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Heats and Temperatures of Transition of Some Aromatic Liquid Crystal-Forming Materials†

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Abstract—The heats and temperatures of transitions were measured for five pure compounds which were known or expected to form mesophases or liquid crystals. The five compounds were N-(*p*-cyanobenzal)-*p*-anisidine, *p*-(4-cyanobenzalamino)-cinnamic acid-active amyl ester, N,N′-terephthalylidene-di-*p*-toluidine, *p*-acetoxy-cinnamic acid, and *p*-[N-(*p*-methoxybenzylidine)-amino]-phenyl acetate. Temperatures of transition for the compounds are reported here for the first time using a well-calibrated differential thermal analyzer. Heats of transitions for the compounds have not been previously reported. They were measured here by differential scanning calorimetry.

Tests were made for phase reversibility of the multiple transitions and the possible changes in heats and temperatures of transition with sample origin, i.e., solvent or melt crystallized.

Introduction

Mesophases in pure compounds are formed in a temperature interval between first-order transitions to the stable crystalline solid and to the normal, isotropic liquid. The intermediate liquid crystal or mesophase possesses considerable molecular order but exhibits properties of a fluid. Of the thousands of compounds known to form mesophases, less than fifty have been examined calorimetrically; and, among these, over half the compounds studied have been reported since 1964. This recent work has been carried out principally in this laboratory[1–3] and by Arnold.[10, 11] Arnold's work has been principally on a series of dialkoxyazoxy benzenes and

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TABLE 1 Compositions of Compounds Studied

Chemical name	Symbol	Formula	Structure
N-(*p*-cyanobenzal)-*p*-anisidine	CBA	$C_{15}H_{12}N_2O$	$CNC_6H_4CH{=}NC_6H_4OCH_3$
N,N′-Terephthalylidene-di-*p*-toluidine	TBT	$C_{22}H_{20}N_2$	$CH_3C_6H_4N{=}CHC_6H_4CH{=}NC_6H_4CH_3$
p-[N-(*p*-methoxybenzylidine)-amino]-phenyl acetate	MBA	$C_{16}H_{15}NO_3$	$CH_3OC_6H_4CH{=}NC_6H_4OCOCH_3$
p-(4-cyanobenzalamino)-cinnamic acid active amyl ester	CBC	$C_{22}H_{22}N_2O_2$	$CNC_6H_4C{=}NHC_6H_4CH{=}CHCOOC_5H_{11}$
p-acetoxycinnamic acid	ACA	$C_{11}H_{10}O_4$	$CH_3CO_2C_6H_4CH{=}CHCOOH$

represents the most valuable calorimetric study on compounds which form smectic mesophases currently available.[10] Previous studies in this laboratory have concentrated on the two other basic mesophase types: the nematic [1, 2] and the unique phases formed by derivatives of cholesterol.[2, 3] The experimental contribution of this paper is the report of heats of transition and transition temperatures measured by differential thermal analysis and scanning calorimetry for five pure compounds which purportedly exhibit only a single mesophase. The techniques have apparently not been applied heretofore to these compounds, although qualitative thermal analysis was reported on other cinnamic acid derivatives which form mesophases as long ago as 1931.[12] Three of the five compounds studied exhibit the nematic-type mesophase. Mesophases have been classically defined by optical methods, and identifications used here are from such literature reports. The names of the compounds studied are given in Table 1. Also given are the molecular formulae, the general structures, and the symbols used hereafter in the text for compound identification. The compound abbreviated as TBT has also been cited as *p*-phthalal-di-(*p*-toluidene).[7] Yet other mesophase-forming compounds have the same molecular formula as TBT.[7] One of these compounds, MBA, has been reported to exhibit a cholesteric-type mesophase.[6] It is a rare example of cholesteric mesophase formed by a compound not containing the basic sterol-like molecular skeleton. It differs also from the behavior of the other derivatives of cinnamic acid, one of which is studied here, ACA, in that neither a nematic nor multiple mesophase of the smectic type are formed.[10, 11] An isomeric compound, the racemic amyl ester reportedly forms only the nematic mesophase.[14]

Experimental

Samples of N-(*p*-cyanobenzal)-*p*-anisidine, *p*-(4-cyanobenzalamino)-cinnamic acid-active amyl ester and N,N′-terephthalylidene-di-*p*-toluidine were obtained from Aldrich Chemical Company, Milwaukee, Wisconsin. Samples of *p*-acetoxy-cinnamic

acid and *p*-[N-(*p*-methoxybenzylidine)-amino]-phenyl acetate were obtained from Eastman Organic Chemicals, Incorporated, Rochester, New York. The acid was reported by Eastman "Information Sheet 122-965" to be a liquid crystal from 205–220°C. All materials were recrystallized twice from hot ethanol and dried at 1 torr 24 hours at 50°C. Vacuum thermogravimetry indicated that all materials were essentially solvent free after this drying.

