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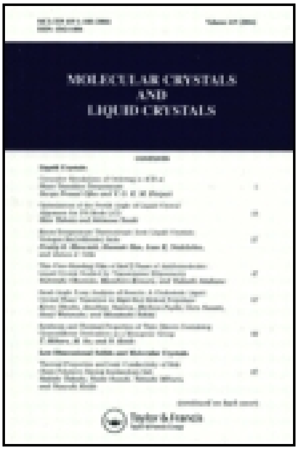

Molecular Crystals and Liquid Crystals

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Calorimetric and Dielectric Investigations of MBBA (N-(p-methoxybenzylidene)-p-butylaniline) and HAB (4,4′-di-n-heptyloxyazoxybenzene)

J. K. Mościcki [a], X. P. Nguyen [a], S. Urban [a], S. Wróbel [a], M. Rachwalska [b] & J. A. Janik [c]

[a] Institute of Physics of the Jagiellonian University, Cracow

[b] Institute of Chemistry of the Jagiellonian University, Cracow

[c] Institute of Nuclear Physics, Cracow

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Calorimetric and Dielectric Investigations of MBBA (*N*-(*p*-methoxybenzylidene)-*p*-butylaniline) and HAB (4,4′-di-*n*-heptyloxyazoxybenzene)

J. K. MOŚCICKI, X. P. NGUYEN, S. URBAN and S. WRÓBEL
Institute of Physics of the Jagiellonian University ,Cracow†

and

M. RACHWALSKA
Institute of Chemistry of the Jagiellonian University, Cracow

and

J. A. JANIK
Institute of Nuclear Physics, Cracow

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Part I of this paper presents the results of calorimetric investigations of *p*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA) and 4,4′-di-*n*-heptyloxyazoxybenzene (HAB). In both these substances two modifications of the solid phase, a metastable and a stable one, have been found to exist. Part II presents the results of measurements of the complex dielectric permittivity $\varepsilon^* = \varepsilon' - j\varepsilon''$ for the solid and liquid phases of both substances. The metastable modification of MBBA was found to feature a dielectric relaxation process in the kilohertz range associated with the rotational motions of the tail groups about the long axes of the molecules. No such process was revealed in the case of HAB. In the liquid phases of these two compounds relaxation processes were observed in the microwave-frequency range; these are interpreted as being due to the rotation of entire molecules about their own long axes. The existence of such motion in the smectic phase C of HAB seems to be not in agreement with the predictions of McMillan's theory.

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† Address: Institute of Physics of the Jagiellonian University, 30-059 Krakow, ul. Reymonta 4, Poland.

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INTRODUCTION

Temperature-dependence measurements, although they are extremely tedious and time-consuming, of specific heat by means of an adiabatic calorimeter, provide much fuller and more precise information regarding the thermodynamic properties of the examined substances than that acquired by the commonly used DSC methods. On the other hand, since in most liquid-crystalline substances the molecules possess permanent dipole moments, dielectric measurements are very useful for studying the reorientational motions of molecules in the various phases.

This paper is concerned with the calorimetric and dielectric relaxation measurements of MBBA (*N*-(*p*-methoxybenzylidene)-*p*-butylaniline) and HAB (4,4′-di-*n*-heptyloxyazoxybenzene). The substances examined are different both as regards molecular structures and liquid-crystalline properties. For instance, MBBA has only a nematic phase, whereas HAB also has a C-type smectic phase. However, it was thought that it would be interesting to see whether such different types of liquid crystals could have similar properties.

I CALORIMETRIC INVESTIGATIONS

1 MBBA

Detailed information on the calorimetric investigations of MBBA is available in Ref. 13. Figure 1 shows the specific heat *vs.* temperature curve. It distinctly shows the existence of two modifications of different thermodynamic properties in the solid phase; these are the metastable (upper curve) and stable phases (lower curve). An interesting point is the existence of a $c(T)$ anomaly in the vicinity of 212–217°K in the metastable modification. Andrews[2] suggests that this anomaly is associated with a change in the freedom of the conformational motions of the tail groups in the MBBA molecules.

2 HAB

The basic goal of the calorimetric investigations of HAB was to find whether the solid phase of this substance features two modifications, as is the case for MBBA. Therefore, the HAB specimen was submitted to thermal treatment just like the MBBA specimen. The sample material used in the calorimetric measurements was manufactured by the firm W. MERCK (for spectroscopic purpose).

