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Thermotropic Liquid Crystals with Nitrocinnamylidene Unit

by

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19 ABSTRACT (Continue on reverse if necessary and identify by block number) Highly polarizable organic molecules in an ordered morphology are sought after for their non-linear optical properties. Among the polymeric systems that have received a lot of attention are poly(diacetylenes) and poly(methacrylates) with liquid crystalline side chains. Although many poly(diacetylenes) have been studied there is none with the side group in strong interaction with the conjugated polymer chains. We reason that poly(diacetylenes) with strongly polarizable side chains attached directly to the conjugated chains should have very interesting optical properties. Furthermore if the monomers are liquid crystalline poly(diacetylenes) with very high order should be obtainable via polymerization in crystalline and/or liquid crystalline states. For ferroelectrical optical displays, on the other hand, polarizable chiral smectic C liquid crystals are desirable. Our approach to these areas started with the design and synthesis of a polarizable mesogen 3-aryl propylenylidene anilines. (AW) ↗ (Cont. on reverse)			
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Thermotropic Liquid Crystals with Nitrocinnamylidene Unit

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Introduction

Low molar mass liquid crystals of schiff base (-CH=N-) type have been long time recognized and studied¹. However, liquid crystals containing conjugated Schiff base (-(CH=CH)_n-CH=N-) are still not explored extensively. Back in 1929, D. Vorlander first introduced molecules of conjugated Schiff base (-(CH=CH)_n-CH=N, n= 1 and 2) type², which were synthesized by reacting either 5-phenyl-1-pentadiene or 7-phenyl-1-heptatriene with different p-substituted anilines. The resulting molecules are either non-liquid crystals or monotropic materials. A plausible reason may be due to the absence of suitable tails at both ends. In order to further explore this topic, we report here the first example of liquid crystals containing 4-nitrocinnamylidene (4-O₂N-Ph-CH=CH-CH=N-) unit.

Monomeric liquid crystals (MCLs), can be readily functionalized and coupled to form oligomers of liquid crystals. Also, flexible-center dimer, dimeric liquid crystals (DCLs), can be prepared by coupling two mesogenic cores with aliphatic spacer chain³. It was previously argued that the central flexible spacer has profound effect on the final mesomorphic properties of DCLs and can distinguish them from MCLs. It is therefore interesting to study the effect of spacer on DCLs and compare the difference between DCLs and MCLs. In this study, MCLs and DCLs were synthesized and carefully examined.

Also, DCLs with four different spacers were prepared in order to investigate the function of spacers.

Results and discussion:

Syntheses of monomers ((1) and (4)) and dimers ((7), (10), (14), (15) and (16)) are depicted in Scheme 1 and 2, details are given in experimentals section. Figure 1 showed DSC thermograms of MCLs ((1) and (4)) and DCLs ((7) and (10)). A summary result was given in Table 1.

Cinnamylidene-P-octyloxyaniline was synthesized primarily by reacting cinnamaldehyde with p-octyloxyaniline and exhibits no mesomorphic property. Apparently, terminal nitro group is essential for the construction of liquid crystal. As seen from Table 1, DCLs (7) and (10) possess higher melting and cleaning points than MCLs (1) and (4). The density of nitro groups in either MCLs or DCLs are approximately the same. Whatever, both ends of DCLs are fixed due to the intermolecular interaction of terminal mesogenic units; this contributes to the higher transitions of DCLs than MCLs'. Also, monomer (4) has the higher enthalpy change of melting process than monomer(1) (29.2 compared with 26.78 Cal/g). Simply depicted from chemical structure, monomer (4) with terminal -OH has extra intermolecular hydrogen bonding compared to monomer (1). This hydrogen bonding may be the cause of higher enthalpy and also Tm of monomer (4) to (1). X-ray diffraction may be used to further verify this point.

Flexible spacers play important role of the final properties of DCLs'. Previously, Griffin's study on diester dimers⁴ showed that the flexibility of the central spacers is deturious to mesogenic behavior because of the large amount of nonlinear geometies the molecule can adopt if the center is

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flexible. Dimer (10), with central triethylene glycol as spacer, will interfere the packing of the terminal nitrocinnamylidene group to a higher degree as compared with dimer (7), where less flexible octanedioxy group was used as central spacer. This effect was revealed by the apparently lower T_m and T_c of dimer (10) than dimer (7). In addition, the solubilities of dimer (7) and (10) differ dramatically as shown in Table 2. The deteriorious effect of triethylene glycol may well enhance the solubility of the corresponding dimer (10).