Prior to actual calorimetry, a sample of each compound was submitted to differential thermal analyses (DTA) by heating

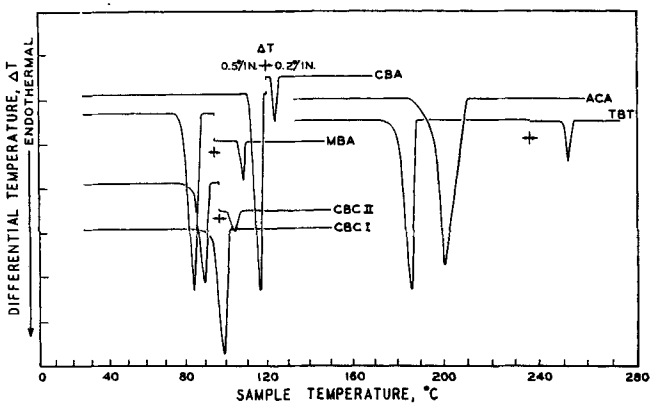

Figure 1. Heating differential thermograms (10°C/min heating rate, ~0.03 g sample).

followed by cooling at a rate of 10°C/min under 760 torr of helium. This established the location of the solid → liquid crystal and isotropic liquid → liquid crystal transition temperatures to ± 0.1°C. The differential thermograms are shown in Figs. 1 and 2. The sensitivity of the differential temperature, ΔT, is shown on the figures above the double arrows. In Fig. 1, the sensitivity to the left of the break is 0.5°C/inch and to the right of the break, 0.2°C/inch. The divisions on the ΔT axis correspond to inches in the original data. The ΔT sensitivities in Fig. 2 are indicated in the same way. A Du Pont 900 Differential Thermal Analyzer equipped with the microsample block was used to obtain the thermograms. Extensive

earlier work indicates that the heating rates used in this study are sufficiently slow for the establishment of equilibrium conditions. The temperatures shown in Table 2 are from maxima and minima in DTA traces. Temperatures are reported to 0.1°C, although mesophase transitions are generally reproducible to only 6°C. Thermograms of the mesophase systems are given because of their value for classification of transitions by empirical type[9] and for comparison with earlier work.

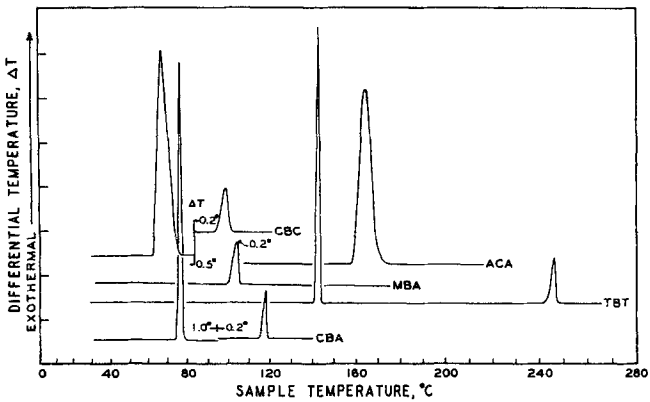

Figure 2. Cooling differential thermograms (10°C/min cooling rate, ~0.03 g sample).