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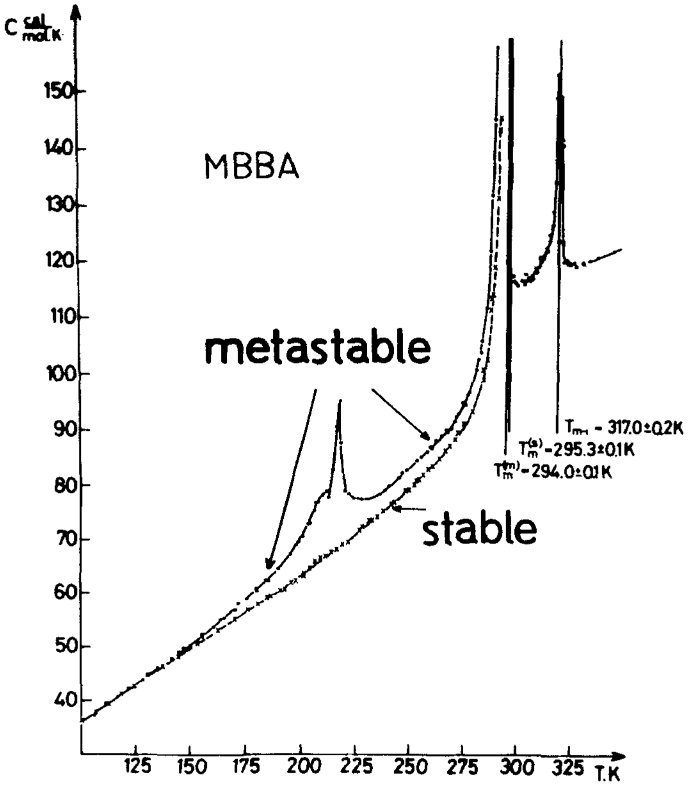

FIGURE 1 MBBA. Specific hear *versus* temperature.

Figure 2 shows the results of measurements of the specific heat of HAB as a function of temperature in the range from 90 to 420°K. The error of the $c(T)$ measurements for temperatures below about 360°K was smaller than 1 %, whereas above this point it reached 2–3 %. The upper curve was obtained after the sample was quickly cooled ($v = -2.5$°K/min) from the isotropic phase to liquid nitrogen temperature. (All calorimetric measurements began at about 90°K). In the heating process the melting point of the sample was never achieved because above 340°K the metastable solid phase modification obtained thus spontaneously transformed (in an exothermal process) into the stable modification. Subsequent research has shown that, like the case of MBBA, the stable modification can be acquired only through a transformation from the metastable modification. The transition time is up to well over ten hours, but may be reduced to several hours by applying thermal pulses, i.e. a one minute period of heating, then 30 minutes of temperature stabilization over and over again. In contrast to

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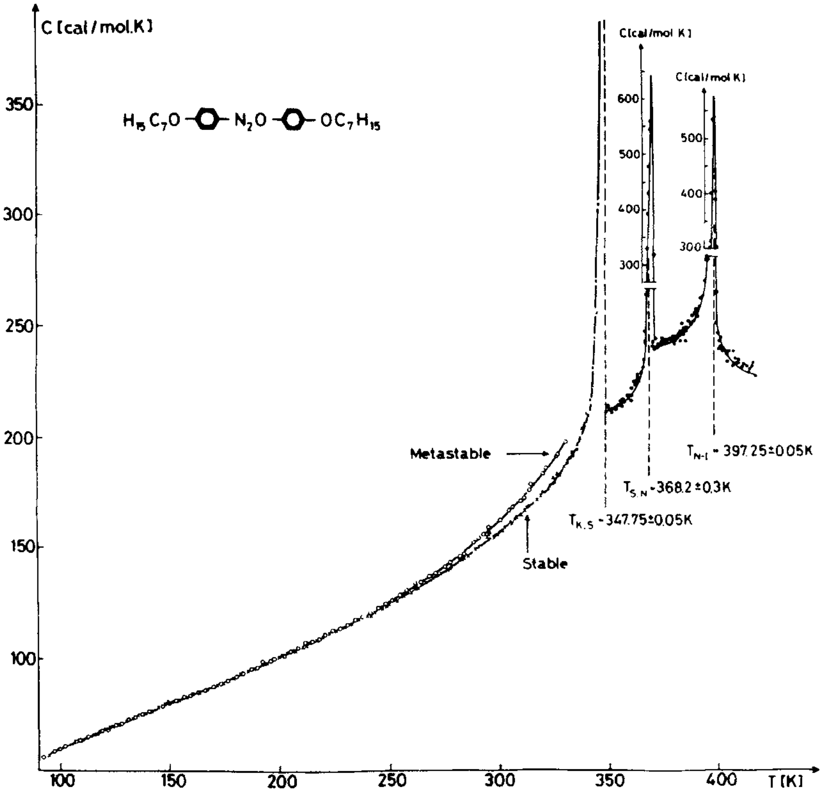

FIGURE 2 HAB. Specific heat *versus* temperature.

MBBA, the metastable modification of HAB does not demonstrate an anomaly in the specific heat.

