

Conformational change induced in mesomolecules by smectic A—nematic—isotropic liquid phase transitions

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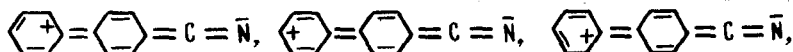
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A method of polarization infrared spectroscopy is proposed for studying the conformation of mesomolecules at phase transitions in liquid crystals. Experiments reveal that a change in the conformation of the aromatic skeleton of the molecules is induced by phase transitions in two cyanobiphenyl liquid crystals and that the conformation depends on the orientational and translational order.

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1. The conformational changes in mesomolecules induced by phase transitions in liquid crystals are currently the subject of intense experimental^{1–3} and theoretical⁴ study. The conformational changes in the aromatic molecular skeleton have received very little study, in contrast with the aliphatic end chains. The only results which have been obtained on the skeleton to date are the fragmentary results found by various NMR techniques.^{5,6} Experiments of this type are very complicated, because it is necessary to selectively introduce deuterium and ¹³C and ¹⁵N isotopes into the molecules; as a result of the difficulties, greatly different results have been reported for the same entities,^{5,6} and conflicting interpretations have been offered.^{1,7} There is accordingly a need for new methods of study, based on different physical principles. In this letter we wish to propose a method of polarization infrared spectroscopy of the absorption induced by a mesomeric effect.

2. A classical example of an effect of mesomolecular interactions on the conformation of a molecule is biphenyl, for which the dihedral angle ϕ between the benzene rings has the values 42° , 30° , and 0° in the gas phase, in an isotropic solution, and in a crystal, respectively.⁸ On the other hand, biphenyl and polyphenyl fragments are parts of many mesomolecules, e.g., the cyanobiphenyls, which will be discussed below. The new method can be outlined as follows: In the biphenyl molecule, the characteristic valence vibration of the C–C bond between the benzene rings (the α bond) is not active in infrared absorption by virtue of the selection rules. In cyanobiphenyl, the conjugation of the strong $C\equiv N$ electron-acceptor group with the biphenyl skeleton leads to resonant valence structures of the type



and to a polarization of the π -electron system of the molecule in the ground state (a mesomeric effect). The dipole moment of the π system, μ (r) (the mesomeric mo-

ment), increases linearly with the length r of the conjugate chain in substituted benzene and biphenyl,⁹ and the increment in this moment, $\Delta\mu$, in the transition from benzonitrile to cyanobiphenyl depends on the angle ϕ : $\Delta\mu = \Delta\mu_{\max} \cos^2 \phi$ (Ref. 10). From the experimental data⁹ on μ and from the length ratio of the conjugation chains in these compounds we find $\Delta\mu = 0.28$ D, $\Delta\mu_{\max} = 0.37$ D, and $\phi = 30^\circ$ (corresponding to the isotropic solution), in agreement with the value for biphenyl.⁸ Now the vibration of the α bond changes the π -conjugation length and the mesomeric moment $\Delta\mu_{\max}$ and thus becomes active in infrared absorption. The integrated optical density of the sample in the infrared absorption band of the α vibration is $I_\alpha \sim \langle (\partial \Delta\mu / \partial r)^2 \rangle \sim \langle \cos^4 \phi \rangle$, where the angle brackets denote a statistical average. Changes in the intensity of this band can thus be used to study the changes in the average angle between rings, $\bar{\phi}$, defined by $\bar{\phi} \equiv (\langle \cos^4 \phi \rangle)^{1/4}$.

3. To eliminate the parasitic effect of multiple scattering and the errors associated with the polarizers (polarizers are usually somewhat less than perfect in the infrared region), it is convenient to use liquid-crystal films in cells with a homeotropic orientation of molecules for the polarization infrared measurements. It can be shown that the quantity $N_\alpha = I_{\alpha\perp} / I_{\alpha i}$, the ratio of the optical densities of the α band in the spectral component of the mesophase which is normal to the director (\perp) and in the isotropic-liquid phase (i), is related to the orientational-order parameter S and to the angle ϕ by

$$N_\alpha = \frac{(1 - S)}{\varepsilon_\alpha} \frac{\langle \cos^4 \phi \rangle}{\langle \cos^4 \phi_i \rangle}, \quad \varepsilon_\alpha = \frac{\rho_i n_{\alpha\perp,i}^b}{\rho n_{\alpha i}^b} \left(\frac{f_{\alpha i}^b}{f_{\alpha\perp}^b} \right)^2; \quad (1)$$

here ρ_i and ρ are the densities of the phases, $n_{\alpha\perp,i}^b$ and $f_{\alpha\perp,i}^b$ are the background refractive indices and elements of the local-field tensor in the α absorption band, and ϕ_i is the value of the angle ϕ in the isotropic phase. For the characteristic valence vibration of the $C \equiv N$ bond (β), which is oriented along the long axis of the molecule, as α is, we have $N_\beta = (1 - S) / g_\beta$. Since the difference between the frequencies ν_α (1287 cm^{-1}) and ν_β (2222 cm^{-1}) is much less than their separation from the lowest electronic-transition band, which determines the values of $n_{\perp,i}^b$, we can ignore the difference between g_α and g_β . Then from (1) we find

$$\bar{\phi} = \arccos \left[\cos \phi_i \left(N_\alpha / N_\beta \right)^{1/4} \right]. \quad (2)$$

