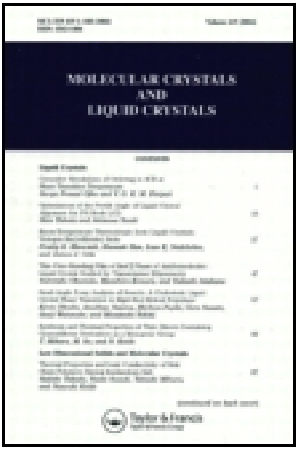

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Dielectric Relaxation in the Metastable Modification of the Solid Phase of *p*-Methoxybenzylidene-*p*′-*n*-Butylaniline (MBBA)

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The paper presents an analysis of the results of studies of dielectric relaxation in the metastable modification of solid MBBA. The experimental values of permittivity $\varepsilon'(\omega)$ and losses $\varepsilon''(\omega)$ can be described by a skewed Davidson–Cole arc. To get an understanding of the relaxation process, the model of "defect" diffusion of Glarum is considered and the Fröhlich–Kirkwood factors of interdipolar correlation are calculated. This constitutes a basis for proposing a model which assumes correlation between the rotation of the dipolar methoxy group about the O—C bond of the molecule and the conformational motions of the butyl group causing local fluctuations ("defects") in the crystal lattice.

1 INTRODUCTION

The existence of two monotropic modifications of the solid phase of *p*-methoxybenzylidene-*p*′-*n*-butylaniline (MBBA), viz., a metastable and a stable one, was first revealed in calorimetric measurements.[1] It was found that every time a sample of MBBA is frozen the metastable modification becomes formed. The stable form is obtained by maintaining the sample at a temperature of about 100 K below the freezing point for several hours and then heating it to about 20 K below the melting point; the outcome of this heat treatment is an irreversible transition of the metastable form into the

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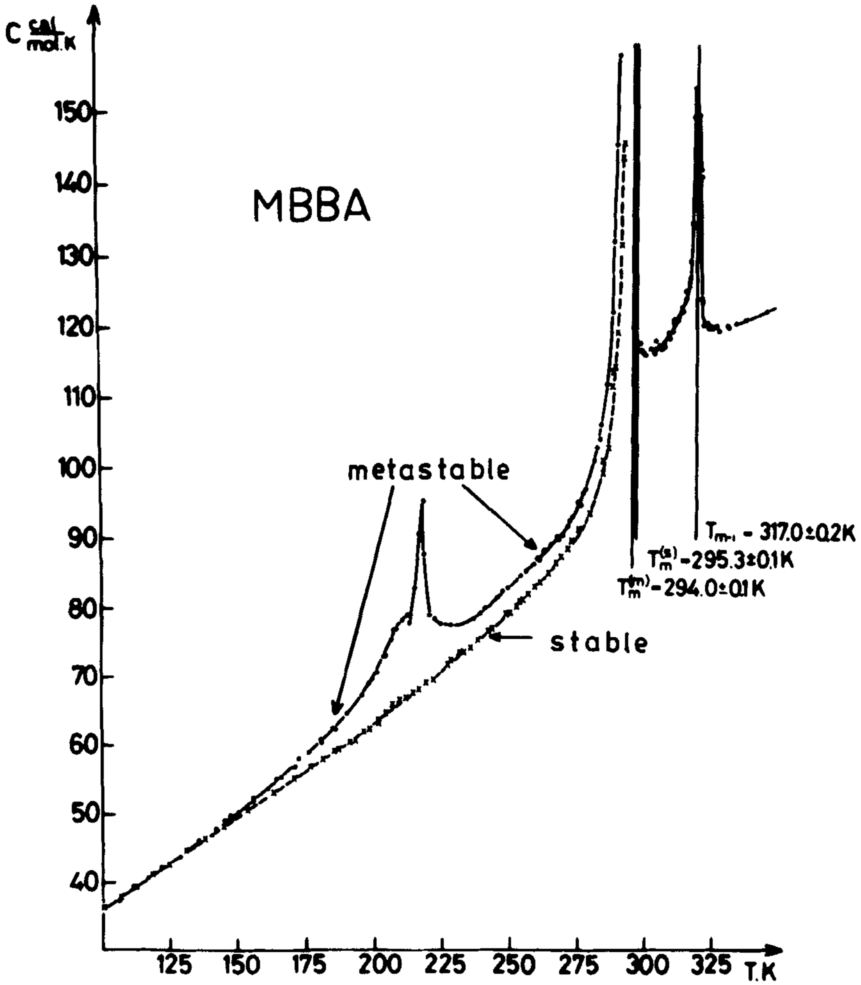