After the stable modification is cooled to 90°K and then reheated the lower curve in Figure 2 is obtained. At the 330°K point the difference of specific heat values of the two modifications, $(c_{\mathrm{met}} - c_{\mathrm{stab}})/c_{\mathrm{stab}}$, amounts to 5 %. The reproducibility of the results of the measurements in both modifications was excellent.

TABLE I

Temperatures, enthalpies and entropies of phase transitions in HAB: K–S—from solid to smectic, S–N—from smectic to nematic and N–I—from nematic to isotropic.

Transition	K–S	S–N	N–I
T[K]	347.75 ± 0.05	368.20 ± 0.30	397.25 ± 0.05
ΔH[cal/mole]	9860 ± 830	650 ± 150	770 ± 110
ΔS[cal/mole · K]	30.3 ± 4.6	1.68 ± 0.45	2.06 ± 0.3

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Table I gives the values of temperature, enthalpy and entropy of the phase transitions acquired when the stable modification of HAB is heated. The values of the transition temperature are in good agreement with literature data.[3,15]

II DIELECTRIC INVESTIGATIONS

1 MBBA

Measurements of the complex dielectric permittivity, ε^*, were carried out on non-oriented samples in two frequency ranges: the kilohertz range from 0.03 to 300 kHz (by the Schering bridge technique) and the microwave range from 1.0 to 10 GHz (by the short-circuited wave-guide technique[20]). The accuracy of the ε' and ε'' measurements was better than 4% and 7% in the wave-guide version and 2% and 3% in the bridge version, respectively. The MBBA specimens were synthesized in the laboratories of the Institute of Organic Chemistry and Technology, Technical University of Warsaw.

a) Radio-frequency range The measurements of ε' and ε'' in the solid phase of MBBA were made in the range from about 180°K to about 280°K every 10 degrees (the metastable modification) or every 15 degrees (the stable modification) at seven field frequencies ν: 0.3, 0.8, 3.0, 10.0, 30.0, 100.0 and 300.0 kHz. The reproducibility of results obtained for the two modifications at various cooling rates was very good. No ageing of the sample throughout the measurements was observed; the melting point was 293.5°K and the clearing point 320°K.

Figure 3 shows the results of measurements of ε' and ε'' *vs.* temperature for the metastable and stable modifications of solid MBBA. The fundamental difference between the dielectric properties of the two modifications is quite evident. In the metastable form there is dipole absorption and dispersion which do not appear in the stable modification. At the lowest frequencies, near the melting point, there appears in both modifications a distinct increase in the dielectric losses, presumably associated with ionic conduction.

The values of $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ found for the metastable modification can be described on the (ε', ε'') plane by the Cole–Davidson equation[7] with the parameter β equal about 0.5,

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + j \cdot 2\pi\nu \cdot \tau)^\beta} \qquad \text{(II.1)}$$

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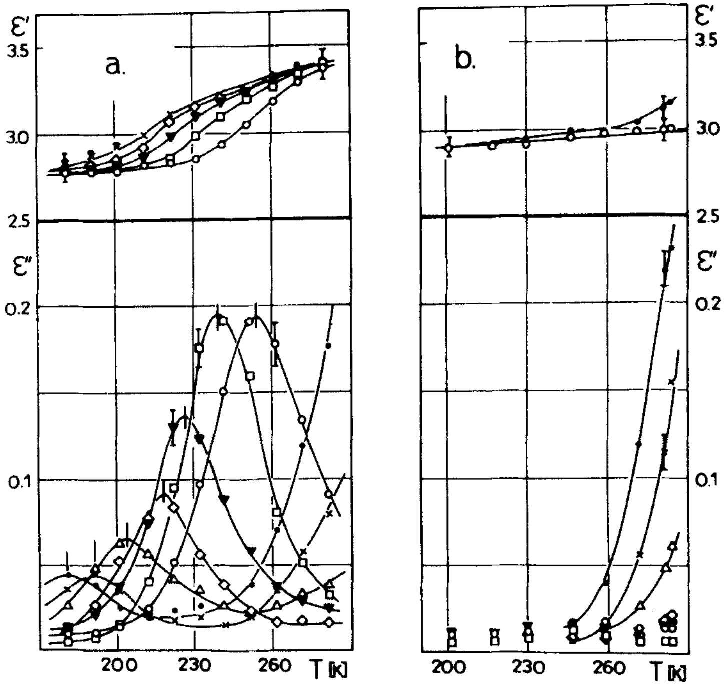

FIGURE 3 MBBA. Temperature dependence of the dielectric losses ε'' and dielectric constants ε' for two modifications of the solid phase: a = metastable and b = stable, with frequency ν as a parameter: ● = 0.3 kHz, X = 0.8 kHz, △ = 3.0 kHz, ◇ = 10 kHz, ▼ = 30. kHz, □ = 100 kHz, ○ = 300 kHz.