The heats of transition were measured independently by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-1B instrument operated at a scanning rate of 10°C/min on both heating and cooling cycles. This apparatus was calibrated over the temperature and sensitivity ranges used for calorimetry by measuring the known heats of fusion for semiconductor-grade indium, pure tin and lead, and zone-refined dotriacontane. The techniques of sample containment, chart integration, and calculation were essentially the same as those described earlier.[1,2]

The calorimetric values are shown in Table 2. The values listed as "first heating" are for ethanol-recrystallized material. The values for "second heating" were obtained on melt-recrystallized

TABLE 2

THERMAL DATA ON LIQUID CRYSTAL-FORMING COMPOUNDS
COMPOUNDS RECRYSTALLIZED FROM ETHANOL

Compound Symbol	Heating						Cooling*					
	T_b, °C	T_m, °C	T_e, °C	ΔH Cal/g	ΔH Kcal/ Mole	ΔS,** Cal/ Mole, °K	T_b, °C	T_m, °C	T_e, °C	ΔH Cal/g	ΔH Kcal/ Mole	ΔS,** Cal/ Mole, °K
CBA	111.4	117.1	119.4	25.3	5.98	15.3	74.3	76.3	77.9	22.6	5.34	10.1
	122.6	124.2	125.5	0.63	0.15	0.38	115.1	119.0	119.7	0.66	0.16	0.41
TBT	172.2	186.7	189.3	27.8	8.69	18.9	140.6	143.3	143.9	28.0	8.75	21.0
	248.9	252.6	255.3	0.88	0.27	0.51	241.8	246.0	247.7	0.78	0.24	0.46
MBA	74.8	85.2	88.0	21.2	5.71	15.9	-	-	-	-	-	-
	106.0	109.0	110.9	0.80	0.22	0.58	100.7	104.1	104.9	0.80	0.22	0.58
Second Heating	59.1	70.4	72.9	16.7	4.50	13.1	-	-	-	-	-	-
	104.5	108.9	109.7	0.76	0.21	0.55	100.6	103.5	104.4	0.79	0.21	0.58
CBC	83.7	99.6	103.1	18.8	6.52	17.5	63.7	67.2	77.4	13.6	4.72	13.9
	← No Liquid Crystal Phase →						94.4	99.5	102.6	0.29	0.100	0.27
Second Heating	75.2	90.0	93.9	13.5	4.68	12.9	54.3	57.7	62.0	13.7	4.75	14.4
	100.4	105.7	108.4	0.25	0.087	0.23	93.3	96.3	99.1	0.27	0.094	0.25
ACA	185.1	208.7	212.2	36.9	7.61	15.8	158.8	174.8	182.3	22.8	4.70	10.5
	← No Liquid Crystal Phase →											
Second Heating	165.5	199.3	203.1	24.4	5.03	10.7	145.4	164.1	174.1	22.7	4.68	10.7
	← No Liquid Crystal Phase →											

*The order of temperatures in the cooling mode has been reversed to facilitate comparison with the heating mode.
**Calculated at T_m

T_b Temperature at onset of heating endotherm or conclusion of cooling exotherm.
T_e Temperature at conclusion of heating endotherm or onset of cooling exotherm.
T_m Temperature at vertex of heating or cooling endotherm or exotherm.
Second heating refers to material recrystallized from the melt.

material. Each compound was scanned three times using fresh samples. The average deviation in calorimetric values between samples with similar thermal histories was $< \pm 3\%$. Transition temperatures and calorimetry obtained from heating curves are considered to be more reliable than those from cooling.

Results

N-(*p*-cyanobenzal)-*p*-anisidine (CBA) exhibits an easily defined solid → nematic mesophase transition as follows:

Heating Cooling

$$\mathrm{C} \xrightarrow[25.3\ \mathrm{cal/g}]{117.1^\circ\mathrm{C}} \mathrm{N} \xrightarrow[0.63\ \mathrm{cal/g}]{124.2^\circ\mathrm{C}} \mathrm{L} \xrightarrow[0.66\ \mathrm{cal/g}]{119.0^\circ\mathrm{C}} \mathrm{N} \xrightarrow[22.6\ \mathrm{cal/g}]{76.3^\circ\mathrm{C}} \mathrm{C}$$

All of the calories observed on heating cannot be accounted for on the cooling scan, possibly due to imprecision caused by the long tail on the nematic → solid exotherm. This tail is probably due to the slow crystallization rate and resultant imperfection of the solid phase formed from the relatively viscous, supercooled nematic mesophase. When the sample of melt-recrystallized material is allowed to stand overnight, the full 25.3 cal/g solid → nematic transition is recovered on reheating. When the rapidly quenched solid phase is subjected to a 10°C/min heating scan, a few minutes after formation, a large exotherm is observed near 100°C due to the formation of stable crystals of the solid phase from supercooled nematic or the liquid. However, a small total heat difference is again noted. Prolonged standing produces complete recrystallization. The calorimetry given in Table 2 suggests that this conversion is principally, if not totally, from the nematic mesophase. The solid → nematic endotherm which follows on further heating occurs at the previously stated temperature and requires 25.2 cal/g. The ethanol- and the melt-recrystallized material appear to be thermally identical.