FIGURE 1 Specific heat vs temperature.

stable one within several hours. Only melting the sample and re-freezing it can restore metastable modification.

The specific heat vs. temperature curve for the metastable modification (see Figure 1) features a complex anomaly with a broad maximum in the vicinity of 212 K and a narrow one near 217 K. No specific heat anomaly has been detected for the stable modification. The two modifications have different melting points—the metastable one melts at 294.0 K, whereas the stable one at 295.3 K.

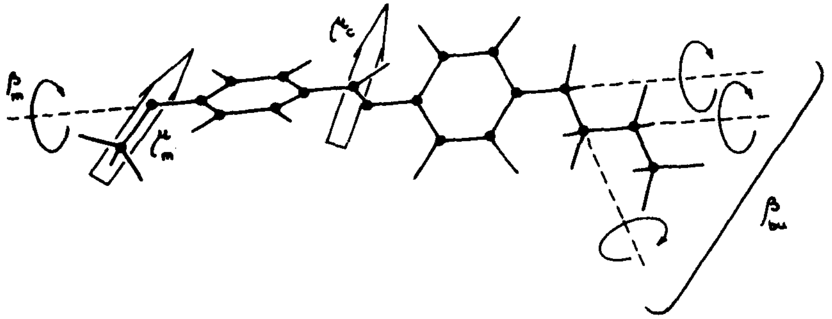

FIGURE 2 The scheme of MBBA molecule: the dipole moments of central group (μ_c) and methoxy group (μ_m), as well as a possible conformational reorientations of end chains are marked.

Experimental studies[2–4] of the solid phase of MBBA were devoted above all to the relationship between the kinetics of the "metastable-to-stable modification" transition and the heat treatment of the sample. The nature of the differences between the physical properties of the two modifications has not yet to be understood.

Results of calorimetric experiments on MBBA[1] were used by Andrews[5] as a basis for certain model considerations concerning the differences in the molecular dynamics of the substance's two solid phase modifications. The assumptions of Andrews' model exclude conformational motions of the MBBA molecule in the stable modification. In the metastable form, on the other hand, they allow the existence of conformational jumps of the end groups of the molecule at temperatures exceeding the 212–217 K transitions; the broad maximum at 212 K is thought to correspond to a "melting-freezing" of β_{bu} motions of the butyl chain, whereas the narrow peak at 217 K to the "melting-freezing" of β_{m} motions of the methoxy group (Figure 2).

In our group we have carried out measurements of the complex dielectric permittivity $\varepsilon^* = \varepsilon' - j\varepsilon''$ of MBBA's solid phase in both the kilohertz[6,7] and gigahertz[7] range of frequencies. They revealed the existence of a dielectric relaxation process only in the metastable modification, with relaxation times of order of 10^{-5}–10^{-6} sec.[6,7]† The preliminary analysis of the results presented in Refs. (6 and 7) suggested a possible explanation of the observed relaxation effect on the basis of Andrews' model. In this paper we shall consider this problem in detail.

As is seen in Figure 2, the MBBA molecule possesses two permanent dipole moments, viz., one associated with the central group ($\mu_c = 1.6$ D)

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† The results of these investigations have been confirmed by Agarval *et al.*[8]

and the other with the methoxy group ($\mu_m = 1.3$ D). It is rather improbable that such large and unsymmetrical molecules as MBBA may perform, as a whole, reorientation motions in the solid phase. This is indicated, for example, by the X-ray diffraction measurements made for both modifications of solid MBBA.[2] The acquired diffraction spectra feature sharp, well shaped Bragg reflections, whereas for rotational phases (in plastic crystals) the X-ray spectra demonstrate strong diffuse scattering.[9] Hence, in what follows we shall assume that the observed dielectric relaxation process in the metastable modification of solid MBBA is associated with the reorientation motions of the end groups in the molecule, in particular, those of the methoxy group.