The dielectric increment (being the difference between the values of permittivity at high temperatures—here 290°K and low temperatures—here 180°K) is about 0.6, which corresponds to a dipole moment of about 1.2 D.

The relaxation times, τ, determined from the positions of the $\varepsilon''(T)$ loss maxima for each of the frequencies, vary from 8.0×10^{-4} sec to 8.5×10^{-7} sec in the range of temperatures from 191°K to 254°K. The character of the $\tau(T)$ dependence above and below the temperature of about 218°K differs slightly.[16] The value of τ extrapolated to the melting point is about 5.0×10^{-8} sec. The Arrhenius activation enthalpy of the observed relaxation process, averaged over the entire range of temperatures examined, equals (8.7 ± 1.0) kcal per mole.

As reorientational motions of entire MBBA molecules in the solid phase are rather improbable, we put forth a possible explanation of the observed dipole relaxation, namely, that it is due to intramolecular reorientation jumps of the tail groups (the OCH_3 groups mainly) about the long molecular

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axes. Both the magnitude of the calculated dipole moment (typical values of the dipole moment of methoxy groups in many compounds are of the order of 1.3 D[9]) and the relatively small value of relaxation time near the melting point speak in favor of this view. It is interesting that this interpretation corroborates the model considerations of the thermodynamic properties of MBBA's metastable modification of Andrews.[2] A detailed discussion of the observed relaxation process and in particular the mechanism of dielectric dispersion and absorption both above and below 218°K will be presented in a future paper.[16]

b) *Microwave-frequency range* Measurements of ε^* in the gigahertz range comprises the main temperature ranges of the nematic and isotropic phases of MBBA. Measurements were made in the temperature range from about 260°K to about 340°K every several degrees for the following five field frequencies ν: 1.0, 1.6, 1.8, 2.9 and 9.9 GHz. Reproducibility of results was excellent. The substance was found to age rapidly, however, which effected a difference in the values of the clearing points for samples measured at the various frequencies.

Figure 4 presents the results of ε' and ε'' measurements in the microwave band as a function of temperature for three condensed phases of MBBA. The dependence $\varepsilon_s'(T)$ at a frequency of 300 kHz, accepted as the static dielectric permittivity, is also plotted. The dependence of ε' and ε'' on temperature and frequency alike indicates the occurrence of dielectric dispersion in both of MBBA's liquid phases in the examined frequency range. The distribution of measurement points in the (ε', ε) plane could be described well by the Cole–Cole equation[6]:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (j \cdot 2\pi\nu \cdot \tau)^{1-\alpha}} \tag{II.2}$$

Figure 5 depicts typical Cole–Cole arcs obtained for the nematic and isotropic phases of MBBA. The estimated values of relaxation time in the nematic phase ranged from 2.0×10^{-10} sec to 1.6×10^{-10} sec in the temperature range from 295°K to 305°K, whereas in the isotropic phase from 1.5×10^{-10} sec to 1.2×10^{-10} sec in the 322°K to 335°K range, respectively. The accuracy of the estimated relaxation time is not better than 10%.

The Arrhenius enthalpy of activation determined from the temperature-dependence of the relaxation time was found to equal (4.6 ± 0.2) kcal per mole for the isotropic phase and (3.8 ± 0.3) kcal per mole for the nematic phase.

The Cole–Cole plots obtained for the nematic phase gives a non-zero difference between $\varepsilon_s^{\text{extr}}$ and ε_s. This difference is quite large, and is above all

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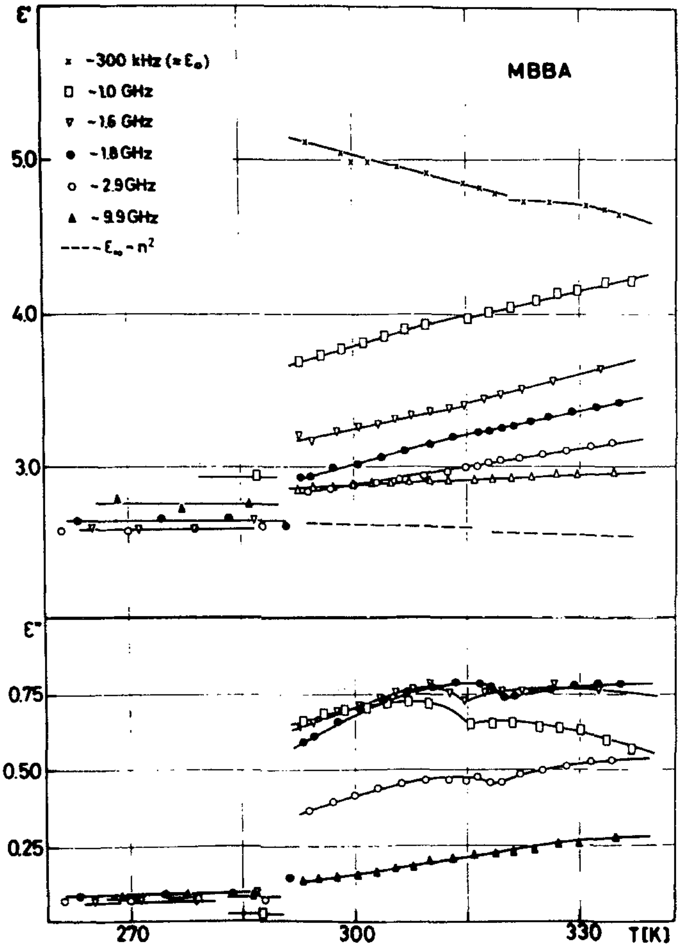

