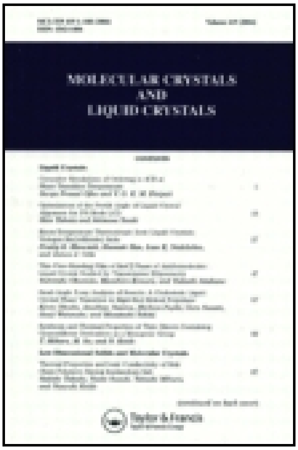

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Motional and Relaxational Processes in Amorphous and Crystalline Phases of Methoxybenzylidene-butylaniline II. Raman Spectroscopy of MBBA in its Solid and Nematic Phases

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Raman spectra for 4-methoxybenzylidene-4'-butylaniline (MBBA) in its nematic liquid crystal phase and in all its solid phases were measured in the frequency range 5–1700 cm^{-1}. Clear modifications have been observed at the phase transitions, not only in the low frequency range, but also in the internal vibrational modes. Different stages of the structural order in the successive polymorphic modifications are evidenced. In addition, the changes which occur in the intramolecular part of the spectra reveal that phase transitions directly affect the butyl tail while others are related to conformational modifications of the core of the molecule.

INTRODUCTION

Methoxybenzylidene-butylaniline (MBBA, formula: $CH_3—O—C_6H_4—CH{=}N—C_6H_4—C_4H_9$) after quenching from the room temperature nematic liquid crystal

(NLC) phase to the amorphous phase C_0 yields, by slow reheating, a succession of solid phases C_1, C_2, C_3 and C_4 obtained between T_g = 205 K and T = 296 K.[1] All four of these phases can be cooled to low temperature without other transition. The phases C_1 and C_2 are smectic bilayered.[2] Conversely, the phases C_3 and C_4 are crystalline. Another sequence of phase transitions is obtained by slow cooling of the nematic state which yields two crystalline phases C_6 and C_5.

Recent neutron scattering experiments[3] indicate that the densities of states in the phases C_0 and C_1 show a similar and structureless shape at the same low temperature of 100 K. On the other hand, the densities of states in the crystalline phases C_3, C_4 and C_5 exhibit strong differences with marked structures which may originate from conformational changes of molecules. Moreover, in the low frequency range (0–30 cm^{-1}), the shape of the densities of states of the crystalline phases C_4 and C_5 can be approximately described by the usual Debye model. Conversely, the amorphous and smectic phases and the crystalline phase C_3 definitely exhibit a systematic deviation which is the stronger as we follow the sequence C_3 towards C_0. At highest temperatures, a general softening of the densities of states is observed.

The neutron spectra show clearly a quasielastic broadening on a time scale 10^{-11}–10^{-12} s not only in the NLC phase but also in the crystalline phase C_6. In both of these phases, the motions do not correspond to rotational motions of the molecule around its long axis. They are rather related to orientational fluctuations of parts of the molecule, in particular of the butyl chain. This idea is strengthened by the dependence of the Elastic Incoherent Structure Factor (EISF) as a function of temperature which excludes well-defined discrete equilibrium positions. Furthermore, there is evidence for a weak broadening of the spectra in both crystalline phases C_4 and C_5 which indicates the occurrence of other motions.

Many Raman studies have been already made.[4–13] In the earliest, the existence of metastable phases was not known. Moreover, because the appearance and the survival of these metastable phases are directly dependent on the cooling rate, more recent spectra which were reported are likely to result from a mixing of several phases.

In the present study, the Raman spectra were systematically measured for all the phases. It is known that the intensity and the width of lines may directly depend on the molecular surroundings. Considering previous assignments, our purpose was to identify the lines which present the strongest modifications at the different phase transitions and to obtain information about the dynamics of the different parts of the molecule. This study is of great interest for the interpretation of our Incoherent Quasielastic Neutron Scattering (IQNS) experiments, especially for the motions of the end butyl chain for which characteristic modes are observed.