2 DISCUSSION OF RESULTS

a Analysis of the relaxation process

Figure 3 shows the results of ε^* measurements for the metastable modification of solid MBBA at several temperatures depicted in the complex ε'' vs. ε' plane in the form of Argand diagrams. For each temperature the experimental points can be described by skewed arcs in accordance with analytical Davidson-Cole formula:

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = (1 + j\omega\tau_r)^{-\beta}, \tag{1}$$

where ε_0 and ε_∞ are the low- and high-frequency limits of the dielectric constant, ω is the circular frequency of the measuring field, τ_r is the effective dielectric relaxation time and β is a phenomenological parameter.

The skewed shape of the ε'' vs. ε' plots is evidence of the complex nature of the examined relaxation process. Relaxation spectra of this kind have been observed in a number of organic compounds,[10–13] and the molecular interpretation of results has been based on various model assumptions. In the present study we shall deal with a simple, one-dimensional model of "defect" diffusion worked out by Glarum.[14] In this model a one-dimensional system of identical polar molecules is considered. Each dipole is supposed to reorient itself in some manner leading to a single relaxation time. Let us further assume, however, that a number of "defects" are presented as points in our one-dimensional system, and that the motion of this points can be described by diffusion equation. The instant a "defect" reaches a dipole, the latter undergoes immediate and total relaxation. Then the molecular

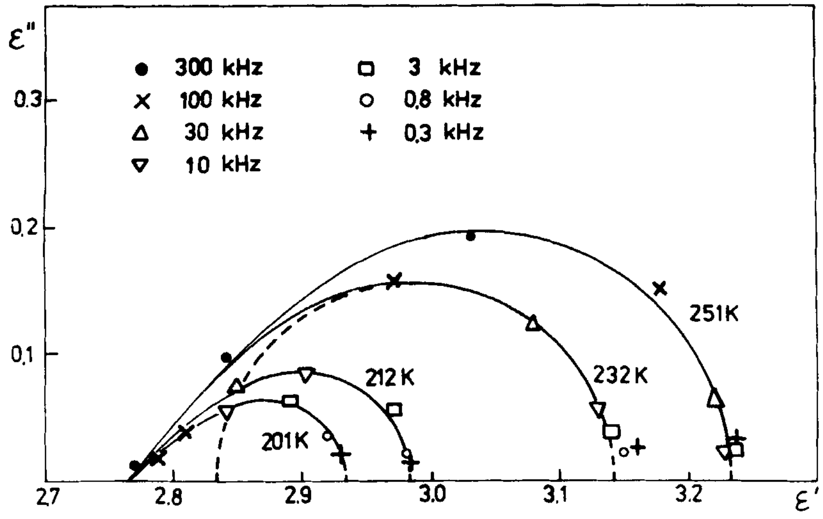

FIGURE 3 The Davidson–Cole diagrams for four different temperatures of the metastable modification of solid MBBA.

relaxation function is given by the expression:

$$\varphi(t) = \exp\left(-\frac{t}{\tau_r}\right)\cdot[1 - p(t)], \tag{2}$$

where $p(t)$ is the probability that a "defect" achieves a dipole within time t. The first term of this function describes the relaxation of the system without any "defects," whereas the other relaxation of the system due to "defect" diffusion.

If the mean distance of the "defect" from a dipole is L_0 and the "defect" diffusion coefficient is D, then after Hunt and Powles[15] the function (2) takes the form:

$$\begin{aligned}\varphi(t) &= \exp\left(-\frac{t}{\tau_r}\right)\cdot\exp\left(\frac{t}{\tau_d}\right)\cdot\left\{1 - \operatorname{erf}\left(\frac{t}{\tau_d}\right)^{1/2}\right\},\\ \operatorname{erf}(x) &= (2\pi)^{-1}\int_0^x \exp(-y^2)\mathrm{d}y,\end{aligned} \tag{3}$$

where $\tau_d = L_0^2/D$ is the time constant of the diffusion of "defects." It should be stressed that the model does not make any assumptions regarding the nature of this "defects."