FIGURE 4 MBBA. Temperature dependence of the dielectric losses ε'' and dielectric constants ε' for the isotropic, nematic and solid phases, in microwave frequency range.

the dielectric dispersions observed in the megahertz range of frequencies[1,17,18] associated with the rotation of molecules about the short molecular axes.

Dielectric relaxation at gigahertz frequencies is associated primarily with the reorientational motions of the molecular dipole moments about the long molecular axes. The MBBA molecule possesses two permanent nonzero dipole moments associated with the CH=N group (1.6 D) and the OCH_3 group (1.3 D). The CH=N dipole moment is practically perpendicular to the long axis of the molecule, whereas the methoxy group's moment

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makes with this axis an angle of about 70°. Since the small difference $\varepsilon_{\infty}^{\text{extr}} - \varepsilon_{\infty} = 0.1$ ($\varepsilon_{\infty} = n^2$, n being the mean refractive index) is presumably due to resonance absorption in the far infrared,[21] it seems that the observed microwave absorption and dispersion in the nematic phase of MBBA is caused by rotational motions of the two dipole moments about the long molecular axis.[16]

The relaxation process in MBBA's isotropic phase was observed earlier.[1,5,12] The value of the relaxation time obtained according to our measured data is in good agreement with the results of Price *et al.*[1,12] but our activation enthalpy value is much lower (compared with 7.2 kcal per mole of Price *et al.*). As is seen in Figure 5, in the isotropic phase there is a relaxation process having a broad spectrum of relaxation times, as revealed by a lowering of the Cole–Cole arc. Both the cited authors and we agree that the main mechanism of this relaxation seems to be rotational jumps of the molecules about their long axes.

A comparison of the activation enthalpies and the relaxation times extrapolated to the clearing point for the two liquid phases is extremely interesting (Table II). Apart from the relatively considerable errors of the determined qualities, everything seems to point to a confirmation of the expectations of

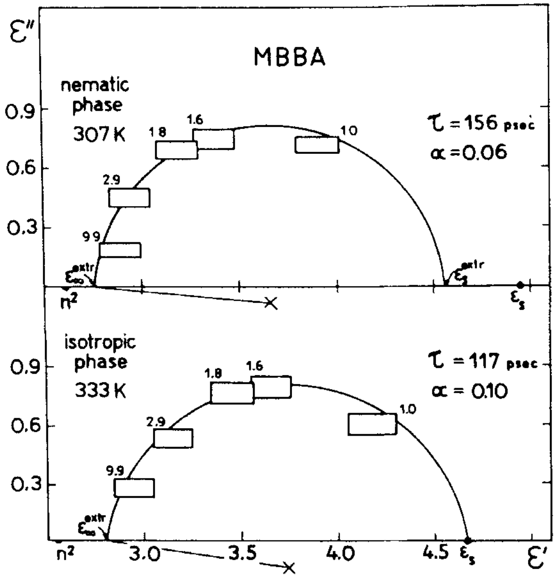

FIGURE 5 MBBA. Representative Cole–Cole diagrams for the nematic and isotropic phases in microwave frequency range. The rectangles correspond to the experimental errors of ε' and ε'', frequencies in GHz are given above them.

TABLE II

Values of activation enthalpy for isotropic and nematic phases of MBBA and the macroscopic dielectric relaxation times extrapolated to the clearing point (320 K).

Phase	Activation enthalpy kcal per mole	Relaxation time at clearing point
Nematic	3.8 ± 0.3	1.25×10^{-10} sec
Isotropic	4.6 ± 0.2	1.60×10^{-10} sec

Tsvetkov's theory[19] which predicts both faster rotation and a lower activation barrier for the motion about the long molecular axis in the nematic phase than in the isotropic phase.

