

EFFECT OF MOLECULAR STRUCTURE ON THE CRYSTAL-NEMATIC PHASE TRANSITION

A. C. GRIFFIN

*Department of Chemistry, University of Southern Mississippi,
Hattiesburg, MS 39401 U.S.A.*

(Received September 27, 1976)

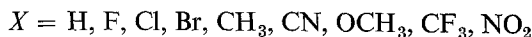
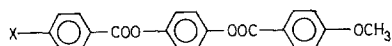
A systematic study of the crystal-nematic phase transition for a series of unsymmetrical *p*-phenylene bis (*p*-substituted benzoates) is reported. Differences in molecular structure along the series are in the nature of one small, compact terminal substituent. Enthalpy and entropy measurements are reported for the crystal-nematic transition as obtained by differential thermal analysis. A correlation between the thermodynamic data and molecular structure is presented.

Substances which undergo the melting process in a stepwise manner have been known for some time [1]. Compounds which lose their crystal structure to form a liquid which has anisotropic properties are known as liquid crystals or mesomorphs. This liquid crystalline phase is thermodynamically stable and transforms to the normal, isotropic liquid at a higher temperature. Liquid crystals have as their principal structural features rigid molecular frameworks and high length: breadth ratios. Early investigations [2–4] into structural features which promote liquid crystallinity (mesomorphism) were fruitful. By the middle 1960's explanations had been advanced as to why some organic molecules form liquid crystalline phases and some do not. Trends in mesophase-isotropic liquid transition temperatures were rationalized in terms of molecular structure even for subtle differences as in homologous series. The advent of differential thermal analysis and its use by Johnson, Barrall, and Porter [5] revolutionized the study of the mesomorphic state. They showed it possible to use this rapid, accurate method to measure not only transition temperatures but also transition heats (enthalpies). From these two quantities transition entropies are obtainable. (It should be noted here that Arnold [6] had done previous work in liquid crystals by adiabatic calorimetry. His work, although excellent, uses an extremely slow and cumbersome technique.) It is much more satisfying to discuss transition temperatures in relation to the associated heat and entropy terms which define it rather than to rely on temperatures alone to rationalize effects of structural modifications on liquid crystalline properties. Dewar and Griffin [7] have recently shown that use of transition temperatures alone to interpret molecular interactions leads in some cases to incorrect conclusions. There is currently a body [8] of thermodynamic information and theories on the mesophase-isotropic transition. Although considerable thermodynamic data is available on the solid-mesophase transition, there has

been little attention paid to organizing this data into a meaningful theory. This is surprising in light of the widespread interest in the use of liquid crystals as part of optical displays [9] which require low crystal-mesophase ($C \rightarrow M$) transition temperatures.

Notable attempts have been made to correlate molecular parameters with thermodynamic data for the crystal-mesophase transition. Levine [10] examined a number of nematogenic compounds and found no obvious correlation of enthalpy of fusion with structural features. Smith [11] reported data for a series of benzylideneanilines and suggested that possible complicating effects such as metastability and low temperature solid phases require further investigation. Work relating positional isomerism in cholesteryl halobenzoates to changes in crystal-cholesteric transition thermodynamics has been reported by Barrall, *et al.* [12].

In an effort to contribute to current knowledge of structural factors related to the $C \rightarrow N$ transition we report here the results of a systematic study of the crystal-nematic transition in a series of unsymmetrical *p*-phenylene bis (*p*-substituted benzoates) shown below



This series of molecules was chosen because the only difference along the series is in the electronic nature of the small, compact terminal substituents, X . This perturbation of molecular electronic properties is the probe used to investigate factors bearing on the $C \rightarrow N$ transition. Data for and discussion of the $N \rightarrow I$ transition for these compounds has been reported [13].

Experimental

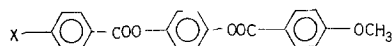
Synthesis and spectroscopic data of the compounds used in this study have been previously reported [13]. Temperature measurements were obtained using a temperature calibrated Stone differential thermal analyzer, Model 202, with a SH11BR2 sample holder, platinum differential thermocouple, and aluminum sample containers. Transition heats were obtained on the same instrument calibrated for enthalpy determinations by fusion curves of ultra-purity indium and lead reference standards. Samples were weighed to six places and heated from room temperature to well above the mesophase-isotropic transition at a heating rate of five degrees per minute. Alpha-alumina was the reference substance against which the sample temperature was measured. Planimetry was used to integrate areas under endothermic peaks for enthalpy determinations. Baseline construction was by the method of Young [14]. Pre-transition and post-transition effects are included in transition enthalpies by extrapolating the

baseline to the transition temperature from regions on both the high and low temperature sides in which the heat capacity varies linearly with temperature. Transition entropies were calculated using the following equation:

$$\Delta S = \frac{\Delta H}{T}$$

Thermodynamic data for the crystal-nematic ($C \rightarrow N$) transition are presented in Table 1.