The correlation function $\varphi(t)$ thus defined leads to Glarum's equation for the complex permittivity,

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + j\omega\tau_r}\left\{1 + \frac{j\omega\tau_r}{1 + (\tau_d/\tau_r)(1 + j\omega\tau_r)^{1/2}}\right\} \tag{4}$$

The shape of the Argand plots corresponding to Eq. (4) depends on the relationship between τ_d and τ_r.[14,15] When $\tau_d \gg \tau_r$ a Debye semicircle is obtained, when $\tau_d \approx \tau_r$ a skewed Davidson–Cole arc with a parameter $\beta = 0.5$, and when $\tau_d \ll \tau_r$ a symmetrical Cole–Cole arc[20] with a parameter $\alpha = 0.5$. Skewed arcs corresponding very closely to the Davidson–Cole formula (1) are obtained when $\tau_d \geq \tau_r$. Then, the relation:

$$\beta = \frac{1}{1 + (\tau_r/\tau_d)^{1/2}} \tag{5}$$

is approximated well. It should be noted that extending this model to the three-dimensional case does not affect the shape of the Argand plots, but complicates the analysis of results considerably.[15]

Equations (1) and (4) have been fitted to the experimental data by the conventional least squares method.[16] The found values of parameters τ_r, β and τ_r/τ_d are presented in Figure 4b, c, d. As seen from the comparison in Figure 4, all of the considered parameters of Eqs. (1) and (4) undergo a jump in the vicinity of the complex specific heat anomaly in the metastable modification (Figure 4a). Whence it follows that in this transition there occurs a rather pronounced change of the conditions in which the observed reorientation of the dipole moment takes place. There is, above all, a marked change in the value of the activation barrier, from 6.2 ± 0.5 kcal/mole above the transition to 9.0 ± 0.5 kcal/mole below it. The parameter β (obtained from Eq. (1)) at low temperatures is, within an experimental error, equal to its extreme value of 0.5. In accordance with Eq. (5) this is equivalent in this temperature range to the acceptance of values similar to τ_r by the time constant of the "defect" diffusion. At the 212–217 K transition there is a slight jump of τ_r, while τ_d lengthens out by an order of magnitude.

In the light of these facts, the following molecular interpretation of the results of calorimetric and dielectric experiments of MBBA's metastable modification comes to the fore. At a temperature of about 150 K (where the curves of the specific heat of the stable and metastable modifications become separated, see Figure 1) the methoxy groups start to perform reorientation motions about the O—C bond of the molecule (Figure 2). Such rotation is possible thanks to conformational motions of the butyl chains of neighbouring molecules, thereby causing fluctuations ("defects") in the vicinity of the dipole moment μ_m. The existence of such conformational motions of

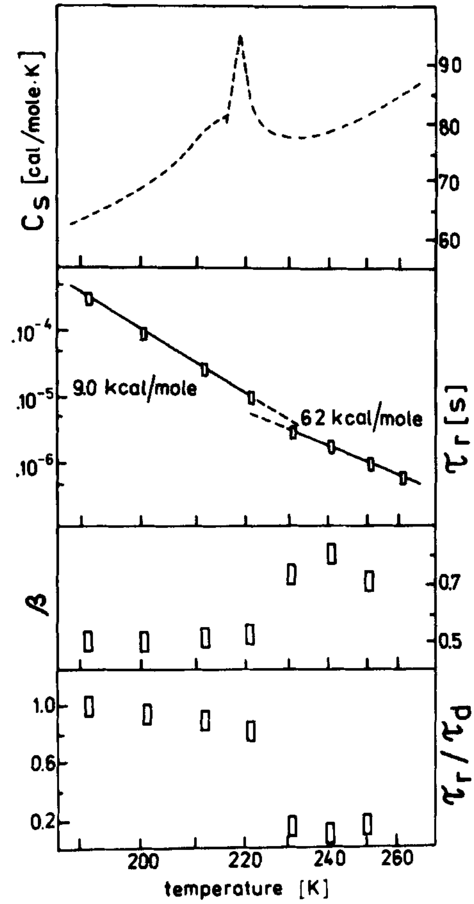

FIGURE 4 Comparison of calorimetric and dielectric results for metastable modification: (a)—specific heat, (b)—relaxation time τ_r, (c)—Davidson-Cole parameter obtained with Eq. (1) and (d)- τ_r/τ_d ratio obtained from Glarum model Eq. (4), vs temperature.