2 HAB

a) Temperature dependence of ε′ and ε″ The dielectric properties of HAB were studied by Maier and Meier[11] (in the radio frequency range) and by Axmann[4] (at three microwave frequencies) for oriented samples. Our measurements of the dielectric permittivity were carried out on non-oriented samples during their cooling and heating. In the radio-frequency range various cooling rates were used in order to be able to examine the behaviour of both solid phase modifications. The temperature-dependence of ε′ at 300 kHz is shown in Figure 6. At room temperature a value of ε′ of 2.77 was

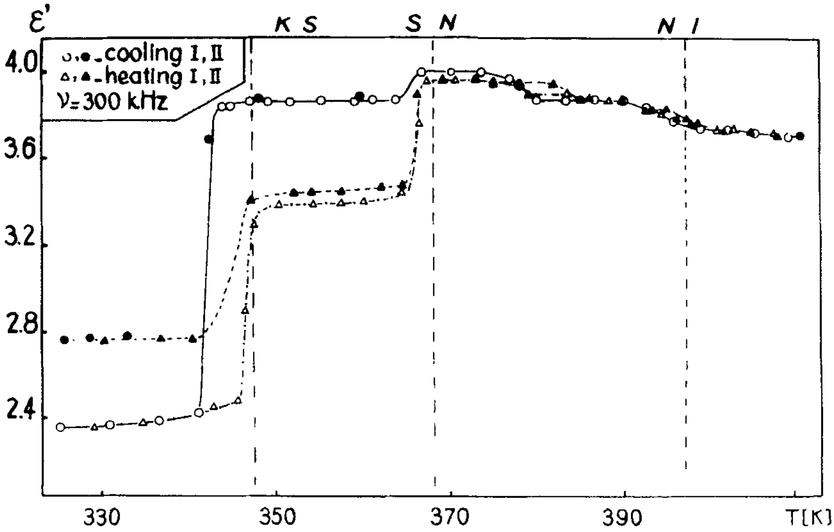

FIGURE 6 HAB. Temperature dependence of ε′ for various thermal treatments of the sample at the frequency of 300 kHz. The fast cooling II was used to study the metastable modification.

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obtained for the metastable modification, whereas for the specimen formed by slow cooling from the isotropic phase (hence, not entirely stable), the value of ε' was 2.30. In contrast to MBBA, no relaxation effect was observed for HAB's metastable phase.

In the smectic phase the values of ε' and ε'' obtained in the radio frequency range and at low microwave frequencies (Figures 6 and 7), become arranged along different curves, depending on the way it was obtained, whether by melting the solid phase or cooling the nematic phase. A similar effect, but much weaker, is observed in the nematic phase at temperatures near the S–N transition. It should be added that an analogous phenomenon had been observed by Gasparoux *et al.*[8] in their investigations on the magnetic susceptibility of compounds with A and C smectic phases. Hence, this effect is a feature of smectic structures, and its survival to HAB's nematic phase seems to indicate the existence of smectic cybotactic groups in it.

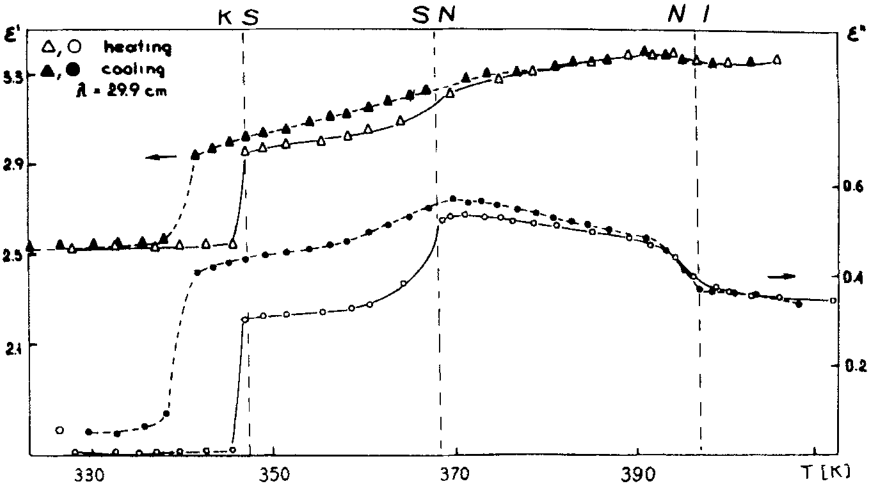

FIGURE 7 HAB. Temperature dependence of ε' and ε'' at the frequency of 1 GHz.

b) Dielectric relaxation in the microwave-frequency range The results of dielectric investigations of HAB presented here for the microwave-frequency range are not yet complete and the quantitative data therefore give only a sense of direction. The ε^* measurements were made at frequencies of 1, 1.8, 3, 6 and 10 GHz in the temperature range comprising all liquid phases. The results of the measurements, presented in Figures 8 and 9, show the existence of distinct dielectric dispersion and absorption in each of the liquid phases. In the Cole–Cole diagrams (Figure 10) the points arrange themselves, as in the case of MBBA, on an arc of a circle of a lowered center (the parameter α