N,N′-terephthalylidene-di-*p*-toluidine, TBT, exhibits a thermal behavior similar to that of CBA as follows:

Heating Cooling

$$\mathrm{C} \xrightarrow[27.8\ \mathrm{cal/g}]{186.7^\circ\mathrm{C}} \mathrm{N} \xrightarrow[0.88\ \mathrm{cal/g}]{252.6^\circ\mathrm{C}} \mathrm{L} \xrightarrow[0.78\ \mathrm{cal/g}]{246.0^\circ\mathrm{C}} \mathrm{N} \xrightarrow[28.0\ \mathrm{cal/g}]{143.3^\circ\mathrm{C}} \mathrm{C}$$

The amount of heat required is nearly independent of direction (melting or freezing) of the phase change. At a cooling rate of 10°C/min, the isotropic–nematic transition supercooled 6.6°C, and the nematic–solid transition supercooled 43.4°C. The thermal behavior of the solid phase appears to be independent of crystallization method.

p-[N-(*p*-methoxybenzylidine)-amino]-phenyl acetate, (MBA), exhibits a thermally reproducible nematic and an irreproducible solid phase. The solid phase apparently reforms slowly at room temperature, and the heat of freezing cannot be measured by the

usual DSC techniques (the blanks in Table 2). When the melt-recrystallized solid was allowed to stand at 20°C for 24 hours and then reheated, the solid → nematic transition occurred at 70.4°C and required only 16.7 cal/g. The nematic → isotropic liquid transition follows as previously given with the transition occurring at the equivalent temperature and heat. This indicates that it is the mesophase and not the isotropic liquid that is in metastable equilibrium with the crystals on rapidly cooling the melt. The addition of a few drops of ethanol to the sample planchet followed by vacuum drying *in situ* results in a solid which converts to the nematic mesophase at 85.3°C and requires 21.1 cal/g. This last experiment rules out the possibility of decomposition products interfering in the solid phase and indicates that the stable crystalline state can be quantitatively formed by this procedure. The solid phase formed from the melt is either a reproducible mixture of the nematic and solid phases or a disordered pure solid phase. Earlier studies have shown that the disordered solid phase is common on cooling of cholesteric liquid crystals.[2, 3]

Solid *p*-(4-cyano-benzalamino)-cinnamic acid-active amyl ester (CBC) recrystallized from ethanol melts directly to the isotropic liquid. No liquid crystal phase forms on heating. On cooling, a liquid crystal phase forms from the melt. Reheating the melt recrystallized material results in a solid → mesophase transition. Further heating gives the mesophase → isotropic liquid transition. Repeated reheatings resulted in some decomposition of the ester as indicated by a faint browning of the sample. Recrystallization from ethanol of the sample exposed to thermoanalysis produced a solid which did not show a liquid crystal transition on first heating but melted directly to the isotropic liquid at 89.0°C. The reduced melting point of this solid, see original in Table 2, is probably due to thermally produced impurities. Recrystallization from ethanol, which involved the removal of the supernatant liquid by filtration rather than evaporation, returned the compound to the initial melting condition of 99.6°C with no mesophase formation on first heating. The existence of a disordered solid phase is difficult to prove in the case of CBC due to a purity loss on heating.

The mesophase type was not identified optically but can be classified on the basis of thermal properties. The relative magnitude of the mesophase heats indicates that CBC forms either a cholesteric or nematic mesophase but not a smectic. Mesophase formation on second heating indicates that the mesophase is likely cholesteric rather than nematic. This conclusion is further supported by an independent mesophase identification for CBC as cholesteric.[6]

p-Acetoxycinnamic acid (ACA) does not appear to form a mesophase under the conditions reported here. The ethanol-recrystallized material melts directly to the isotropic liquid. Cooling of the isotropic liquid produces a solid phase. The solid phase formed from the melt on reheating melted at 199.3°C and required 24.4 cal/g. Recooling the melt produced essentially the same results as before. The reduction in the heat of fusion is probably due to the formation of a less ordered solid phase. Recrystallization *in situ* with ethanol followed by reheating produces the 36.9 cal/g. endotherm at 208.7°C. A mesophase could not be found on careful hot stage microscopy of ACA. If a mesophase is formed, the transition from the solid may be within 1°C of the isotropic–liquid transition. In this case, separation of the phases would be difficult with the present methods.

