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Note

DIELECTRIC AND DTA STUDIES ON *TRANS*-STILBENE AND *N*-BENZYLIDENEANILINE NEAR THEIR MELTING TEMPERATURES

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In recent years, the application of dielectric studies have proved useful for the determination of acuplanarity and other related characteristics of compounds exhibiting liquid crystalline properties [1,2]. The vast majority of compounds exhibiting such properties have flexible aromatic rings as end groups attached to a rigid central group like $>C=C<$ and $>C=N-$, etc. [3,4]. A survey of the literature reveals that only few attempts have been made to establish the criticalness of length-to-breadth ratio in such molecules from the physicochemical characteristics of the fragments of these molecules [5]. As a part of our investigations on the fragments of potentially mesomorphic systems [6,7], we report here the dielectric and DTA studies on *trans*-stilbene and *N*-benzylideneaniline near their respective melting temperatures. The present studies were aimed at investigating the behaviour of these compounds in the crystalline, molten liquid and supercooled regions.

EXPERIMENTAL

The samples of *trans*-stilbene and *N*-benzylideneaniline used in the present investigations were essentially the same as used in earlier studies [7]. The dielectric constants were determined using a Wayne Kerr Universal Bridge B 221 A in combination with an autobalance adapter AA 221. The details of the technique and the cell assembly employed for capacitance measurements have been described elsewhere [8]. The uncertainty in the values of dielectric constants reported here are within ±0.1%. DTA studies were carried out at a heating rate of $1^\circ C\ min^{-1}$ using alumina as reference material in an apparatus assembled and calibrated in our laboratory [9].

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RESULTS AND DISCUSSION

The dielectric constants for the two compounds at various temperatures near their respective melting temperatures are recorded in Table 1 and plotted in Figs. 1 and 2. It is observed that the change in dielectric constant with temperature shows certain interesting features. When solid *trans*-stilbene is heated, its dielectric constant increases only gradually and falls steeply at the melting point; thereafter it increases linearly with temperature. Upon cooling the liquid, the dielectric constant of the melt is reproduced until the melting point, while on further cooling it does not fall on the

TABLE 1

Dielectric constants of molten *trans*-stilbene and *N*-benzylideneaniline at various temperatures near the melting temperature

Temp. (K)	Dielectric constant	
	Heating cycle	Cooling cycle
trans-Stilbene		
373.15	3.295	
378.15	3.303	
383.15	3.314	3.387
386.15	3.321	3.657
388.15	3.331	3.658
390.15		3.641
393.15	3.358	3.633
396.15		2.398
397.15	3.430	
398.15	2.272	2.273
403.15	2.199	2.200
408.15	2.179	2.179
413.15	2.143	2.143
418.15	2.097	2.096
423.15	2.068	
N-Benzylideneaniline		
313.15		3.567
316.15		4.388
318.15	3.516	4.372
320.15	3.586	4.342
323.15	3.865	4.331
324.15	4.002	
325.15	4.298	4.280
326.15	4.253	4.252
328.15	4.212	4.213
330.15		4.178
330.65	4.170	
333.15	4.129	4.128

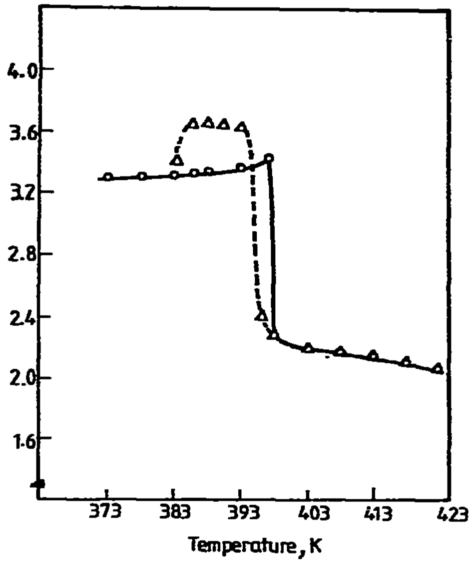

Fig. 1. Dielectric constant of *trans*-stilbene as a function of temperature. ○, Heating cycle; △, cooling cycle.