EXPERIMENTAL

Raman spectra were measured for all solid phases and the NLC state with a resolution of 2 cm^{-1} in the frequency range 5–250 cm^{-1} and of 3 cm^{-1} in the range 250–1750 cm^{-1} on a triple monochromator T800 Coderg spectrometer. The

514.5 nm line of an argon laser was used and the incident power at the sample was about 50 mW. The spectra were obtained using unpolarized light and were averaged over the data from several scans. Unsuccessful measurements were attempted in the spectral range 2400–3400 cm^{-1} because of an intense background. The sample was in a capillary tube of 2 mm diameter. The quenched phase C_0 was obtained by directly plunging into liquid nitrogen the sample originally in its nematic state. The different solid phases were produced by placing the sample in a nitrogen cryostat. From the quenched phase C_0 which was measured at 80 K, the phases C_1, C_2, C_3 and C_4 were successively obtained by reheating the sample at 210, 225, 255 and 275 K respectively. Then, each of these four phases was cooled and measurements were performed at 80 K. By slow cooling of the sample (< 2K/mn) from the NLC phase, the crystalline phases C_6 and C_5 were successively produced and measured at 260 K and 80 K respectively. The crystalline phase C_4 was also measured at 260 K for the propose of comparison with the crystalline phase C_6 at the same temperature.

LOW FREQUENCY SPECTRA

The low frequency spectra (0–250 cm^{-1}) of MBBA are shown in Figure 1 for the different solid phases C_0, C_1, C_2, C_3, C_4 and C_5 at 80 K and for the NLC phase at

TABLE I

Low frequency vibrational modes for the solid and nematic phases of MBBA. The nematic liquid crystal (NLC) and crystalline C_6 phases were measured at room temperature and 260 K respectively; the other phases were measured at 80 K.

NLC	C_0	C_1	C_2	C_3	C_4	C_5	C_6
						7	
						10	
				15		17	
	22			18			21
		30		25	28	28	
			36		35	39	
				45			
					53	57	
					74		
					86	85	
	100	100		93			100
			106		109	107	
					114		
			120	125		120	
				133		139	135
					146		
						170	175
186			186	183		180	
	194	192			192		
	214	208			210		
					245	242	

TABLE II

Internal vibrational frequencies of the different phases of MBBA. The more intense lines are underlined: the weaker are in *italics*.

NLC	C_0	C_1	C_2	C_3	C_4	C_5	C_6
						306	
		312	*314*	314		*314*	
330				*330*	*332*	338	338
	345	*340*	*345*		*342*	*351*	
		362	*365*	*362*	*358*	*365*	*362*
				383		*382*	
414	418	418			416	418	418
				442	*446*	450	450
						506	
				527	*532*		
550	*554*	*563*			*562*	*559*	
					602		
608	*614*	*610*		*611*	*614*	*610*	
634	636	635	634	635	634	635	634
643	644	643	642	642	642	*643*	
724	720	720	718	718	717	717	718
						723	
	734	734		*738*	*732*		
762	*762*	762	*760*	762	762	760	760
780	782	781					
						792	790
798	800	798	798	797	798	802	798
824						823	*823*
	834	832	*830*	*830*	*832*	*839*	
					842	*850*	
					878		
890	890	888	884	880	888	888	886
		905	905	904	908	902	900
940	945	*940*					
					970	*970*	
978	982	982	*979*	*978*	980	*984*	*980*
1016	1016	1016	1014	1014	1014	1014	1012

TABLE II (*continued*).

NLC	C_0	C_1	C_2	C_3	C_4	C_5	C_6
						1030	
			1058	*1052*		*1055*	
						1074	
						1094	
1106	1107	1107	1106	1105	1106	1108	1108
				1116	1114		
1162	1164	1166	1164	1165	1159	1166	1169
					1172		
			1183	1184	1182		
1192	1194	1194	1192	1192	1192	1192	1196
1250	1252	1251	1249	1248	1248	1246	1246
						1255	1254
		1273	*1272*	1272	*1272*		
		1288	1286	1286	*1288*	1287	1286
1302	1304	1304	1302	1300	*1302*	1302	1304
1310	1314	1314	1314	1312	1310		
					1328		
			1360	*1360*	*1360*		
1368	1368	1370	1370	1370	1370	1367	1370
1421	1421	1422	1421	1422	1422	1416	1418
					1436	1444	*1444*
					1456	1456	*1458*
				1462	*1466*		
1502	1501	1499	1498	1498	1500	1495	1504
						1502	
1573	1573	1572	1573	1573	1574	1575	1576
				1580			
1595	1595	1593	1594	1594	1594	1595	1596
				1600		*1606*	
1624	1624	1624	1624	1625	1624	1624	1624
				1642			
				1678			

