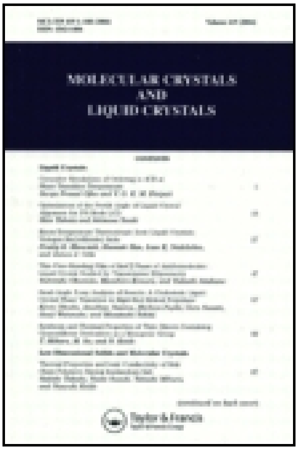

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Dielectric Low-Frequency Relaxation in a Swallow-Tailed Liquid Crystal

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Version of record first published: 04 Oct 2006.

To cite this article: M. Massalska-arodź , H. Stettin & H. Kresse (1989): Dielectric Low-Frequency Relaxation in a Swallow-Tailed Liquid Crystal, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 177:1, 155-161

To link to this article: http://dx.doi.org/10.1080/00268948908047779

Mol. Cryst. Liq. Cryst., 1989, Vol. 177, pp. 155–161
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Printed in the United States of America

Dielectric Low-Frequency Relaxation in a Swallow-Tailed Liquid Crystal

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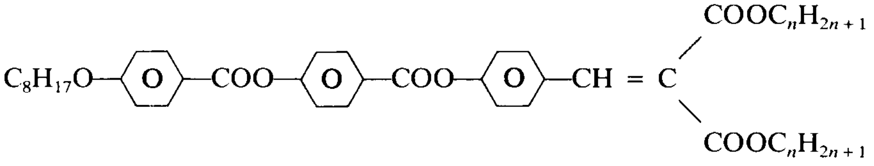
(*Received March 15, 1989; in final form June 22, 1989*)

The relaxation of the parallel permittivity component has been observed in the liquid crystalline substance of swallow-tailed molecules with extra CN-side group. The data has been examined with help of the many-body cooperative model and the results compared with some earlier ones.

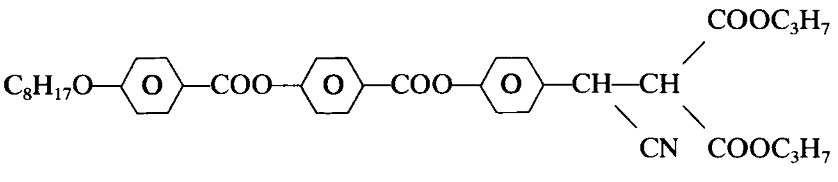
Keywords: substituted benzylidene malanotes, liquid crystals, dielectric relaxation, molecular motion

INTRODUCTION

The swallow-tailed compounds[1,2] are an interesting form of liquid crystalline substances with non-rod-like molecules. The dielectric relaxation investigations of two substituted benzylidene malonates



with $n = 5$ (No 1) and $n = 10$ (No 2) have shown an unexpectedly high value of the dipole–dipole correlations in the nematic and smectic A phase.[2] In spite of that the Cole–Cole presentation of the data turned out to give the Debye form that is observed for the compounds of elongated molecules. Hence comes the study of the dynamical properties of the third swallow-tailed compound with molecules modified by an CN-side group (No 3)



with the following phases

$$\mathrm{Cr}\ 333\ \mathrm{K}\ \mathrm{S_A}\ 373\ \mathrm{K}\ \mathrm{N}\ 404\ \mathrm{K}\ \mathrm{Is}.$$

In the paper the experimental dielectric data of these three examples are examined in terms of the many-body cooperative model using Dissado-Hill correlation parameters,[3,4]

EXPERIMENTAL

The dielectric permittivity measurements have been performed on the sample oriented by a magnetic field of about 0.7 T on the cooling runs in the temperature range from 378 K to 335 K. The static dielectric constant has been measured at 1 kHz for both directions of the field applied. The study of the parallel permittivity dispersion and absorption has been carried out in the frequency range from 0.1 kHz to 100 kHz. For the investigations the modified Sawyer-Tower bridge has been used with the capacitor characterized by the 2 cm^2 area and by the 0.2 mm distance between the electrodes.

RESULTS AND DISCUSSION

Figure 1 presents the parallel, the perpendicular and the average static dielectric constant vs temperature of compound No 3. In Figure 2 dispersion and absorption curves are observed for parallel dielectric permittivity component in the kHz-frequency range. In the smectic phase both the static dielectric constant as well as the dielectric absorption intensity go down with decreasing temperature indicating the decrease of the effective dipole moment coupled with the electric field.