Another interesting point will be the effect of the central spacers' length on the products' transition temperatures. As seen from Table 1, compound (15), with tetraethylene glycol as central spacer, possesses lower T_m and T_c as compared with those of compound (14), which has shorter triethylene glycol spacer. Increasing central spacer's length by one ethylene glycol unit results in material with 35 - 37°C lowered thermal transition temperatures. Whatever, further attempt to disclose the relationship between central spacers' length and mesomorphism turned out to be ambiguous. Compound (16) with its longest spacer, pentaethylene glycol, possesses a very narrow mesogenic range. This, of course, may be due to the presence of large quantities of impurities. Further purification is needed for compound (16),

Recently, microscopy and X-ray were used to identify the the textures of monomers and dimers, which all these monomers and dimers turned to be nematic above their melting points. In order to evaluate the effect of tails in monomeric system, two other monomers with longer tails ($O_2N-Ph-CH=CH-CH=N-Ph-O-(CH_2)_n-CH_3$; $n = 11$, (17); $n = 15$, (18)) were synthesized. Compound (17) and (18) appears to be smectic above their melting points (for (17), $T_m = 64^\circ C$ and $T_c = 118^\circ C$; (18), $T_m = 94^\circ C$ and $T_c = 144^\circ C$ according to microscopy).

Apparently, tails with longer length will enhance the packing in the liquid crystalline state of the corresponding substrates. The low melting point and broad liquid crystalline state of compound (17) make it interesting to further explore this system.

Table 1. Summary data from DSC thermograms

	T _m (°C)	T _c (°C)
	(H, Cal/g)	(H, Cal/g)
(1)	108	135
	(26.78)	(0.27)
(4)	124	156
	(29.20)	(0.47)
(7)	192	238(Dec.)
	(27.25)	---
(14)	151	181
	(26.52)	---
(15)	114	146
	---	---
(16)	114 ---> 117 (?)	

Table 2. Solubility test of MCLs (7) and (10) at room temperature.

	NMP	DMSO	Acetone	Chloroform	CF ₃ CO ₂ H
(7)	N	N	N	N	S
(10)	S	S	N	S	S

N : not soluble S : soluble

Experimental:

Purification and Handlings of Laboratory Materials

4-Octyloxyaniline (99%; Aldrich) and 4-fluoronitrobenzene(99%; Aldrich) were vacuum distilled and stored in refrigerator. THF was distilled from CaH_2 and stored under Argon. 4-Nitrocinnamylidene (98%; Aldrich), 4-nitrophenol (99%: Aldrich), Hydrazine hydrate (hydrazine content 55%; Aldrich) and palladium on activated carbon (palladium content 5%; Aldrich) were used without further purification.

Synthesis

(4-Nitrocinnamylidene)-P-aminoctyloxybenzene (1): 4-Nitrocinnamylidene (0.995mmole) and 4-octyloxyaniline (0.995mmole) were heated at reflux for 2 hrs with 20mL of ethanol under argon atmosphere. Reaction vessel was cooled to room temperature. The yellow product was filtered and recrystallized with ethanol (0.220g; 60%). IR spectrum (KBr pellet); cm^{-1} : 1620, 1600, 1515. $^1\text{H-NMR}$ (CDCl_3); δ : 7.3-8.4(m, aromatic H's in $-\text{Ph-NO}_2$ and CH's in $-\text{CH=N-}$, 5), 6.6-7.3(m, aromatic H's in $-\text{Ph-O-}$ and CH's in $-\text{CH=CH-}$, 6), 0.6-2.2(m, $-(\text{CH}_2)_6-\text{CH}_3$, 15).

