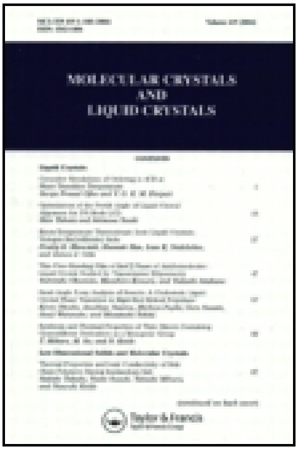

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Thermotropic Liquid Crystals IV. Anomalous Melting Behavior of Nematogenic Azobenzene Derivatives

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Thermotropic Liquid Crystals IV. Anomalous Melting Behavior of Nematogenic Azobenzene Derivatives

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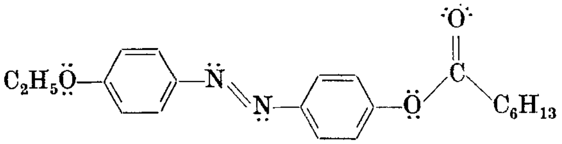
Monotropic solid phase modifications of *p*-azoxyanisole presumably with molecular arrangement similar to the parallel structures of the nematic phase, have been reported.(1) We wish to call attention to a nematogenic compound which, during heating, appears to crystallize from the nematic phase at a temperature *higher* than the initially observed solid-nematic transition. This is apparently due to a superheating through a solid phase modification stable only over a temperature range of a few degrees in the vicinity of the solid-nematic transition. This behavior was discovered while examining the series of 4-ethoxy-4′-*n*-alkanoyloxyazobenzenes by differential thermal analysis. We observed pronounced anomalies for data obtained from crystals prepared from solution as compared with those obtained from the nematic melt. This series was first prepared by Vorländer,(2) who apparently did not observe the initial solid-nematic transition by use of ordinary melting-point apparatus.

The DTA data for *trans*-4-ethoxy-4′-*n*-heptanoyloxyazobenzene (Formula 1, Vorländer reports solid-nematic transition at 68.5°)



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are illustrated in Figs. 1 and 2. The DTA curve (heating mode) is given in Fig. 1 for a sample of this compound obtained by recrystallization from an ethanol solution at room temperature. There is a pronounced endotherm at 61.5° corresponding to transition from solid to nematic mesophase; a very small endotherm is also evident at 67°. Figure 2 shows data for the same compound for which crystals were formed by cooling from the nematic phase. Again a pronounced endotherm exists at 61.5° but the second endotherm at 67° has become equal in size indicating a significant interphase transition. There is also evident a significant exotherm immediately following the endothermic transition at 61.5°.

This behavior was further investigated by examination of the melting behavior by means of a Kofler hot-stage polarizing microscope. If the stable room temperature solid phase of *trans*-4-ethoxy-4′-*n*-heptanoyloxyazobenzene is slowly heated without disturbance, one invariably observes melting into the nematic phase at 61.5°. At this point new, very long, needle-like crystals can sometimes be seen to form in the nematic melt; the extent of this crystal growth depends on the thermal history of the sample. This second crystalline phase is stable only over a short temperature range and then melts to form the nematic phase at 67°.

These phenomena cannot be ascribed to impurities in the sample. All compounds in the series of *trans*-4-ethoxy-4′-*n*-alkanoyloxyazobenzenes were carefully purified by multiple recrystallization and analyzed. Comparison of the ultraviolet spectra with that of *trans*-azobenzene shows almost identical band contours with maxima at 238 and 340 nm, which is good evidence for the absence of *cis* isomer. The mass spectrum for the 4′-*n*-heptanoyl derivative has a strong molecular ion at m/e 354 and no evidence for homologous impurities

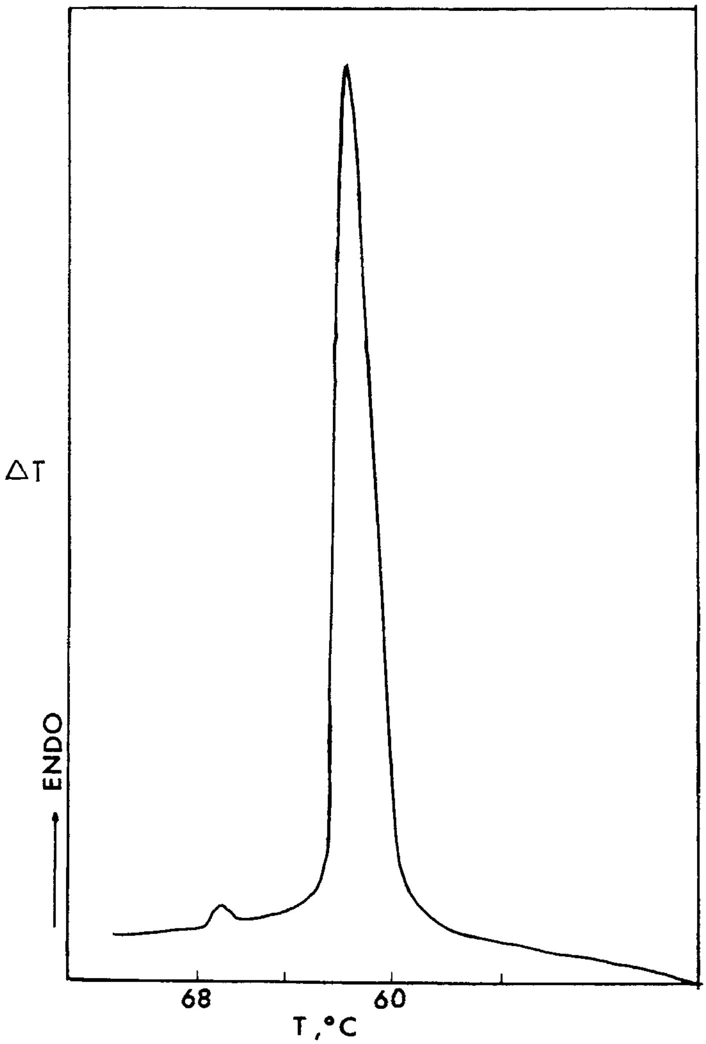

Figure 1. Differential thermogram (heating mode) for *trans*-4-ethoxy-4′-*n*-heptanoyloxyazobenzene recrystallized from ethanol.