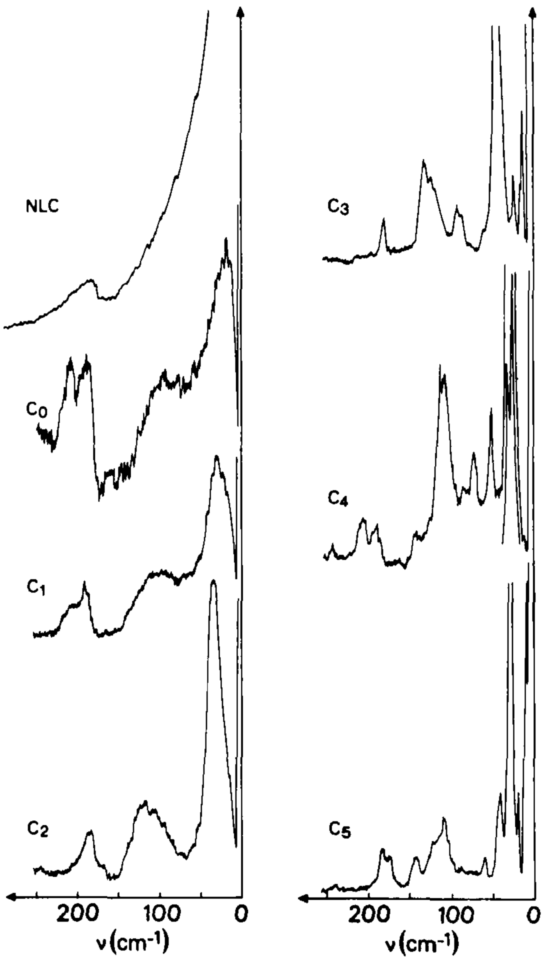

FIGURE 1 Low frequency Raman spectra for the different phases of MBBA. The NLC phase was measured at room temperature. The solid phases were measured at 80 K.

room temperature. In Figure 2, the phases C_4 and C_6 are compared at 260 K. In the NLC phase, the spectrum is structureless up to 186 cm^{-1} where the first line appears. This band exists also with various structures in all the solid phases and different assignments were put forward by several authors.[4,5,12,13] Nevertheless, all of them agreed that this band is due to an internal mode. So, we are led to situate the limit of the external modes at about 160 cm^{-1}. The quenching of the NLC phase to the C_0 phase yields the appearance of a structure in the low frequency spectra (Figure 1). Two broad peaks clearly appear at 22 and 100 cm^{-1}. The general shape of the spectra in the range 5–160 cm^{-1} remains similar when passing to the phases C_1 and C_2. Nevertheless, the band at 22 cm^{-1} in C_0 is shifted to 30 cm^{-1} in C_1 and 36 cm^{-1} in C_2. The band at 100 cm^{-1} which is observed in C_0 and C_1 is also shifted to 120 cm^{-1} in C_2. Simultaneously, these bands become definitely

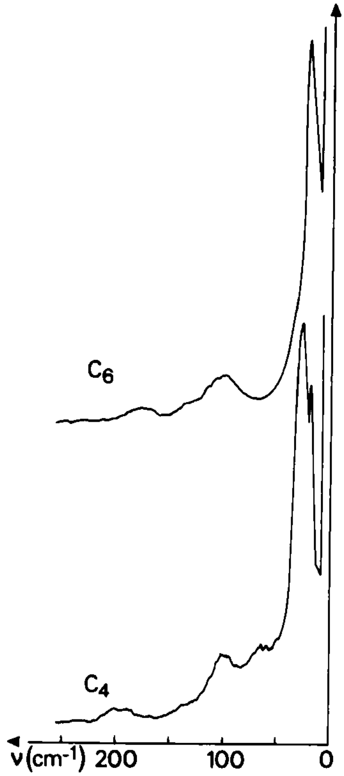

FIGURE 2 Low frequency Raman spectra for the phases C_6 and C_4 at the same temperature 260 K.

sharper. This is probably related to the degree of order in the sample. Indeed, recent studies have shown that the phases C_1 and C_2 could be smectic bilayered.[2] In the (frozen) nematic phase C_0, there is no long range translational order. The smectic phases are a little more ordered by the existence of layers of molecules, but there is still a lack of translational order within these layers. Thus, the coherence lengths of the modes are much smaller than the optical wavelengths. The momentum selection rule is broken and all the modes can give contributions to the Raman spectrum.[14] However, it appears that the shape of the low frequency spectra (< 160 cm^{-1}) is not drastically changed, particularly at the $C_0 \rightarrow C_1$ transition and we are led to conclude that the local order is not strongly modified at this latter phase transition.

