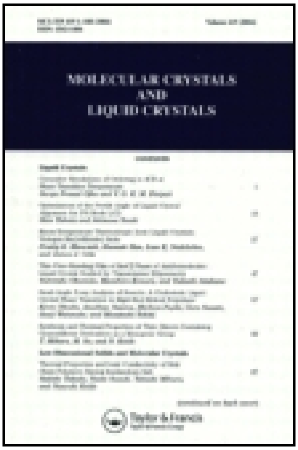


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Comparison of Dielectric Relaxation for a Mesogen and a Non-Mesogen

Victor Naumenko [a] & Vladimir Bezborodov [a]
[a] Institute of Applied Physics Problems, 220064, Minsk, U.S.S.R.

Version of record first published: 22 Sep 2006.

To cite this article: Victor Naumenko & Vladimir Bezborodov (1990): Comparison of Dielectric Relaxation for a Mesogen and a Non-Mesogen, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 192:1, 113-117

To link to this article: http://dx.doi.org/10.1080/00268949008035616

Mol. Cryst. Liq. Cryst. 1990, Vol. 192, pp. 113–117
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

COMPARISON OF DIELECTRIC RELAXATION FOR A MESOGEN AND A NON-MESOGEN

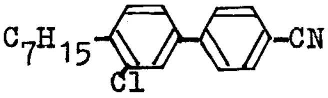
VICTOR NAUMENKO AND VLADIMIR BEZBORODOV
Institute of Applied Physics Problems, 220064
Minsk, U.S.S.R.

Abstract The influence of chemical modification destroying liquid-crystalline properties on dipole relaxation of a polar nematogen is investigated.

It is well-known (see e.g. Sonin[1], Abdulin et al.[2]) that an introduction of lateral substituents into a rigid core of a rod-like mesogenic molecule leads, as a rule, to a decrease of the temperature of transition to isotropic liquid and to narrowing of the temperature interval for mesomorphic state up to a complete ceasing of the mesophase. Today concepts treat above as follows: in the molecular system considered, there is no characteristic orientational correlation in the mutual arrangement of the molecules at any temperature in contrast to relative translational freedom. The reason for such changes in the molecular behaviour is whether some weakening of the lateral intermolecular interactions due to an increase in the 'thickness' of the molecules or, as opposite case, forming of new lateral quasi-bonds between the molecules due to interactions, for example, among the polar lateral substituents introduced. So there is no anisotropy of physical properties, there are no other features characteristic only forliquid crystals.

On the other hand, it is known (see, e.g., Chandrasekhar[3]) that some physical properties (for example, magnetic birefringence) for the isotropic phase of liquid crystals differ radically (by 100 times) from those for normal organic liquids. This is caused by the fact that a certain degree of the liquid crystalline short-range order can exist. The reasonable question arises: whether the substances being non-mesomorphic due to little modification of their chemical structure have such anomalous properties, having in mind, moreover, that some of these substances do have a mesophase at elevated pressure[3].

As a basic mesogen, we have taken 4'-n-heptyl-4-cyanobiphenyl (7CB) the properties of which are well known[4,5] (nematic phase in the temperature range 19 to 43°C). The chemical modification was in the introduction of chlorine atom into one benzene ring which leads to the structure:



The non-mesogen obtained has a melting point 34.5 °C. A higher melting point as compared to the mesogenic analog but lower than the clearing point of the latter is a familiar result of chemical modifications with ceasing of the mesogenic properties[2].

Dipole relaxation was taken as a physical phenomenon the characterictics of which we had been going to search and apply for describing a degree of the closeness of the two structures. Such a choice is justified by following experimental items: 1) the mesogenic prototype chosen has dipole relaxation frequency for the isotropic phase only 7 times higher[4] than that for the nematic phase (low-frequency part) rather than several orders as in the classical liquid crystals; this is an evidence of a considerable correlation in the arrangement of the close neighbours (short-range effects) in the isotropic phase; 2) just in such systems, some physical properties (e.g., the magnetic birefringence) of the isotropic phase differ markedly from those of normal organic liquids.

Below are the plots of the relaxational peak frequencies and the corresponding dielectric loss peaks as functions of reciprocal temperature for 7CB (on data from the work of Davies et al.[4]) and for our chloroderivative modified.

As expected, the relaxation times for the derivative chlorosubstituted have been somewhat longer (~ 4 times) than for the isotropic phase of 7CB. Evidently, this is related to an additional hindering which is rendered by the phenyl-chlorine dipole interactions to the molecule rotations. Also, to the above reasons, probably, related is the steeper slope of the $\log f_m(T^{-1})$ plot due to a higher activation enthalpy for the molecule rotations in this compound (~ 60 $kJ.mole^{-1}$ against 26 $kJ.mole^{-1}$ for 7CB).