at 14 amu intervals either side of the molecular ion. Major fragment ions were observed at m/e 121, 149, and 242 corresponding to expected cleavage at both aryl-nitrogen bonds and at the CO—O bond with β-hydrogen rearrangement, respectively.

The anomolous differential analysis behavior can be explained with reference to the schematic free-energy diagram shown in Fig. 3.

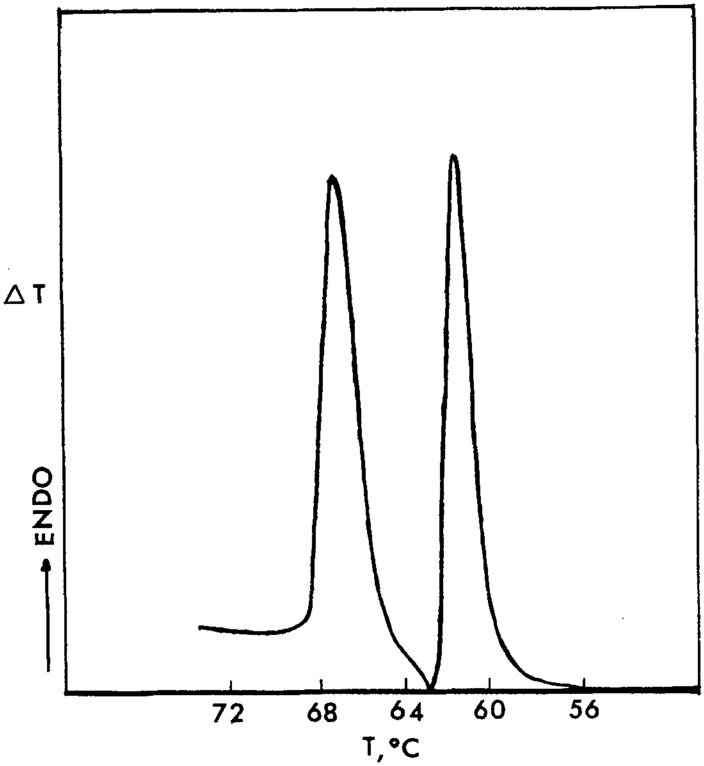

Figure 2. Differential thermogram (heating mode) for *trans*-4-ethoxy-4′-*n*-heptanoyloxyazobenzene crystallized from the nematic phase.

The solid form stable at room temperature is labeled S_2; the higher temperature solid form is labeled S_1, whereas the nematic phase is labeled N. As the sample is heated the free-energy curve for phase S_2 is followed past point A (intersection of curves for S_2 and S_1) to the point B, the S_2–N melting point at 61.5°. This requires superheating through the S_2–S_1 transition. The formation of solid phase

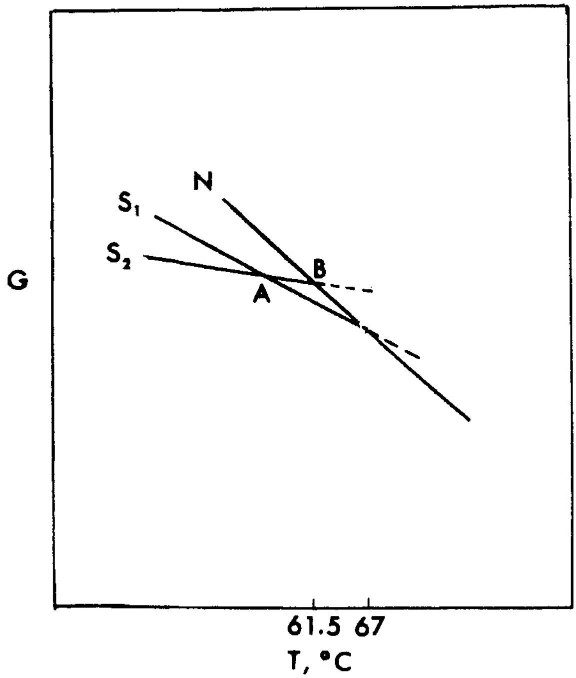

Figure 3. Idealized free energy versus temperature diagram for *trans*-4-ethoxy-4′-*n*-heptanoyloxyazobenzene.

S_1 from the nematic melt is kinetically more favorable and the S_1 crystals begin to form. These are, of course, formed exothermally and the extent of formation will depend on the pre-history of the sample. When the sample is formed by previous cooling from the nematic phase some thermodynamically unstable solid, S_1 is present. This has been confirmed by investigation of the infrared spectrum of a sample formed from the melt wherein changes in spectral features have been observed on long standing, identified with the slow process, $S_1 \rightarrow S_2$ at room temperature. When phase S_2 melts at point B, some solid phase S_1 crystallites remain to act as nucleation sites for formation of S_1. These nucleation sites will not be present in crystals grown from ethanol solution at temperatures below the S_1–S_2 transition.

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REFERENCES

1. Robinder, R. C. and Poirier, J. C., *J. Amer. Chem. Soc.* **90**, 4760 (1968).
2. Vorländer, D., *Z. Physik. Chem.* **126**, 449 (1927).