Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Synthesis of novel liquid crystal compounds with aromatic amide mesogenic cores

Dong Zhang; Qi-Feng Zhou; Yu-Guo Ma; Xin-Jiu Wang; Xin-Hua Wan; Xin-De Feng

To cite this Article Zhang, Dong , Zhou, Qi-Feng , Ma, Yu-Guo , Wang, Xin-Jiu , Wan, Xin-Hua and Feng, Xin-De(1997) 'Synthesis of novel liquid crystal compounds with aromatic amide mesogenic cores', Liquid Crystals, 23: 3, 357 — 363
To link to this Article: DOI: 10.1080/026782997208280
URL: http://dx.doi.org/10.1080/026782997208280

LIQUID CRYSTALS, 1997, VOL. 23, NO. 3, 357–363

Synthesis of novel liquid crystal compounds with aromatic amide mesogenic cores

by DONG ZHANG, QI-FENG ZHOU,* YU-GUO MA, XIN-JIU WANG,
XIN-HUA WAN, XIN-DE FENG

Institute and Department of Polymer Science and Engineering, College of
Chemistry, Peking University, Beijing 100871, P.R. China

(*Received 22 December 1994; in final form 20 March 1997; accepted 14 April 1997*)

The synthesis and properties of a new series of compounds having aromatic amide mesogenic cores are reported. Most of these new compounds are thermotropic mesogens. In consideration of the fact that aromatic amides form crystals of high melting point which is unfavourable for the formation of thermotropic liquid crystals, we make use of lateral substitution to decrease both the packing efficiency and the hydrogen bonding, so that the melting temperature of the aromatic amides is sufficiently depressed. The lateral substituent used in these new compounds is bromine. In order to investigate the influence on properties of the end groups, different alkoxy, alkyl and other groups are used at the two ends of the rod-like molecules. The two ends are either identical or different, with an electron-donating alkoxy as one end and the electron-accepting cyano group as the other. The results indicate that appropriate lateral and terminal substitution is essential for the aromatic amides to form thermotropic liquid crystals. The peculiar mesophase characterized by an X-ray diffraction pattern of a SmC phase, but a texture of a nematic phase is also noted.

1. Introduction

1,4-Phenylene rings are often found in the rod-like mesogenic cores of liquid crystalline compounds. Two 1,4-phenylene rings may be connected by a single covalent bond as in the cases of biphenyl and *p* terphenyl derivatives. Otherwise, they are connected by a linking group such as an ester, ether, methylene, imine, diazo, azoxy, ethylene, and others [1]. However, the amide linkage is considered undesirable for the formation of thermotropic liquid crystals. The extensive hydrogen bonding among the molecules of aromatic amides would result in too high a melting point. The hydrogen bonding may also interfere with the parallel molecular alignment that is required by liquid crystalline phases. It is for this reason that few compounds with only an amide linkage between 1,4-phenylene rings have been reported to form liquid crystals upon heating. Certain aromatic polyamides, such as *p*-polybenzamide and poly-1,4-phenylene terephthalamide, are able to form liquid crystals with solvents, but also lack thermotropicity.

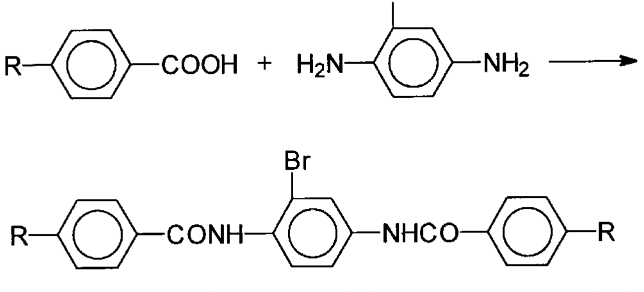
In this paper we report the synthesis and properties of a new series of low molar mass liquid crystalline compounds that are aromatic amides. We hope this new series of thermotropic liquid crystal compounds will not only enrich the family of known liquid crystals, but also be applicable in liquid crystal devices.

The synthesis and chemical structures of the compounds, **A**, having identical end groups (R) are given in scheme 1. Those for the compounds **B** having two different end groups (R_1 and R_2) are given in scheme 2.

2. Experimental

2.1. *Materials and synthesis of 2-bromophenylene-1,4-diamine*

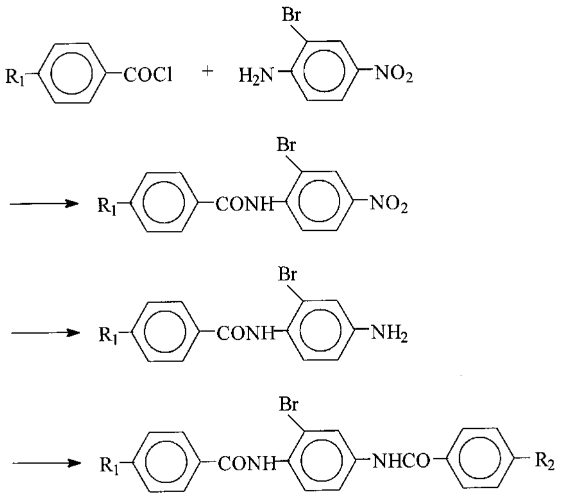
4-Substituted benzoic acids including 4-methoxy-, 4-ethoxy-, 4-propyloxy-, 4-butyloxy-, 4-pentyloxy-, 4-hexyloxy-, 4-heptyloxy-, 4-octyloxy- and 4-cyanobenzoic acids were from Aldrich. No further purification



Scheme 1. Synthesis and chemical structures of the liquid crystalline amides. R may be alkoxy, alkyl, nitro or cyano.