When passing from C_2 to C_3, some analogies can still be found in the spectra. The line at 36 cm^{-1} in C_2 is shifted to 45 cm^{-1} in C_3 and the band at 106–120 cm^{-1} is moved and separated in two lines at 125 and 133 cm^{-1}. Other well-defined lines also appear at 15 and 25 cm^{-1}. In addition, it will be seen later that apart from the frequency range 1150–1250 cm^{-1}, the spectra of the internal modes in C_2 and C_3 exhibit the same features which allows us to assume that the conformation of the core of the molecule is not changed at this phase transition.

Conversely, the transition $C_3 \rightarrow C_4$ shows definitely more important modifications among the external modes. Strong lines are observed at 28 and 35 cm^{-1} and less intense modes at 53, 74 and 86 cm^{-1}. The region 100–160 cm^{-1} is also modified and lines appear at 109, 114 and 146 cm^{-1}. Simultaneously, the spectrum of the internal modes is changed, which allows Dolganov *et al.*[12] to put forward the hypothesis that these effects are due to changes of molecular conformation.

In the spectrum of the phase C_5, intense lines are noted at very low frequencies: 7, 10 and 17 cm^{-1}. A similarity with C_4 is the line at 139 cm^{-1}. From a Raman study of MBBA in the isotropic liquid, NLC and C_6 and C_5 crystalline phases, Vergoten *et al.*[5] attempt to assign the low frequency lines and suggest that the lines in the range 100–120 cm^{-1} and 130–145 cm^{-1} are due to rotational motions of the molecules around their long axis and translational motions, respectively. On the other hand, from infra-red measurements on oriented nematic MBBA, Bulkin *et al.*[15] point out that the band at 135 cm^{-1} is not due to a hindered translation along the long molecular axis, but do not exclude other hindered translation or rotation.

The metastable crystalline phase C_6 does not exist at low temperature. So, we report in Figure 2 the low frequency spectra of C_6 and the stable crystalline phase C_4 at 260 K. It is worth noting that at this temperature, the spectra of C_6 and C_4 are strongly smoothed. Nevertheless, the spectrum of C_6 is very similar to the envelope of the spectrum of C_5 and the lattice is probably conserved in both of these phases, the main change being the occurrence of dynamical disorder. Our neutron studies have effectively shown that these phases are dynamically disordered.[3]

INTERNAL MODE ANALYSIS

General features—The internal mode spectra are reported in Figure 3 and Figure 4. The spectra of the NLC and C_0 phases are similar (Figure 3). This result is not surprising because we may admit that the state of the NLC phase is frozen in the quenched phase C_0. Changes appear at the phase transition $C_0 \rightarrow C_1$: the wide band at about 346 cm^{-1} in C_0 is clearly separated into two lines at 340 and 364 cm^{-1}, the band at 890 cm^{-1} in the NLC and C_0 phases is also split into two lines at 888 and 905 cm^{-1}. At the transition $C_1 \rightarrow C_2$, much stronger modifications are observed. In particular, the lines at 418 and 980 cm^{-1} and the less intense wide band at 832 cm^{-1} disappear. The frequency range 1260–1320 cm^{-1} is modified. The lines of C_2 remain in C_3, but are more narrow. In the latter phase, the line at 315 cm^{-1} appears a little more intense, but the most significant changes are the appearance in C_3 of a new line at 1184 cm^{-1} and differences in the range 1260–1320 cm^{-1}. In the phase C_4, the major modifications to be noted are as follows: the line at 980 cm^{-1} is visible again and the range 1150–1200 cm^{-1} is strongly modified. The spectra of the phases C_5 and C_6 exhibit practically the same features.

Spectral range 170–210 cm^{-1}—We have assigned the bands in the range 170–210 cm^{-1} to internal modes. However, their existence and their shape are strongly influenced by the changes of phases. The wide band at about 186 cm^{-1} in the NLC