Table I



X	$T_{C \rightarrow N}^a$	$\Delta H_{C \rightarrow N}^b$	$\Delta S_{C \rightarrow N}^c$
H ^d I	159.0	7.41	17.14
F II	155.0	6.87	16.04
Cl III	196.1	7.03	14.98
Br IV	213.1	6.49	13.35
CH ₃ V	204.1	7.67	16.07
CN VI	181.1	8.15	17.94
OCH ₃ VII	217.0	8.68	17.71
CF ₃ VIII	228.0	-e-	-e-
NO ₂ ^f IX	200.2	6.70	14.15

^a crystal-nematic transition temperature, °C

^b enthalpy of crystal-nematic transition, kcal/mole

^c entropy of crystal-nematic transition, entropy units

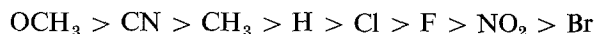
^d This compound has a shoulder on the low temperature side of $C \rightarrow N$ endotherm. If this is due to a crystal-crystal transition the $C \rightarrow N$ transition heat and entropy should be substantially reduced from the values in the table.

^e Due to overlap of this endotherm with $N \rightarrow I$ endotherm at 231°, no accurate determination was possible.

^f This compound undergoes a crystal-crystal transition at 161.5° which has a ΔH of 1.13 kcal/mole and a ΔS of 2.60 e.u.

Results and discussion

If one considers the $C \rightarrow N$ transition enthalpy as a direct measure of the net attractive forces (stability) acting among the molecules in the crystal at a temperature immediately below the $C \rightarrow N$ phase transition, the following stability order is found for this series:



This order suggests a picture of the $C \rightarrow N$ transition as one in which there are two types of opposing forces at work. One factor seems to be intermolecular

attraction caused by substituent polarity and/or the presence of lone pairs of electrons on the substituent. (These lone pairs may interact with electron-deficient parts of adjacent molecules.) The other factor appears to be the destabilizing effect of electron lone pair repulsions in neighboring molecules. Thus substituents with several lone pairs of electrons and which are without an "insulating" group [15] such as the methyl group in compound VII have a less stable crystal phase than those compounds which either have no lone pairs of electrons or have a smaller number of them. Compounds such as II, III, and IV are destabilized (relative to the others) by the large contribution of repulsive forces caused by the three lone pairs of electrons surrounding each of the halogen atoms. There appears no obvious correlation between the enthalpies of the $C \rightarrow N$ and of the $N \rightarrow I$ transitions [13] for a given substituent. Identical molecular structural features do not affect the $C \rightarrow N$ and $N \rightarrow I$ transitions by identical mechanisms. Entropies of the $C \rightarrow N$ transition are here found intimately related to the enthalpy of that transition. The $C \rightarrow N$ temperatures in these compounds are not identical due to a lack of perfect correlation between heat and entropy terms for this transition. However, the relatively small temperature spread for all $C \rightarrow N$ transitions in the series suggests a strong interdependence of intermolecular order and intermolecular bonding. As noted by Smith [11] low temperature solid phases may well bear on attempts to relate structural parameters to thermodynamic values. Compounds I and IX apparently have crystal-crystal transitions at temperatures between 20° and their $C \rightarrow N$ transition temperature. Other members of the series may show solid phase polymorphism at temperatures below 20° , the lower limit in this investigation. It does appear possible, however, from conclusions drawn here to design molecules with low $C \rightarrow N$ temperatures and high $N \rightarrow I$ temperatures.

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RÉSUMÉ — On communique les résultats d'une étude systématique de la transition de phase entre l'état cristallin et l'état nématique d'une série de benzoates *p*-phénylène bis *p*-substitués asymétriques. Les différences de structure moléculaire des membres de la série sont dues à la nature d'un substituant terminal compact de faible dimension. On décrit les mesures d'enthalpie et d'entropie de la transition entre l'état cristallin et l'état nématique, effectuées par ATD. On présente une corrélation entre les données thermodynamiques et la structure moléculaire.

ZUSAMMENFASSUNG — Eine systematische Untersuchung über den kristallin-nematischen Phasenübergang einer Reihe asymmetrischer *p*-Phenylen-bis-(*p*-substituierter Benzoate) wird bekanntgegeben. Die Unterschiede der Molekularstruktur der Serienglieder bestehen in der Beschaffenheit eines kleinen, kompakten, terminalen Substituenten. Die mittels Differentialthermoanalyse erhaltenen Enthalpie- und Entropiemessungen des kristallin-nematischen Überganges werden beschrieben. Eine Korrelation zwischen den thermodynamischen Daten und der Molekularstruktur wird gegeben.

Резюме — Приведено систематическое изучение кристаллически-нематического фазового перехода для серий несимметричных *p*-фенилен-бис (*p*-замещенных бензоатов). Различия в молекулярной структуре по сериям обусловлены природой одного небольшого, плотного, концевого заместителя. Приведены данные энтальпии и энтропии кристаллически-нематического перехода, полученные с помощью дифференциального термического анализа. Представлена корреляция между термодинамическими данными и молекулярной структурой.