butyl groups are detected by IR-spectroscopy[4] and NMR.[22] The equality of the time constants τ_r and τ_d below the transition is evidence of the mutual linkup of both kinds of conformational motions of the end groups in the neighbouring molecules. It seems that the complex nature of the specific heat anomalies is associated with the gradual release of conformational movements of the butyl chains (the broad component of the peak in the specific heat curve of Figure 1 and Figure 4a) and then, beginning at a certain stage of this process, the rotation of the methoxy groups becomes liberates considerably, as revealed by the shortening of time τ_r and lowering of the activation barrier. Just above the transition the time constant of "defect" diffusion

τ_d is much longer than τ_r, for the conformational motions of the long butyl chains are slower than the reorientation of the smaller methoxy groups.

b Dipole correlations

More light on the character of the observed rotational motion of the methoxy groups in the metastable modification of solid MBBA may be cast by an analysis of the temperature dependence of the dielectric increment $\varepsilon_0 - \varepsilon_\infty$. To do this, let us consider the Fröhlich–Kirkwood equation[17] which may be written in the form:

$$g = \frac{Mk_BT}{4\pi N_A \rho \mu_m^2} (\varepsilon_0 - \varepsilon_\infty) \cdot \left(2 + \frac{\varepsilon_\infty}{\varepsilon_0}\right), \tag{6}$$

where M is molecular mass, k_B is the Boltzmann constant, N_A is Avogadro's number, ρ is the density of the substance, and μ_m is the dipole moment of rotating methoxy group. The parameter g is the so-called dipole correlation factor which may be defined as:

$$g = 1 + \sum_{k=2}^{N} \langle \cos \theta_{1k} \rangle, \tag{7}$$

where summation extends over the nearest neighbours of the arbitrarily chosen dipole, while θ_{1k} is the angle between the chosen and kth dipole moment. When there is no correlation between neighboring dipoles, $\sum \langle \cos \theta_{1k} \rangle = 0$ and $g = 1$. When there are antiparallel correlations $g < 1$, whereas when they are parallel we have $g > 1$.

The factor g was calculated by taking the values of ε_0 and ε_∞ from the parameters of the fit of experimental points to Eq. (1), whereas the density ρ was found by extrapolating the results of $\rho(T)$ measurements for the nematic phase;[18] this was thought to be justified because the observed changes in density of nematogens in the nematic—solid phase transition are small.[19] The results of calculations are shown in Figure 5.

As is seen in this figure the g-factor also changes jumpwise in the 212–217 K transition, its temperature dependence being weaker below than above the transition. It is also important that the g values are smaller than unity in the entire temperature range of the metastable modification. For this is proof of antiparallel interdipole correlations. The question arises, however, of how such correlations are realized. It seems rather doubtful that there is a direct correlation between methoxy groups in neighbouring molecules. Therefore, let us consider the possibility of the existence of intermediate correlations.

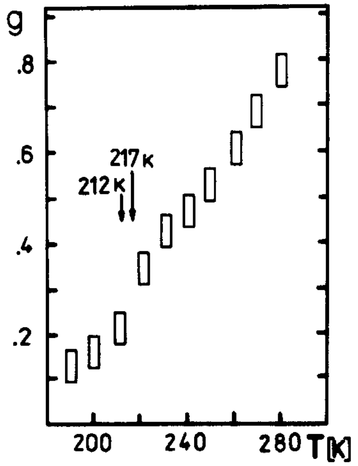

FIGURE 5 Temperature dependence of dipole correlation factor for metastable modification of solid MBBA.