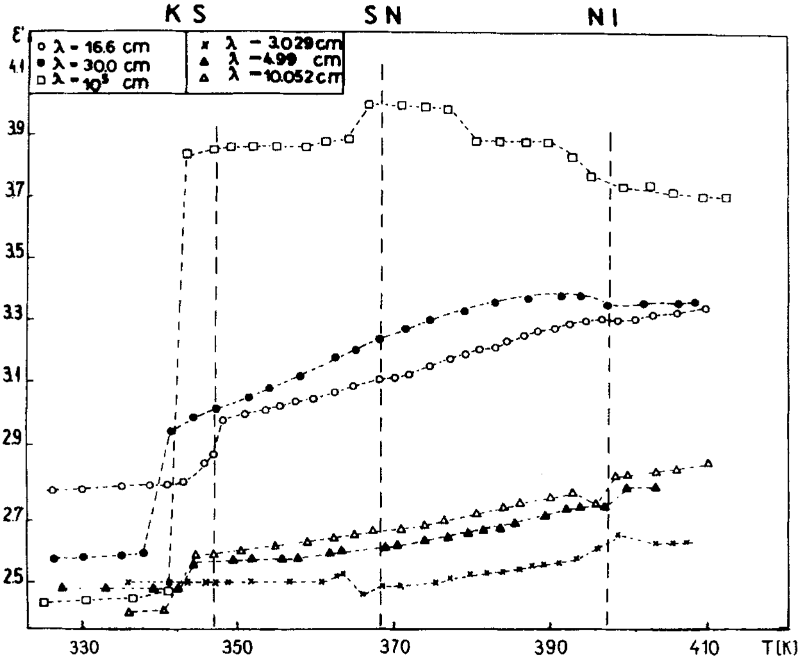

FIGURE 8 HAB. Temperature dependence of ε' for several microwave wavelengths.

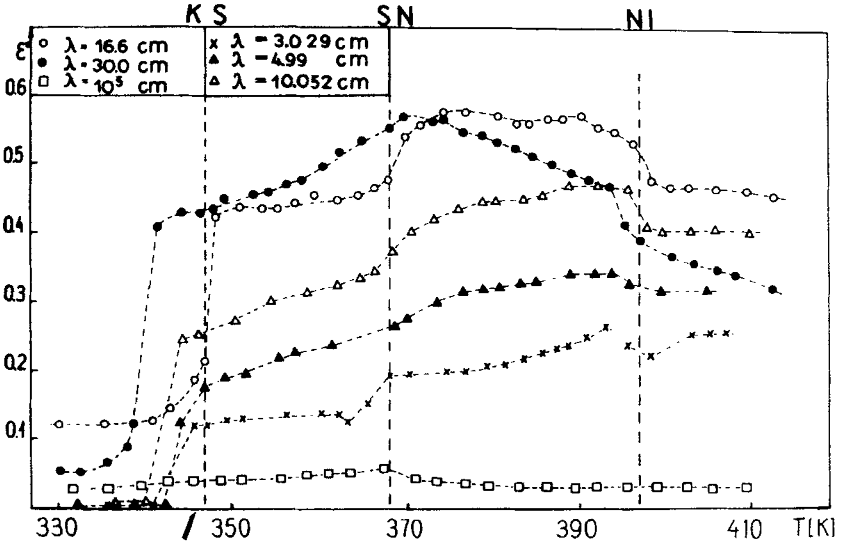

FIGURE 9 HAB. Temperature dependence of ε'' for several microwave wavelengths.

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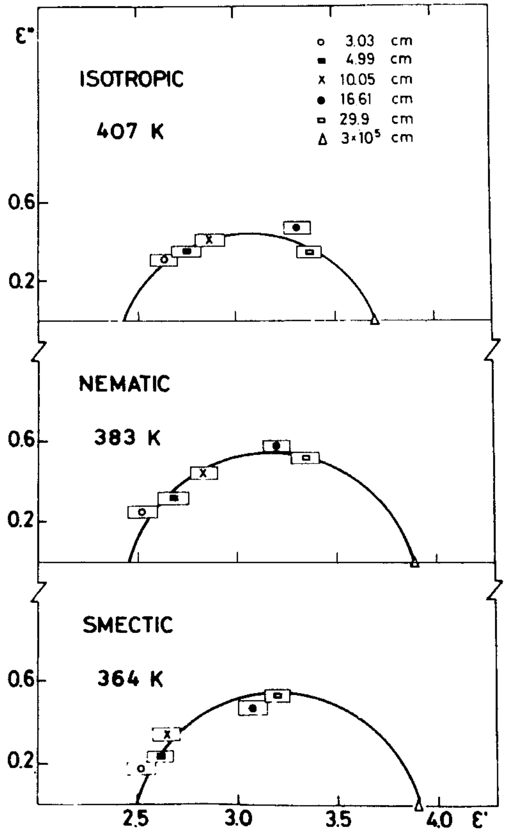