The relaxation observed is connected with the reorientation of the molecules around the short axis, as is the case for liquid crystals with typically elongated molecules. To analyze the experimental data the following form for the complex electric susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ has been proposed

$$\chi(\omega) = \chi'(O)\ (1+i\omega/\omega_{\max})^{1-n}\,{}_2F_1(1-n,1-m;2-n;(1+i\omega/\omega_{\max})^{-1}) \qquad (1)$$

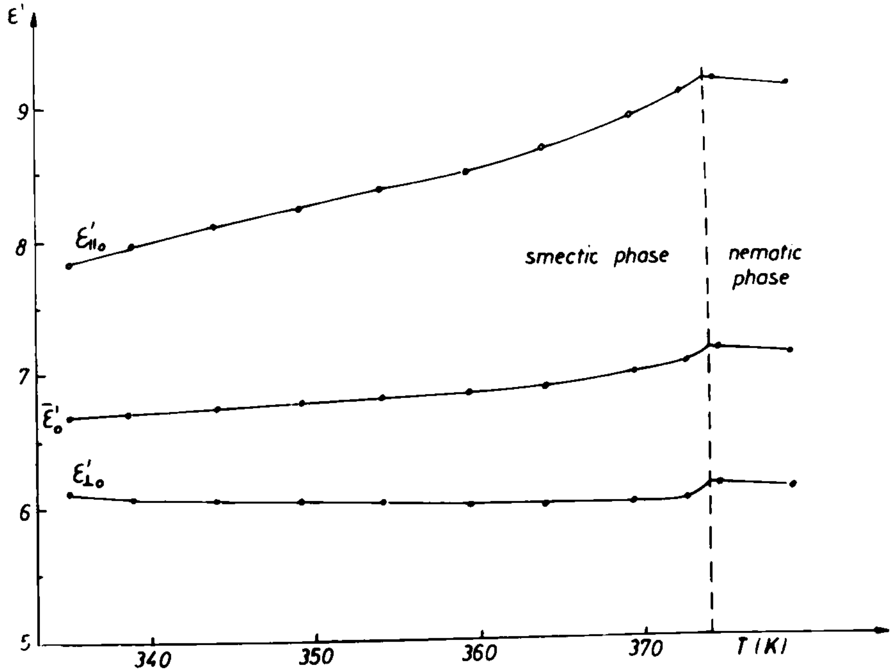


FIGURE 1 The parallel, perpendicular and average static dielectric constants vs temperature, measured at 1 kHz for compound No 3. Due to increasing conductivity the measurement has been stopped at 378 K.

where ${}_2F_1$ is the hyper-geometric Gauss function and $\omega_{\max} = 2\pi\nu_{\max}$ is the characteristic relaxation rate.[3,4] The low-frequency and high-frequency limits of this expression have the following form

$$\chi''(\omega) \sim \chi'(\omega) \sim (\omega/\omega_{\max})^{n-1} \quad \text{for } \omega > \omega_{\max} \tag{2a}$$

$$\chi''(\omega) \sim (\chi'(O) - \chi'(\omega)) \sim (\omega/\omega_{\max})^{m} \quad \text{for } \omega < \omega_{\max} \tag{2b}$$

observed for various not perfectly ordered materials[3,4,6] with n and m in the range (0,1). The pair of the Dissado-Hill correlation parameters n and m theoretically introduced in Equation 1, describe the deviation of the observed relaxation process from the Debye form recovered by the pair $n = 0$ and $m = 1$. In the relaxation phenomenon regarded not as a single-particle process but as a cooperative one this deformation of the Debye picture can be caused by the existence of short and long range correlations of the motion i.e. of some structural regularities on a local and long-range levels. The n and m parameters, respectively, are the measure of structural order in the sample on these two levels.

In Figure 3 dielectric relaxation data for the compound investigated are presented in a double logarithmic scale[6] in the compact form: The response curves of each temperature from the range between 335 K and 378 K have been shifted along

