^{-1} at 123 K. The temperature dependence of the 118 cm^{-1} band leads to the conclusion that it can be assigned to a rotatory lattice mode about the long axis. Complete results concerning this latter compound will be published elsewhere.

CONCLUSION

Infrared and far infrared spectra of MBBA and EBBA have been recorded and complete assignments have been given. This work has to be used as a basis of future investigation on the influence of external electric or magnetic fields on the vibrational spectra of mesomorphogenics.

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