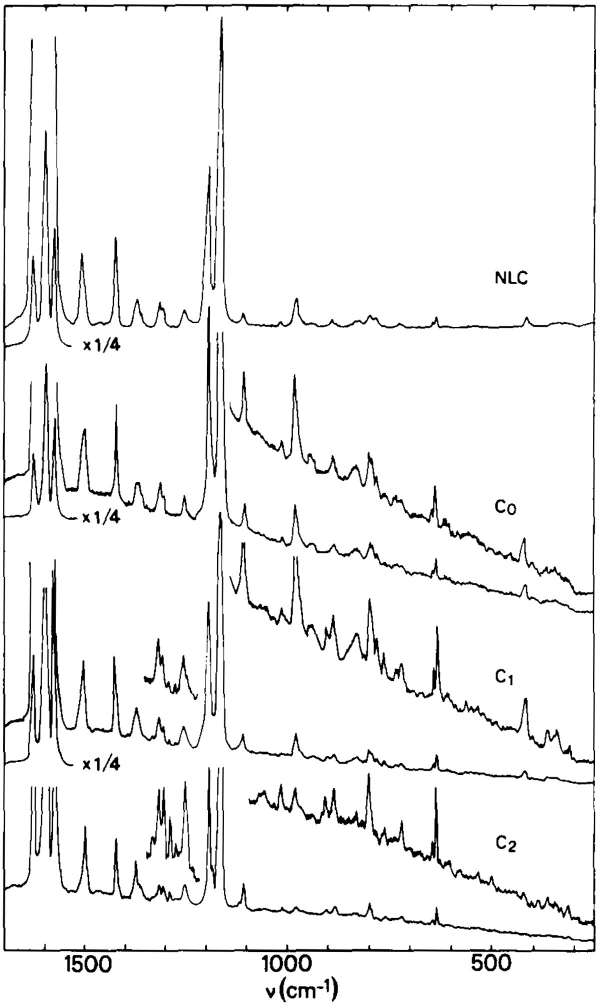

FIGURE 3a Raman spectra for the NLC, C_0, C_1 and C_2 phases in the range 250–1700 cm^{-1}. (NLC: room temperature, C_0, C_1 and C_2: 80 K).

phase is moved and gives two peaks of equal intensity at 194 and 214 cm^{-1} in the phase C_0. By quenching the NLC phase into C_0, the motions have been frozen, but we may assume that, from a structural aspect, the phase C_0 is essentially the same as the NLC phase. Thus, these two peaks should also exist in the NLC phase but are strongly broadened by the dynamical disorder. The line at 214 cm^{-1} is reduced in intensity in C_1 and it totally disappears in C_2 where a single line is observed at 186 cm^{-1}. In C_3, its widths becomes much more narrow at 183 cm^{-1}. On the other hand, two lines at 192 and 210 cm^{-1} appear again in C_4. In a Raman study of the isotropic liquid, NLC and C_6 phases, Borer *et al.*[4] indicate that these bands can probably be assigned to a torsional mode. For benzylidene-aniline (BA),

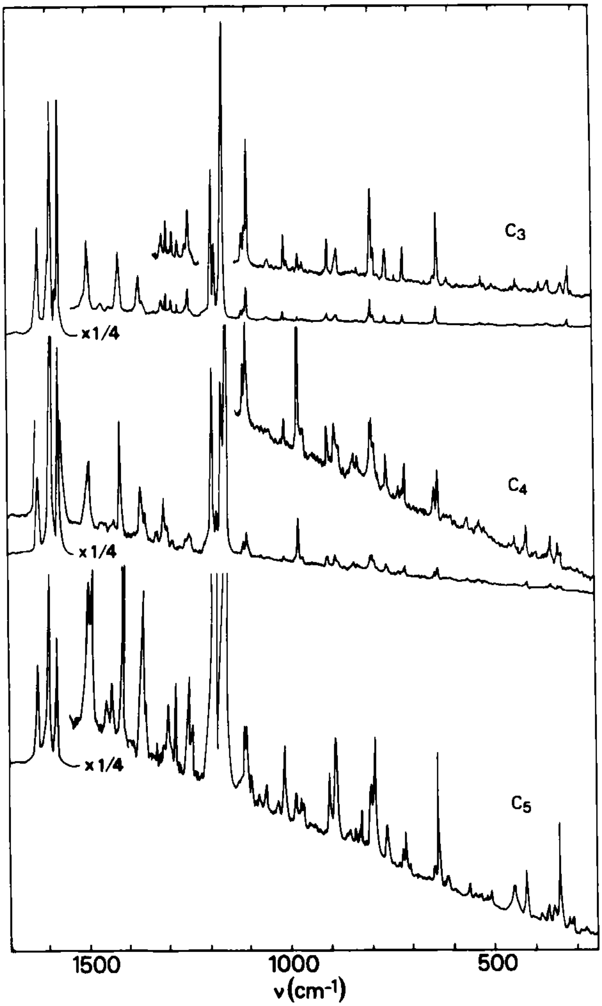

FIGURE 3b Raman spectra for the phases C_3, C_4 and C_5 at 80 K.