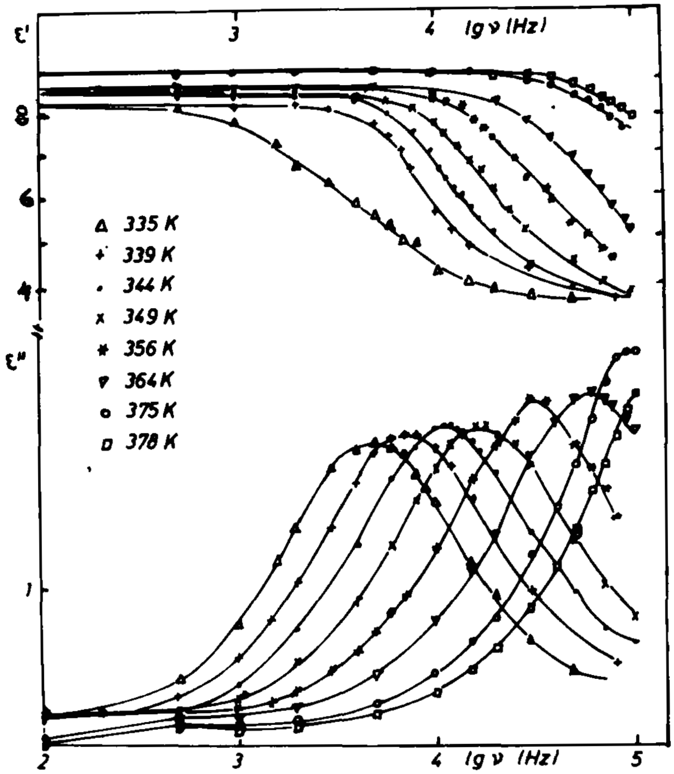


FIGURE 2 The absorption and the dispersion of the parallel permittivity component.

both coordinates to have the single master absorption and the single master dispersion curve. Such a scaling procedure is possible owing to the form of the frequency dependence of susceptibility (and permittivity) given by Equation 2. The scaling has been done with respect to the $\nu_{\max}$ in the chosen temperature of 344 K. The experimental points for this temperature are the only ones in the absolute scale in the figure. The points in the circles are the normalisation shift points.[3,4,6] The shift point characteristic for each temperature is common for scaling both the dispersion and the absorption curves which makes the procedure more precise and more convincing. The trace of these points can describe the temperature dependence of both the static permittivity and the relaxation rate. The *n* and *m* parameters determined from the slope of the linear wings of the master absorption curve are collected in Table I. There are also results for two swallow-tailed compounds investigated earlier[2] and for 4-*n*-heptyloxyphenyl 4'-*n*-octyloxybenzoate with elongated molecules[5,6] determined in the same manner. The value of the *n* parameter is close to the Debye limit only in the case of the reorientations of the rod-like molecules around the short axes, which corresponds to their weak correlations of the local range. The local order of the molecules in the smectic A phase of the swallow-tailed compounds is higher especially for the compound under study. Ac-