FIGURE 10 HAB. The Cole–Cole diagrams for the isotropic, nematic and smectic phases.

is of the order of 0.2). The values of dielectric relaxation times calculated for the various phases are as follows:

$$\tau_I = 0.6 \times 10^{-10}\ \text{sec} \quad (\text{at } 407^\circ\text{K}),$$

$$\tau_N = 1.1 \times 10^{-10}\ \text{sec} \quad (\text{at } 383^\circ\text{K}),$$

$$\tau_S = 2.0 \times 10^{-10}\ \text{sec} \quad (\text{at } 363^\circ\text{K}).$$

The observed process of dielectric relaxation is presumably linked with the rotation of molecules about their long axes. The existence of this process in HAB's isotropic and nematic phases had been suggested earlier by Axmann[4] who performed dielectric measurements at three frequencies above 9 GHz, hence, very far from the critical frequency. The value of the activation enthalpy estimated from the temperature-dependence of the relaxation times is of the order of 5 kcal per mole for all three liquid phases.

The most important result of this study is the finding of the existence of the dielectric relaxation phenomenon in the smectic phase of HAB. This fact contradicts the prediction of McMillan's theory,[14] which states that in C-type smectic phases dipole correlations cause the long molecular axes to become inclined, while the dipole–dipole interactions are strong enough for the rotation of the molecules about their long axes to become frozen (such rotation is possible in A type smectic phases, however).

III CONCLUSIONS

Despite the distinct differences in the structure of MBBA and HAB molecules, these substances do demonstrate many similar properties.

In both cases there are two modifications in the solid phase: the metastable and stable modifications. The lack of the relaxation process and anomalies in the specific heat in HAB's metastable modification seems to be caused by the more developed and more flexible tail groups of the molecules of this compound, as compared with those of analogous groups in the case of MBBA.

The values obtained for dielectric relaxation times and the barriers hindering dipole rotation in the liquid phases of the two compounds imply that in the isotropic and nematic phases, and in the smectic phase of HAB, the mechanisms of molecular reorientation are very similar.

References

1. V. K. Agarwal and A. H. Price, *Trans. Faraday Soc.*, **70**, 188 (1974).
2. J. T. S. Andrews, *Phys. Lett.*, **46A**, 377 (1974).
3. H. Arnold, *Z. f. Phys. Chem.*, **226**, 146 (1964).
4. A. Axmann, *Z. Naturforsch.*, **21a**, no. 5, 615 (1966).
5. J. L. Bartaschevsky, W. M. Dolgov and W. A. Krasovsky, presented at Second Soviet Union Conference on Liquid Crystals, Ivanovo 1973.
6. K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**; 341 (1941).
7. D. W. Davidson and R. H. Cole, *J. Chem. Phys.*, **19**, 1484 (1951).
8. F. Hardouin, H. Gasparoux and P. Delhaes, Preprint of the Université de Bordeaux I, 1975.
9. N. E. Hill, W. E. Vaughan, A. H. Price, and M. Davies, Dielectric Properties and Molecular Behaviour, Acad. Press London, 1969, Chap. I.
10. J. A. Janik, J. M. Janik, J. Mayer, E. Ściesińska, J. Sciesinski, T. Waluga, W. Witko, and J. Twardowski, *J. de Phys.*, **36**, C1-159 (1975).
11. W. Maier and G. Meier, *Z. Naturforsch.*, **16a**, 1200 (1961).
12. P. Maurel and A. H. Price, *Trans. Faraday Soc.*, **69**, 1486 (1973).
13. S. Meyer, T. Waluga, and A. J. Janik, *Phys. Lett.*, **41A**, 102 (1972).
14. W. L. McMillan, *Phys. Rev.*, **A8**, 1921 (1973).
15. A. Mircea-Roussel and F. Rondelez, *J. Chem. Phys.*, **63**, no. 6, 2311 (1975).
16. J. K. Mościcki, *et al.* to be published.
17. F. Rondelez, D. Diguet, and G. Durand, *Mol. Cryst. Liquid Cryst.*, **15**, 183 (1971).

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18. F. Rondelez and A. Mircea-Roussel, *Mol. Cryst. Liquid Cryst.*, **28**, 173 (1974).
19. V. N. Tsvetkov, Vyestnik LGU, **10**, 40 (1969).
20. S. Wróbel, J. A. Janik, S. K. Mościcki, and S. Urban, *Acta Phys. Pol.*, **A48**, 215 (1975).
21. M. Evans, M. Davies, and I. Larkin, *Trans. Faraday Soc.*, **69**, 1011 (1973).

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