Vergoten *et al.* predicted a mode at 179 cm^{-1} due to CCX deformations (X is the atom in the *para*-position on the aniline ring) and N=C—C deformations which correspond to motions of the central part of the molecule.[16] However, this band does not appear in the measured spectrum of BA, but was effectively observed in the isotropic liquid, NLC and C_6 phases of MBBA.[5, 6] Mizuno *et al.*[17] have measured the low frequency Raman spectra of three solid phases which they called annealed, metastable and stable phases. The annealed phase has no correspondence with any of our spectra; this probably results from a mixing of phases, but the metastable phase could correspond to C_5 and the stable to C_4. These authors note that the bands in the range 170–200 cm^{-1} are very likely due to the internal twisting rotation of the benzene rings out of the C=N—C plane. We have no precise assignment

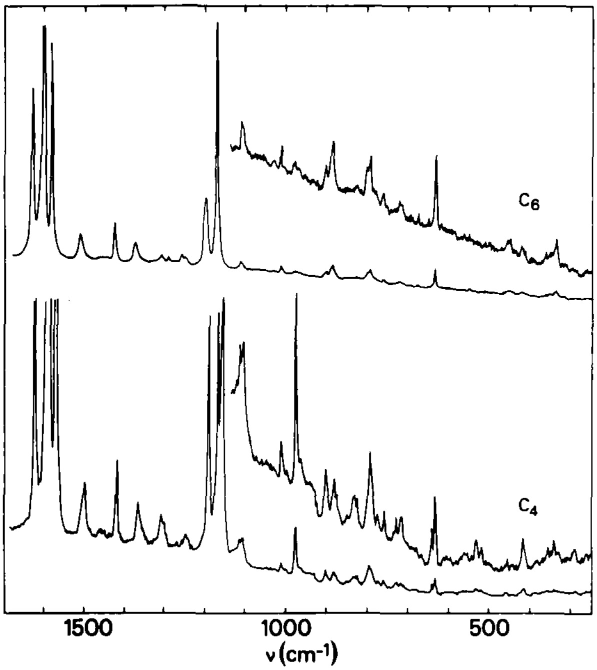

FIGURE 4 Raman spectra for the phases C_6 and C_4 at the same temperature, 260 K.

for these bands. However, it must be pointed out that these modes are particularly sensitive to the progressive disappearance of the disorder in the arrangement of the molecules when going from nematic to smectic and then crystalline phases C_0 to C_4, particularly at the transitions $C_1 \rightarrow C_2$ and $C_3 \rightarrow C_4$. On the other hand, no significant change is observed at the phase transition $C_5 \rightarrow C_6$ where the study of the external modes has already evidenced only a small variation of the intermolecular forces.

Spectral range 300–500 cm^{-1}—Bands of very weak intensity appear in all the phases. Their structure generally changes when passing from one phase to another. The broad and structureless band which is observed in the NLC and C_0 phases in the region 300–370 cm^{-1} is more defined in C_1. Two lines clearly appear at 340 and 362 cm^{-1} and a weak intensity line is observed at 312 cm^{-1}. At the phase transition $C_1 \rightarrow C_2$, the intensity of these lines is strongly reduced. In C_3, the latter peak becomes more intense and lines are rearranged at 330, 362 and 383 cm^{-1}. Lines are noted at 332, 342 and 358 cm^{-1} in C_4, at 306, 314, 338 (more intense), 351, 365 and 382 cm^{-1} in C_5 and at 338 cm^{-1} in C_6. In the isotropic liquid, NLC and C_6 phases, Vergoten *et al.*[6] effectively observed bands at 315 cm^{-1} and 340 cm^{-1} and assigned them to out-of-plane deformation of benzene rings and to the accordion mode of the butyl tail, respectively. However, by an analysis of n-alkylbenzene compounds, Yasuniwa *et al.*[18] suggest that constraints from other molecules exist between the benzene ring and the butyl chain of the MBBA molecule. Thus, the accordion mode vibration in the end propyl chain should occur at about 310 cm^{-1}.