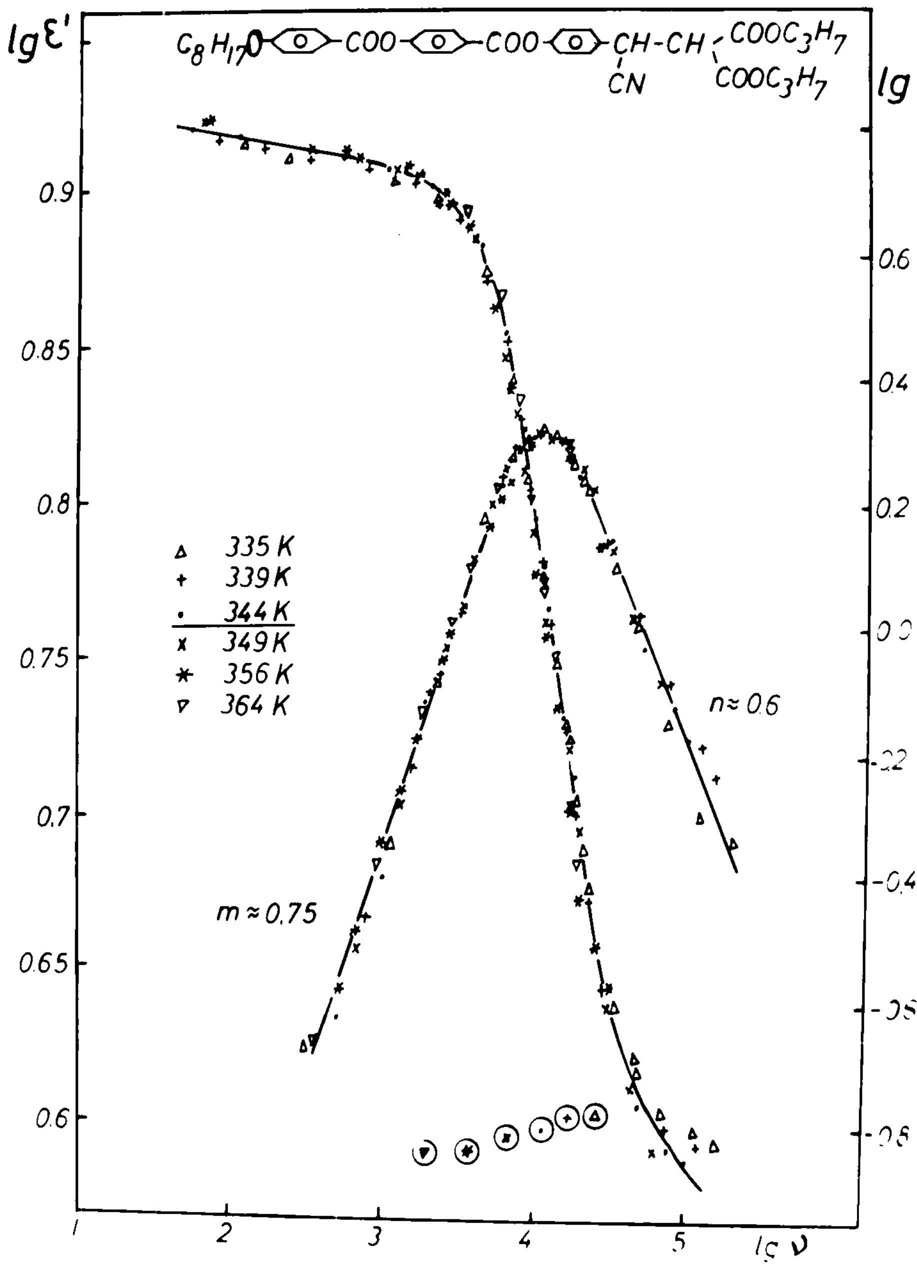


FIGURE 3 The absorption and the dispersion master curves in double logarithmic scale. They have been obtained by the appropriate shift of the response curves logϵ' (logν) and logϵ'' (logν) for each temperature along both coordinate axes. The magnitude of each translation is given by the vector connecting the "datum point"-the dot in the circle-and the encircled point for the respective temperature. The "datum point" has been chosen arbitrarily at ν_{max} = 10 kHz for 344 K where the data are in the absolute scale.

TABLE I

The activation energy, Dissado-Hill correlation parameters and relaxation rates for liquid crystalline molecules

No	Substance	Activation energy [kJ/mol]	Correlation parameters $m \pm 0.1$	Correlation parameters $n \pm 0.1$	Relaxation rate at 350 K [MHz]
1	swallow-tailed	91.7	0.92	0.17	0.22
2	swallow-tailed	90.3	0.92	0.24	0.37
3	swallow-tailed with CN-group	87.5	0.75	0.6	0.12
4	C_8O/OC_7*	110	0.96	0.13	5.0

*4-*n*-octyloxyphenyl 4-*n*′-heptyloxybenzoate

cording to the experimental results (Figure 1, Figure 2 and Reference 2) the enlargement of the *n* value could occur due to the antiparallel pairing, which is favoured for the molecules of such a shape. It seems that due to the more complicated tail with additional strongly dipolar CN-side group in the investigated compound the motion of each molecule needs relatively larger cooperative reorganisation of the neighbours. The geometrical factor plays an important role in the dynamics of the molecules in that type of compounds.[2] The associated long-range order turns out to be similar for all swallow-tailed compounds and is only slightly higher than that for the compound of the rod-like molecules.[6]

For the compound examined the data from the whole temperature range were useful in the determination of the *m* value (Figure 2). In the nematic and in the smectic phase the *m* values i.e. the long range correlations are the same, within the limit of accuracy of the experimental data. It is in agreement with some observations for liquid crystals of rod-like molecules.[5,6,7]

The relaxation rates ω_{max} for the swallow-tailed compounds are relatively low. The highest value was observed for compound No 2 although it consists of the longest molecules.

In all the cases presented in Table I the activation energy is of the Arrhenius type and has a similar magnitude regardless of the molecule's structure. So the correlation parameters seem to be more sensitive to the physical nature of the molecular dynamics than the energy parameter in the form used.

CONCLUSIONS

In the smectic A phase the antiparallel packing of the swallow-tailed molecules with the CN-side groups has been found. The observed kHz-relaxation of parallel permittivity component has turned out to show the power law behaviour. The magnitude of the local order has occurred to be much higher than that for the compounds with elongated molecules and also higher than that for typical swallow-tailed compounds.

Acknowledgments

The authors express their thanks to professor Jerzy A. Janik for his stimulating interest and valuable discussions.

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