4-(6'-Hydroxyhexyloxy)nitrobenzene (2): Suspension of hexanediol (127mmole) and K_2CO_3 (1.8g) in 160 mL of DMAc was slowly heated to 160°C under argon atmosphere. Fluronitrobenzene (12.7mmole) in 30 mL of DMAc was slowly added through dropping funnel. Stir for 2 hrs before precipitated from distilled water. The crude yellow product was redissolved in chloroform and dried with MgSO_4 . Final product (m.p. $69-71^\circ\text{C}$) was obtained by removal of chloroform

followed by recrystallization with toluene. IR spectrum (KBr pellet); cm^{-1} : 3600-3200, 1610, 1600, 1510, 1350, 1260. $^1\text{H-NMR}$ (CDCl_3); δ : 6.8-7.4(m, aromatic H's ortho to $-\text{NO}_2$, 2), 6.6-7.2(m, aromatic H's meta to $-\text{NO}_2$, 2), 4.5-5.0(b, $-\text{OH}$, 1), 3.8-4.4(t, CH_2 's in $-\text{Ph-O-CH}_2-$, 2), 3.4-4.0(t, CH_2 's in $-\text{CH}_2-\text{OH}$, 2), 1.2-2.3(m, CH_2 's in $-\text{O-CH}_2-(\text{CH}_2)_4-\text{CH}_2-\text{OH}$, 8).

4-(6'-Hydroxyhexyloxy)aniline (3): 4-(6'-Hydroxyhexyloxy)nitrobenzene

(41.8mmole) and palladium on activated carbon (0.4g) were suspended in 100 mL of anhydrous ethanol under argon. Hydrazine hydrate (125.4mmole; 3.5 times) was slowly added through dropping funnel. Reaction vessel was slowly heated to reflux (heating rate 10°C/hr) for overnight. Filter through celite and ceramic filtration funnel before precipitating with distilled water. The crude product was recrystallized with toluene under argon (m.p. ; 80%). IR spectrum (KBr pellet); cm^{-1} : 3100-3450, 1510, 1240. $^1\text{H-NMR}$ (DMSO-d_6); δ : 6.4(aromatic H's,4), 3.8-4.3(b, $-\text{OH}$ and $-\text{NH}_2$, 3), 3.5-3.8(t, CH_2 's in $-\text{Ph-O-CH}_2-$, 2), 3.1-3.5(t, CH_2 's in $-\text{CH}_2-\text{OH}$), 0.7-2.0(b, CH_2 's in $-\text{CH}_2-(\text{CH}_2)_4-\text{CH}_2-$, 8).

(4-Nitrocinnamylidene)-p-(6'-hydroxyhexyloxy)aniline (4): Synthesis was

followed the procedure as described for monomer (1). Final product was recrystallized with toluene. IR spectrum (KBr pellet); cm^{-1} : 3160-3600, 1610, 1600, 1575, 1515, 1505, 1340, 1250. $^1\text{H-NMR}$ (CDCl_3); δ : 7.4-8.4(m, aromatic H's in $-\text{Ph-NO}_2$ and CH's in $-\text{CH=N-}$,5), 6.6-7.4(m, aromatic H's in $=\text{N-Ph-O-}$ and CH's in $-\text{CH=CH-}$, 6), 3.7-4.2(t, CH_2 'S in $-\text{Ph-O-CH}_2-$, 2), 3.5-3.7(t, CH_2 's in $-\text{CH}_2-\text{OH}$, 2), 1.0-2.1(M, CH_2 's in $-\text{CH}_2-(\text{CH}_2)_4-\text{CH}_2-$, 8).

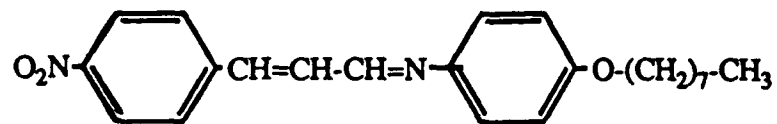
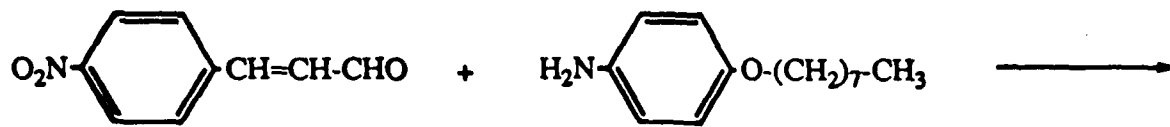
Dinitro compound (5), (8), (9) and (10) and their reduced diamino compounds (6), (11), (12) and (13): Diamino compounds were obtained from the reduction of their dinitro analogues. All of these procedures were described from recent literatural report⁴.