The line at about 415 cm^{-1} which exists in the NLC, C_0 and C_1 phases disappears in the phases C_2 and C_3, but is again found in C_4. This line also exists in the phases C_5 and C_6 but its intensity is much weaker. The modifications of the line which is assigned to out-of-plane deformations of benzene rings coupled with a ϕ-C wagging[6] may originate from conformational changes of the molecule. Especially, the angle between the azomethine plane and the benzene rings should be modified at the phase transitions $C_1 \rightarrow C_2$ and $C_3 \rightarrow C_4$.

Spectral range 500–750 cm^{-1}—Generally, several lines weakly appear in the region 500–650 cm^{-1} (except the peak at 635 cm^{-1} which is intense) but we especially turn our attention to the range 715–740 cm^{-1}, where we expect to find evidence of the methylene rocking mode. Indeed, Snyder[20] points out that the calculated frequencies of the in-phase methylene rocking mode in n-paraffins are 723 cm^{-1} for the *trans* (*tt*) conformation and 734 cm^{-1} for the *gauche* (*tg*) conformations of n-pentane. The band at 724 cm^{-1} in the NLC phase is broadened by the dynamical disorder. In all the other phases, the line at 718 cm^{-1} may be assigned to the CH_2 rocking of the *trans*-conformation of the butyl tail. Moreover, it is noteworthy that a line at 734 cm^{-1} appears in C_0 and C_1. This fact leads to the conclusion that *gauche*-conformations are effectively present, not only in the phases C_0 and C_1, but also in the NLC phase, since the former phases result from the quenching of the latter. It must be pointed out that the line at 734 cm^{-1} totally disappears in C_2 and is practically invisible in C_3. This fact suggests that all the butyl tails are in the *trans*-conformation. In C_4, the relative intensity of the lines at 717 and 732 cm^{-1} is strongly dependent on the temperature (see Figure 3*b*: C_4 at 80 K and Figure 4: C_4 at 260 K) and this confirms the possibility of the existence of *trans*- and *gauche*-conformations of the butyl chains whose proportions are directly connected with the temperature.

Spectral range 750–850—In the NLC phase, we observe essentially four bands at 762, 780, 798 and 824 cm^{-1} (Figure 3). These lines are still present in C_0, but the latter is shifted to 834 cm^{-1}. The transition $C_0 \rightarrow C_1$ does not modify the spectra apart from the line at 762 cm^{-1} which becomes more intense. The main modifications occur at the transition $C_1 \rightarrow C_2$, where the lines at 760 and particularly at 830 cm^{-1} are weakened and the line at 780 cm^{-1} totally disappears. All the lines of the phase C_2 are more narrow in C_3. Conversely, the lines of C_4 are broadened with respect to C_3 at the same low temperature. The motion involved at 780 cm^{-1} may be the rocking vibration of the chain in its *gauche*-conformation, as is the case for n-paraffins.[20]

Destrade *et al.*[7, 8] measured the Raman spectra of MBBA in the isotropic liquid and NLC phases and in three solid forms called A, B and C. A detailed comparison of their spectra with our own measurements shows that the form A probably corresponds to a mixing of the phases C_1 and C_2, the form B to the phase C_4 and that the form C results from a mixing of phases C_6 and C_4. Indeed, by neutron diffraction, Belushkin *et al.*[19] effectively showed that a slow transformation $C_6 \rightarrow C_4$ can occur. From their study, Destrade *et al.* assign the line at 781 cm^{-1} to *gauche*-conformations of the butyl tail and the line at 798 cm^{-1} to the *trans*-conformation, and show that both *gauche-* and *trans*-conformations of the butyl tail exist in the liquid and NLC phases and that the *gauche*-configurations disappear in the form C.[8] They also point out the existence of *trans-* and *gauche*-isomers in the form A. Conversely, in the forms B and C, the butyl tails have the *trans*-conformation.[7]

Due to the presence of the lines at 780 and 798 cm^{-1} in our spectra of the NLC, C_0 and C_1, we may conclude that both *trans-* and *gauche*-conformations of the butyl tail exist in these phases. On the other hand, the lack of the line at 780 cm^{-1} in the phases C_2, C_3, C_5 and C_6 corresponds to the total disappearance of the *gauche*-conformations as is generally observed in solid phases. The formation of the phases C_1 and C_2 in smectic layers is connected with the organization of the tail of the molecules. In C_4, the line at 780 cm^{-1} is not visible at 80 K, but appears at 260 K, which leads us to assume that *gauche*-conformations probably exist in proportions strongly dependent on the temperature.