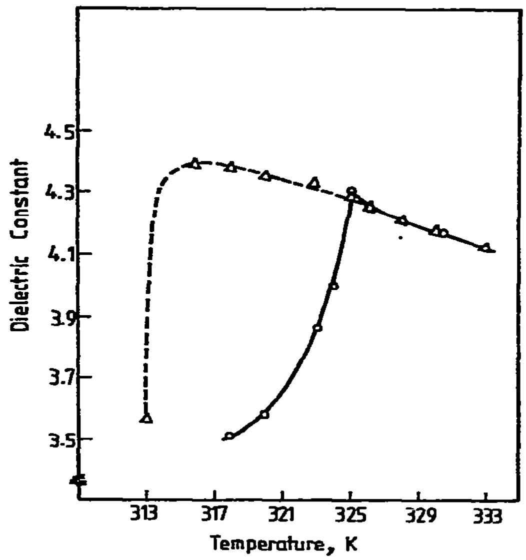

Fig. 2. Dielectric constant of *N*-benzylideneaniline as a function of temperature. ○, Heating cycle, △, cooling cycle.

original (extrapolated) line for the liquid but has a slightly higher value. For solid *N*-benzylideneaniline, the dielectric constant increases with temperature first gradually and then steeply (at a temperature close to the melting temperature) along an exponential curve. Beyond the melting temperature, its dielectric constant decreases almost linearly with increase in temperature. During the cooling cycle, the dielectric constant is reproducible until the freezing temperature, but falls below the extrapolated liquid line when the liquid is supercooled. The dielectric constants for both the compounds tend to a value very close to the dielectric constant of the solid when the supercooled liquid suddenly freezes. On reheating and melting, the data in the liquid state are completely reproduced without any hysteresis.

The steep curvature observed just before the melting temperature in the ϵ vs. T plot for *N*-benzylideneaniline is indicative of a pre-melting phenomenon involving a solid—solid transition while the behaviour in the supercooled region seems to indicate the occurrence of a pre-freezing transition in the liquid state. Such a phenomenon is not uncommon, particularly in molecules with a strong dipolar character, with groups involving torsional oscillations or rotational movements [10,11]. The absence of the steep curvature before melting in the ϵ vs. T plots for *trans*-stilbene is indicative of the fact that there is no such pre-melting phenomenon in *trans*-stilbene involving solid—solid transition. These observations are further supported by the DTA studies.

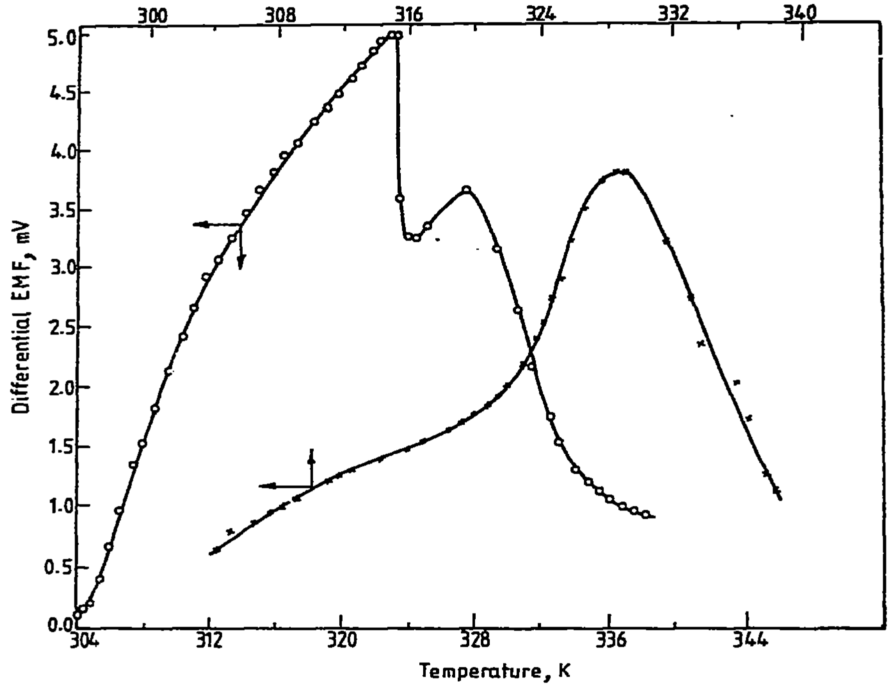

Fig. 3. Thermograms for crystalline (O), and, glassy (X) forms of *N*-benzylideneaniline.

It is observed from the thermograms for *N*-benzilideneaniline shown in Fig. 3 that when the crystalline compound is the starting material, the thermogram passes through a cusp a few degrees before the melting point and then at the melting temperature, as indicated by two maxima in the curve. On the other hand, when the glassy state is the starting material, there is a change in the shape of the curve in the heating zone before the melting point, indicating that the pre-melting transitions are lost in this case and there is only one maximum in the thermogram at the melting temperature. It appears, therefore, that in the supercooled glassy state there is a wide range of clusters of varying degrees of order, so that the transformation of the liquid state does not show any sudden changes. In the case of the crystalline melt, it is possible that cooling to the solid state may have occurred with a near equilibrium between crystalline and non-crystalline clusters, which requires a transition in the solid state between these two prior to melting upon reheating, as shown by the two maxima in the thermogram. The thermograms for *trans*-stilbene show no transition before the melting temperature. Further investigations on such compounds are under way.

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