Dimer (7), (14), (15) and (16): Dimers were synthesized from the condensation of 4-nitrocinnamaldehyde and corresponding diamino compounds, (6), (11), (12) and (13). General procedure is refluxing two equivalents of 4-nitrocinnamaldehyde with one equivalent of diamino compounds in appropriate solvents for 4 hours. Except in the case of dimer (7), where THF was used as reaction solvent, ethanol was employed as solvent for the syntheses of dimer (14), (15) and (16). Dimer (7) was purified by recrystallized with NMP for three times. Dimer (14), (15) and (16) was recrystallized with ethanol.

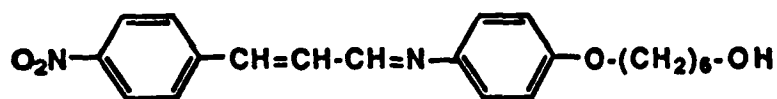
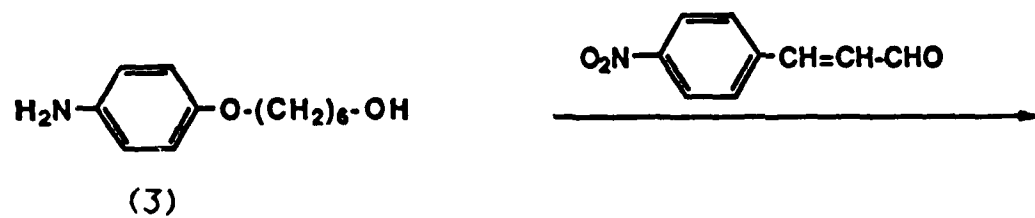
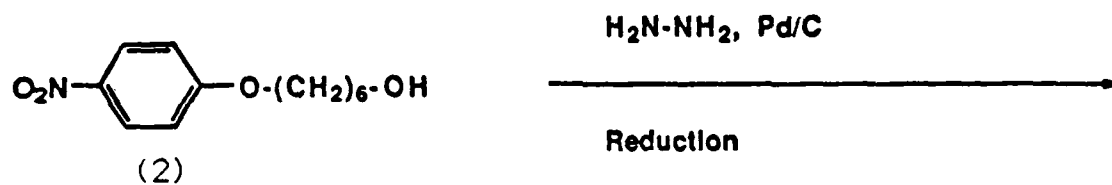
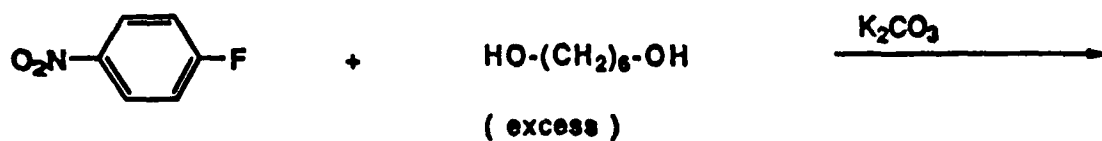
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- (4) Groffin, A. C. and Britt, T. R. J. Am. Chem. Soc. 1981, 103, 4957.

Scheme 1 Synthesis scheme of monomeric liquid crystals (MCL's).



(1)



(4)

Scheme 2. Synthesis scheme of dimeric liquid crystals (DCL's)