4. We used crystals of 4-n-hexyl-4'-cyanobiphenyl (6CB) and 4-n-octyl-4'-cyanobiphenyl (8CB) in the experiments. The transition temperatures ($^\circ\text{C}$) for the transitions between the solid crystal (C), the smectic A phase (SmA), the nematic phase (N), and the isotropic phase (I) for these two materials are as follows: C 14.4° N 28.5° I and C 20.9° SmA 33.5° N 40° I. A perfect homeotropic orientation of the molecules in liquid-crystal layers $20 \mu\text{m}$ thick (for the measurements of N_β) and $40 \mu\text{m}$ thick (N_α) was induced by the walls of a fluorite (CaF_2) sandwich cell; the cell walls had not been subjected to any special chemical or texture-formation treatment. The error in the temperature at which the system was held and the fluctuations in the temperature regulation were $\pm 0.1^\circ\text{C}$. The N_α measurements were less accurate than the N_β measurements (Fig. 1) because of the faintness of the α band (I_α / I_β

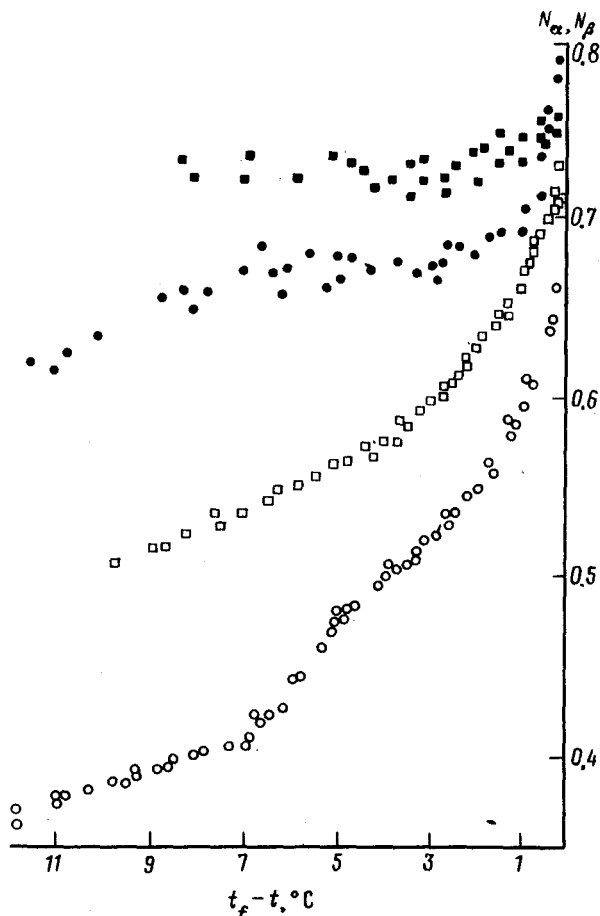


FIG. 1. Temperature dependence of N_β (\square , \circ) and N_α (\blacksquare , \bullet) in the liquid crystals 6CB (\square , \blacksquare) and 8CB (\circ , \bullet). Here t_f is the temperature of the transition between the nematic phase and the isotropic liquid.

$= 0.08$ in the isotropic phase with a fixed cell thickness).

We calculated the values of $\bar{\phi}$ in the mesophase (Fig. 2) from the experimental values of $N_{\alpha,\beta}$ (Fig. 1) and Eq. (2); we found the value $\phi_f = 30^\circ$, which is the same value as was found above. The angle $\bar{\phi}$ changes abruptly at the transition from the isotropic phase to the nematic phase and then decreases with increasing S ($S = 1 - N_\beta - N_\beta g_\beta$), both as the temperature of the nematic phase of both crystals is lowered and in a transition from 6CB to 8CB at a fixed Δt . The change in $\bar{\phi}$ in the nematic phase of these substances is comparable to that for 4-methoxybenzylidene-4'-butylaniline, according to the NMR data.⁵ The accuracy of our method is no worse than that of Ref. 5, and it is better than that of Ref. 6.

The change in ϕ also reflects a pretransitional increase in S in the nematic phase of 8CB near the N-SmA transition. The translational ordering of molecules which occurs at this transition affects the conformation of the aromatic nuclei of these

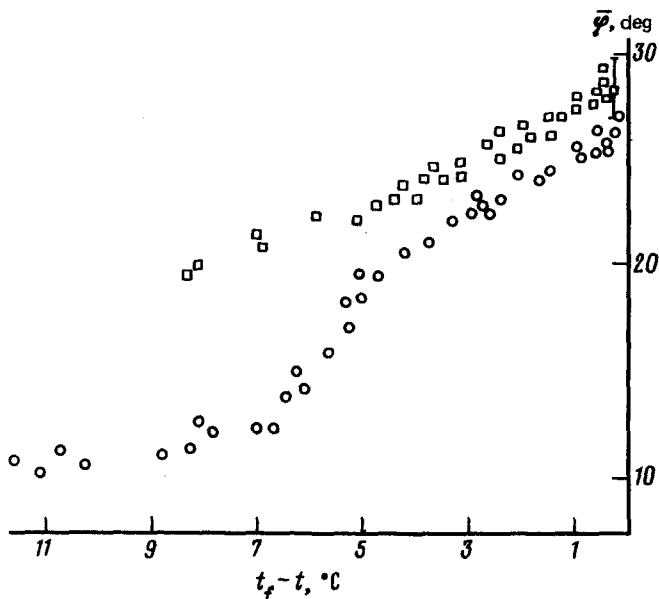


FIG. 2. Change in the dihedral angle $\bar{\phi}$ between the benzene rings of the biphenyl fragment of the molecules in the mesophase of 6CB (\square) and 8CB (\circ).

molecules as strongly as does a change in S in the nematic phase. Our data verify the suggestion^{1,4} that there is a change in the conformation of the aromatic nucleus of the mesomolecules in the mesophase even in a transition between two phases of identical symmetry, N and SmA. The role played by these conformational changes in phase transitions in liquid crystals and also the functional dependence of $\bar{\phi}$ on S require further experimental and theoretical study.

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