If the unit cell of a crystal contains an even number of molecules the most probable arrangement of neighbouring molecules is the antiparallel (or almost antiparallel) one. It should be expected, then, that the methoxy group of one molecule is close as possible to the butyl chain of another molecule. Thence, the methoxy groups would probably be repulsed by butyl chains (Figure 6), that is, in a pair of molecules there would be a certain compensation of dipole moments. Under such conditions the role of conformational motions of butyl groups becomes clear, namely, they are the producers of "defects" which make reorientation of the methoxy groups possible.

Unfortunately, for both modifications of solid MBBA the crystal structures are unknown. So, we must make some speculations concerning the differences in a molecular situation in particular modifications.

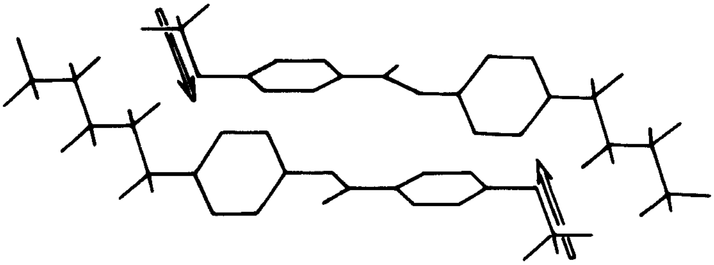

FIGURE 6 Proposed arrangement of two neighbouring molecules in metastable modification of solid MBBA.

It is known from IR-spectroscopy[4] and NMR investigations[22] that in the metastable modification the conformational movements of butyl chains of molecules exist, which disappear when a crystal transforms to the stable form. It proves that in stable modification the molecules are much more close-packed than in metastable one. From thermodynamic and steric considerations it seems that such a situation is adequate to the *trans-trans* (zig-zag) conformation of butyl chains in this modification.

From ultrasonic[21] and NMR[23] investigations it is known that in the liquid-crystalline phases of MBBA and other substances having similar end groups in molecules, the butyl chains perform the conformational movements. As the metastable modification of solid MBBA is formed every time a nematic phase is frozen, we may infer that in this modification the molecules have a mixture of different conformations of butyl chains. Therefore, the packing of molecules in crystal lattice of this form is not so close as in the stable form and the end groups of molecules have sufficient free space to perform the conformational movements. As the unit cell's volume increases with raising temperature, the probability of the conformational movements of butyl chains also increase making the methoxy group reorientations easier. One can obviously assume that there will occur a step increase of the crystal volume at the 212–217 K transition, which should lead to higher mobility of butyl chains and, in consequence, of methoxy groups too. This could be the possible explanation of the experimentally observed lowering of the activation barrier and a decay of the interdipolar correlations revealed by a marked change of the g-factor at this transition and its fast increase with increasing temperature (Figure 5).

3 CONCLUSIONS

In the light of the presented facts and considerations it may be ascertained that Andrews' model does not give a full explanation of the nature of the specific heat anomaly in the vicinity of 212–217 K in the metastable modifications of solid MBBA. It can be undoubtedly said that at this transition the conformational freedom of the molecules' end groups increases distinctly, but it is also a fact that at lower temperatures such motions exist too. Hence, it cannot be stated that the anomaly is associated with a "melting-freezing" process of the end groups of molecules.

The proposed model of the arrangement of the molecules in the crystal lattice of the metastable modification well explains the temperature dependence of all parameters describing the dielectric relaxation process observed in this modification. In addition, if the above mentioned differences in the molecular situation in both modifications are real one can explain also the fact that the process of spontaneous transition from metastable-to-stable modification occurs especially easily at temperatures above the 212–217 K anomaly.[1,2,4] Namely, in high temperatures only in crystal lattice of metastable modification there is a sufficient large free space due to the butyi chains of molecules could "straighten" to *trans-trans* conformation and, then, fall in a cage of a new solid phase.

In order to verify those conclusions, the knowledge of the detailed crystal structures of both solid modifications of MBBA is needed which, however, is rather a difficult experimental problem.

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