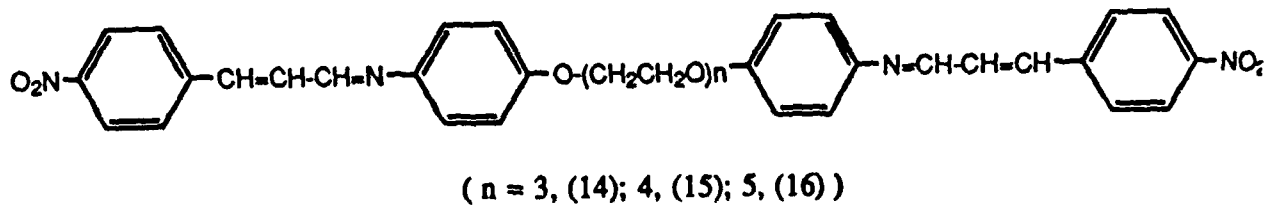
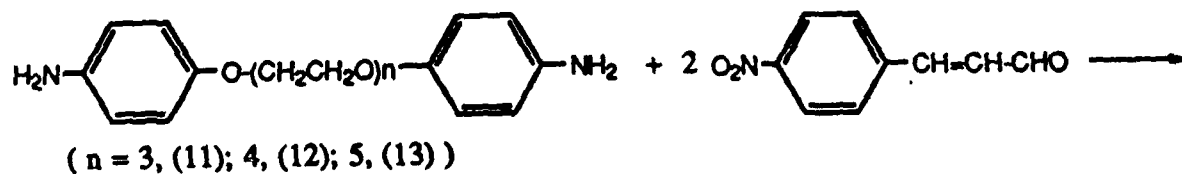
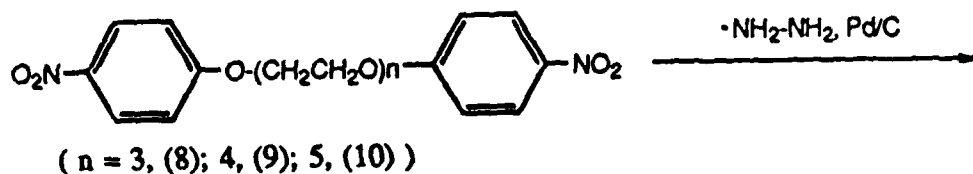
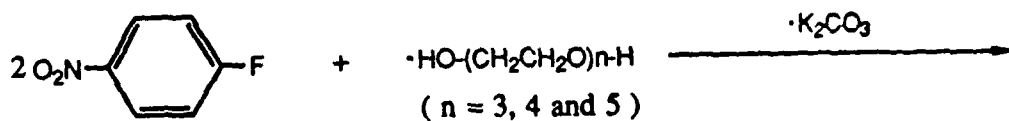
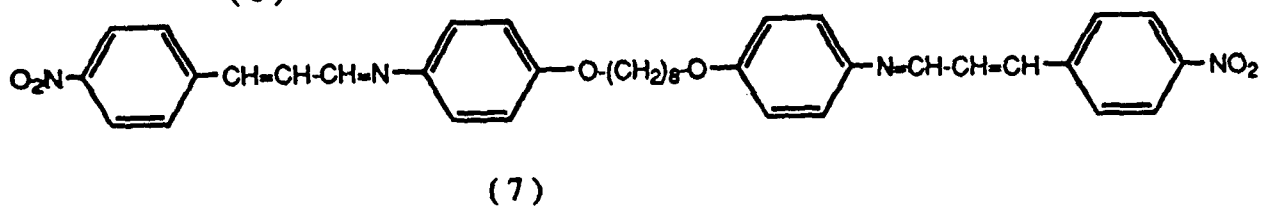
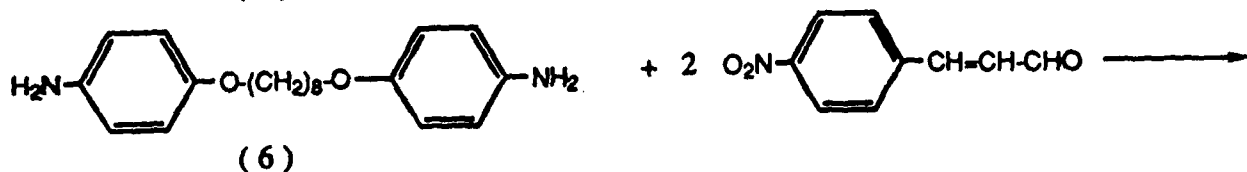