The dielectric permittivity from the low-frequency side of the relaxational region (not shown) and the dielectric loss peaks are in average by 10 to 15 % less for chlorosubstituted derivative.

It is a temperature behaviour of the above quantities near the isotropic phase formation temperature which justifies certainly the similarity of the local arrangement in the substances considered: at first,

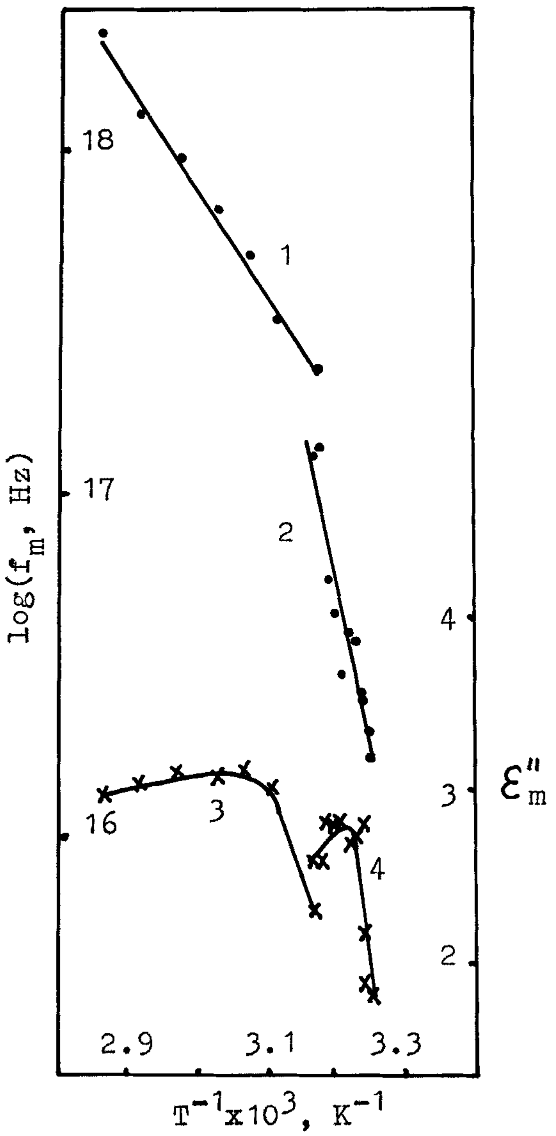


FIGURE 1 Dependence of relaxation peak on reciprocal temperature: 1 - for 7CB (on data of Davies et al.[4]); 2 - for its chlorosubstituted.

Dependence of dielectric loss peak on reciprocal temperature: 3 - for 7CB (on data of Davies et al.[4]); 4 - for its chlorosubstituted.

they increase with the temperature increase and only then the quantities begin to decrease in an ordinary way for such cases. The initial increase can evidently be related to destruction of the local antiferroelectric order in the liquid structure followed by an increase of effective dipole moment and the related quantities observed.

It can be assumed that the introduction of lateral chlorine has not prevent from the antiferroelectric packing in the liquid.

Molecular polarizability calculated from the refractive indices measured for the chlorosubstituted derivative was 3.7 $C.m^2.V^{-1}$ as compared to 4.1 $C.m^2.V^{-1}$ for 7CB[4]; the introduction of chlorine had to lower the polarizability, as we see this here.

As a result, the similarity supposed for the local structures of the two compounds must, in our opinion, lead to the chlorosubstituted derivative to possess a nematic phase at an elevated pressure.

REFERENCES

1. A.S.Sonin, Vvedeniye v Fiziku Zhidkikh Kristallov (Nauka, Moscow, 1983), Chapter X, § 1,
2. A.Z.Abdulin, V.S.Bezborodov, A.A.Minko, and V.S. Rachkevich, Teksturoobrazovaniye i strukturnaya uporiadochennost v zhidkikh kristallakh (Universitetskoye, Minsk, 1987), Chapter 1.
3. S.Chandrasekhar, Liquid Crystals (Cambridge University Press, Cambridge-London-New York-Melbourne, 1977), Chapter 2.
4. M.Davies, R.Moutran, A.H.Price, M.S.Beevers, and G.Williams, J.Chem.Soc.: Faraday Trans.II, 72, 1447 (1976).
5. A.J.Leadbetter, R.M.Richardson, and C.N.Colling, J.de Physique, 36, C 1-37 (1975).