Discussion

The mesophase-forming materials reported here exhibit the same general pattern of heats and temperatures as nematic-forming materials reported previously.[5] The calorically large event is uniformly the solid → nematic transition. The nematic → isotropic liquid conversion is unusually small for a first-order transition, requiring between 0.088 and 0.27 kcal/mole. Supercooling of the liquid → nematic transition is generally less than 5°C; whereas the lower temperature more viscous conversion, nematic → solid, can supercool in excess of 40°C. CBA and TBT exhibit phase transitions similar to *p*-azoxyanisole in being completely reversible. The same solid forms from melt as from ethanol recrystallization. MBA and CBC show a more complex phase behavior more closely akin to

the previously described cholesteric and smectic liquid crystals than to nematic mesophase behavior.

The absence of a liquid crystal phase in ACA is difficult to account for. The material structurally should be capable of the kind of dipole interaction which characterizes other nematic materials. It is possible that phases of ACA are formed through double molecules such as reported for *p*-butylbenzoic acid. The individual molecular weights are among the lowest for which mesophase behavior has been reported. A structurally similar compound, *p*-methoxy-cinnamic acid exhibits a mesophase, 170–186°C,[7, 8] for which a rare example of early calorimetry is available, a nematic–isotropic transition heat of 3.5 cal/g as measured by DeKock and reported by Schenck.[8]

Table 3 compares a summary of transition temperatures measured in this study with those reported in the literature for the same five compounds. A variety of measurement methods have been used with the set presented here being the first developed by differential thermal analysis. The three sets of data in Table 3 on CBA appear to establish the transitions at 116°C and 125°C with

TABLE 3 Transition Temperatures for Mesophase Systems Data of Different Investigators

Compound	Transition	This study	Chemical source	Int. Critical (Ref. 7)	Brown & Shaw
CBA	Crystal–Mesophase	117.1	114	115	
	Mesophase–Liquid	124.2	125	125	
TBT	Crystal–Mesophase	186.7	184–5	186	
	Mesophase–Liquid	252.6		238	
MBA	Crystal–Mesophase	85.2		81.5	
	Mesophase–Liquid	109.0		108	
CBC	Crystal–Mesophase	90.0	96	95	92
	Mesophase–Liquid	105.7	106	107	105
	First Heat, Crystal–Liquid	99.6			
ACA	Crystal–Mesophase	208.7	205		
	Mesophase–Liquid		220		

the minimum possible expected precision of ± 1°C. The mesophase–isotropic transition for TBT is among the highest reported and is probably now the highest temperature reported for mesophase calorimetry. The entropy of transformation is comparable to other materials studied. The high temperature for the mesophase–isotropic transition is probably why it is not yet well defined and has not been reported in several melting point studies of this compound, TBT, see Table 3 and Ref. 13.

For the compound MBA, the isotropic–mesophase transition appears well defined at 108–109°C. The material studied here may be more pure than that previously investigated because of the higher crystal–mesophase transition, 85°C, on first heating. This compound, MBA, has also been cited as *p*-(anisalamino)-phenol acetate.[7] The transitions for the compound CBC have been given several times in the literature, see Table 3. The mesophase–isotropic transition appears to be 106 ± 1°C with greater uncertainty, 90–96°C, for the temperature of the crystal → mesophase transition. The mesophase of CBC has been reported to be of the cholesteric type. The thermal data are consistent with this conclusion. Empirically, the nematic and cholesteric types can be distinguished by the fact that the latter frequently go directly on first heating from crystals to isotropic liquid, with thermal behavior depending on the conditions of initial crystallization [see Table 2 for the marked difference of transition behavior for first heating (ethanol recrystallized) versus second heating (melt recrystallized)]. For ACA, thermal analysis shows a transition of 208.7°C, indicative of a relatively high purity, see Table 3. A second, higher temperature transition, reported for this compound has not yet been revealed by these thermoanalytical techniques.

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