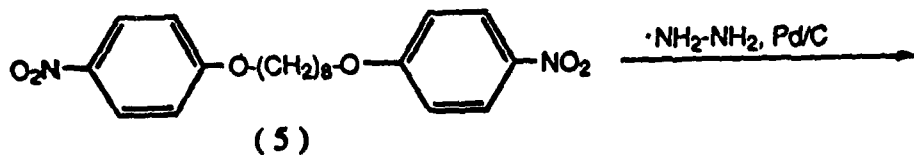
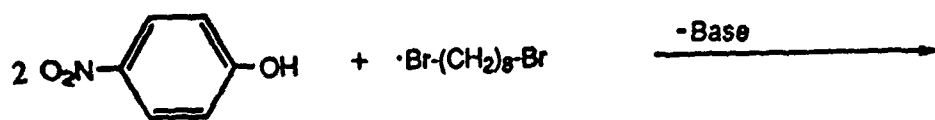
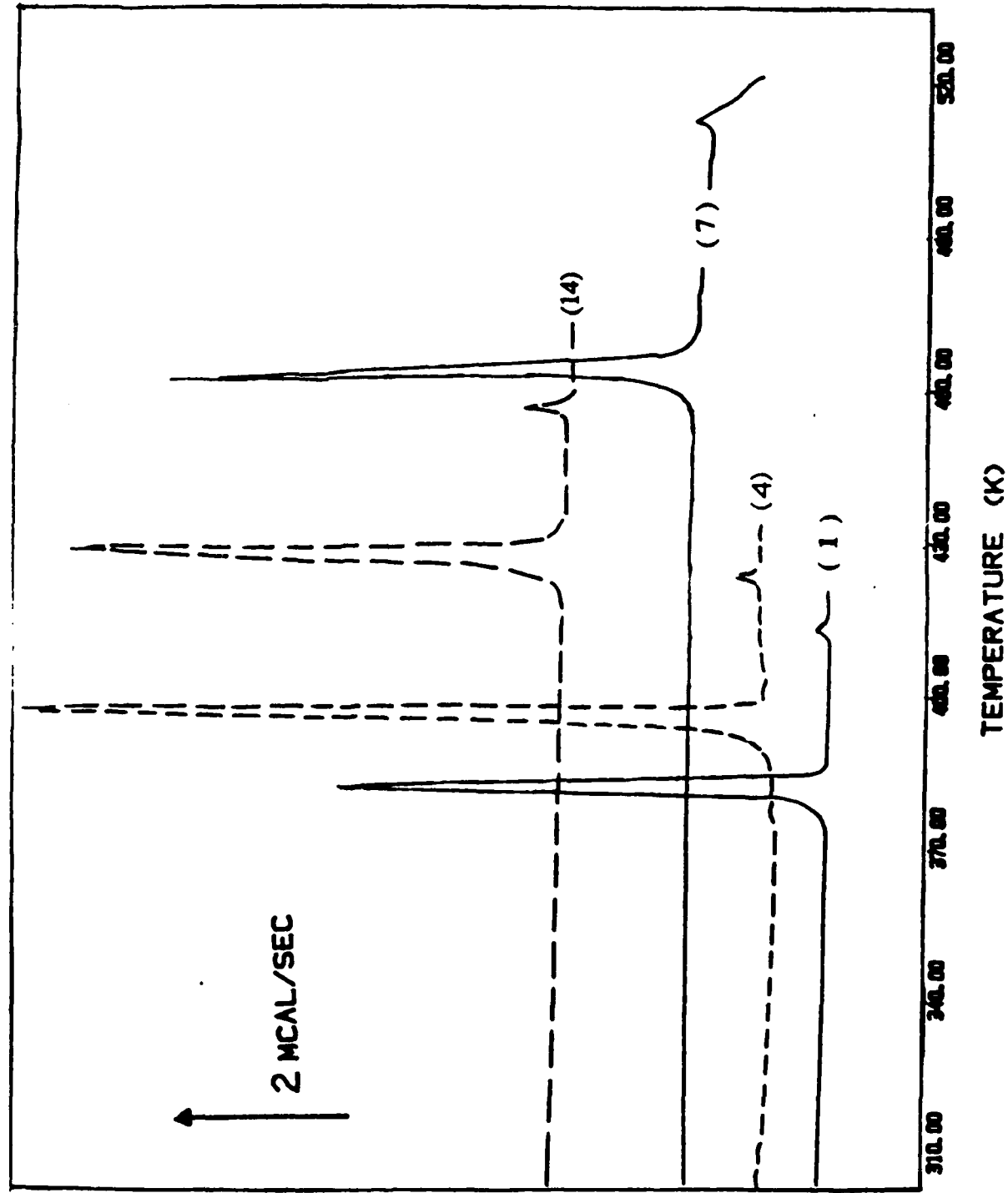


Fig. 1 DSC thermograms of compounds (1), (4), (7) and (14).



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