Spectral range 850–1000 cm^{-1}—Interesting features are to be noted in this region. In the NLC and C_0 phases, three lines are observed at about 890, 940 and 980 cm^{-1}. At the transition $C_0 \rightarrow C_1$, two significant modifications occur. A new line appears at 905 cm^{-1} and the intensity of the line at 940 cm^{-1} is much weakened. The line at 905 cm^{-1} is also observed in the other phases; conversely the line at 940 cm^{-1} totally disappears. The latter line appears in the same phases as the line at 780 cm^{-1}, and therefore may be assigned to vibrations of the butyl tail in *gauche*-conformations. Conversely, the line at 905 cm^{-1} is probably related to the existence of *trans*-conformations. The intense peak at 980 cm^{-1}, which is assigned to out-of-plane deformations of benzene rings and a $CH_{central}$ wagging,[6] practically disappears at the transition $C_1 \rightarrow C_2$, but is found again intensely in C_4. The intensity of this line is weak in the crystalline phases C_6 and C_5. The appearance of the lines at 980 and 415 cm^{-1} in the different phases clearly exhibits an analogous behaviour. Since both these lines deal only with modes of the core of the molecule, we are led to conclude that the conformation of the core changes at the transitions $C_1 \rightarrow C_2$ and $C_3 \rightarrow C_4$.

Spectral range 1100–1250 cm^{-1}—Two intense lines which are assigned to CCH deformations of benzene rings[6,16] are observed at about 1165 and 1192 cm^{-1} in the NLC, C_0, C_1 phases (Figure 5). They become more and more narrow when passing from the smectic phases C_1 to C_2 and then to the crystalline phase C_3 which indicates the progressive appearance of a structural ordering of the molecules. In addition, a new peak clearly appears at 1184 cm^{-1} in C_3. At the transition $C_3 \rightarrow C_4$, the line at 1165 cm^{-1} is split into two lines at 1159 and 1172 cm^{-1}. The changes may originate from the dihedral angles between the azomethine plane and the aniline and benzylidene rings and suggest that two conformations of the core of the molecule are mixed in the phase C_4 as was proposed by Mizuno *et al.*[17] The relative intensity of both of the latter lines are strongly dependent on temperature. We may thus propose that the proportion of each conformation is very sensitive to temperature.

Spectral range 1240–1330 cm^{-1}—The relative intensities are particularly changed in the phase C_2 and to a larger extent in the phase C_3 with respect to the other phases. In this region, we expect to see the CH_2 wagging-twisting modes, but a

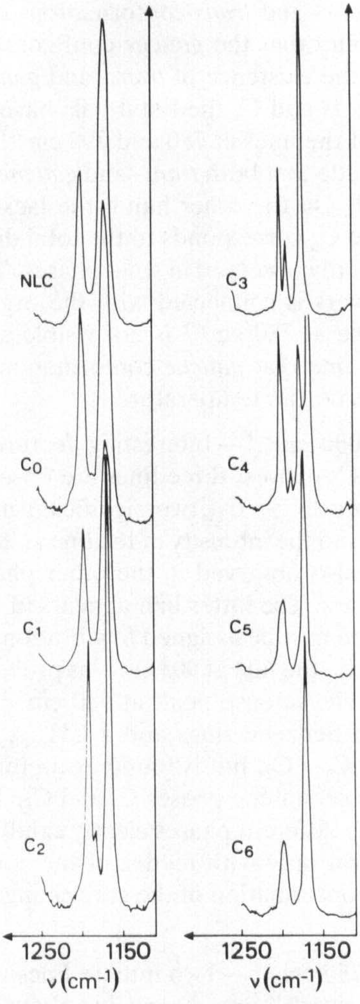

FIGURE 5 Raman spectra for the different phases of MBBA in the spectral range 1120–1250 cm^{-1}.

detailed analysis appears difficult because of the existence of vibrational modes due to the core of the molecule.

CONCLUSION

From this study, we have essentially the following picture: when the sample is quenched from the NLC phase, the disorder of both the centre of mass of the molecule and the conformation of the molecule are frozen. When the sample is heated the succession of phase transitions results from two competing processes: first, the centres of mass of the molecules tend to arrange themselves in compact order so that the succession of polymorphic modifications deals with different stages of the structural order. Second, the butyl tails exhibit a more and more important dynamical disorder in proportion as the temperature increases.

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