---

*Author for correspondence.



Scheme 2. Synthesis of the unsymmetrically substituted amides.

was applied before use. 4-(S)-2-(Methylbutyloxy)benzoic acid was synthesized according to reference [2].

2-Bromophenylene-1,4-diamine was synthesized by two steps.

Step 1: the synthesis of 2-bromo-4-nitroaniline [3]. 4-Nitroaniline (28 g, 0·20 mol) and concentrated hydrochloric acid (374 ml) were stirred and heated to obtain a solution which was quickly cooled to below 45°C. With stirring, bromine (11·0 ml, 0·21 mol) was slowly added dropwise. A yellow precipitate was formed as soon as the addition of bromine commenced. The addition was finished in about 3 h. The reaction was continued with stirring and warming for another 5 h. The system was then heated to boiling for about 10 min. The mixture was cooled and the precipitate was filtered off and washed in turn with water, sodium bicarbonate solution, and water to obtain a bright yellow product. After two recrystallizations from 95% ethanol, needle-like, bright yellow crystals were obtained. The product, 30 g (yield 70%), melted at 103–105°C (Beilstein: 104·5°C).

Step 2: synthesis of 2-bromophenylene-1,4-diamine. In a three-necked flask equipped with an electric stirrer and a condenser, iron powder (45 g, 0·80 mol), water (400 ml) and glacial acetic acid (5·8 ml) were heated to boiling for a few minutes. 2-Bromo-4-nitroaniline (20 g, 0·092 mol) was added. When the reaction had slowed down, a mixture of more 2-bromo-4-nitroaniline (17·5 g, 0·081 mol) and iron powder (10 g, 0·18 mol) was slowly added. After the addition the mixture was heated to boiling for 20 min. Ethanol (200 ml) and acetic acid (3 ml) were added, and the mixture was kept boiling for another 20 min. It was then filtered when it was still hot. Into the filtrate active carbon, sodium hydroxide (to pH 7–8) and a small amount of stannous chloride were added. The mixture was heated to boiling for 10 min. The hot solution was filtered and a light yellow solution was obtained. Upon cooling, partial concentration of the filtrate gave 20 g of needle-like white crystals (yield 62%) that melted at 73–76°C (literature [3]: 74–76°C).

2.2. *Synthesis of the amides*

All the amides with $R_1 = R_2$ were synthesized according to scheme 1 by reaction of the corresponding 4-substituted benzoic acid and 2-bromophenylene-1,4-diamine in the presence of triphenylphosphine/pyridine/hexachloroethane as catalyst [4]. The procedure is described below using the synthesis of 2-bromo-*N*,*N*′-bis-(*p*-ethoxybenzoyl)phenylene-1,4-diamine (compound **2**) as an example.

2-Bromophenylene-1,4-diamine (3·5 g, 0·019 mol), triphenylphosphine (11·5 g, 0·044 mol), hexachloroethane (12·5 g, 0·053 mol), 4-ethoxybenzoic acid (7 g, 0·042 mol), and dried pyridine (40 ml) were placed in a flask and stirred. The reaction was continued for 1 h. The mixture was then heated to boiling for a few minutes, and allowed to cool. The mixture was then poured into ice-water while stirring. The resulting precipitate, was then filtered off and washed in turn with deionized water, ether, benzene, and ethanol. The product was recrystallized from DMF/water with active carbon as decolourizer. A needle-like white product was obtained in a yield of 74% (6·8 g). It melted at 241°C and formed a liquid crystal phase which became isotropic liquid at 250°C. The elemental analysis gave (%) C: 59·79, H: 5·03, N: 5·70 (calc. C: 59·64, H: 4·80, N: 5·80). NMR (δ, ppm) of the product: 1·35–1·38 (6H, t, $2 \times CH_3$); 4·09–4·15 (4H, q, $2 \times CH_2$); 7·04–8·23, (11H, m, aromatic), 9·85, 10·27 (2H, s, $2 \times NH$).

When R_1 and R_2 are different (table 1, compounds **11** and **12**), three steps are needed to synthesize the compounds. In the first step, 2-bromo-4-nitroaniline and an equivalent amount of 4-R_1-benzoyl chloride (R_1 = ethoxy or CN) are reacted in the presence of pyridine to form 3-bromo-4-(*p*-R_1-benzamido)nitrobenzene. This product is then reduced by Fe/H^+ in DMF/H_2O to form 3-bromo-4-(*p*-R_1-benzamido)aniline. This aniline reacts in the third step with 4-R_2-benzoic acid (R_2 = CN or 4-(S)-2-methylbutoxy) to yield the unsymmetrically substituted amides by using a procedure similar to that described in the previous paragraph.

2.3. *Characterization techniques*

The proton NMR spectra were obtained with a Bruker ARX400 spectrometer by using d_6-DMSO as solvent and TMS as internal standard. The elemental analyses were obtained using Carlo Erba 1106. The mass spectra were taken with a VG-ZAB-HS. A Shimadzu DSC-50 differential scanning calorimeter (DSC) was used for determining the thermal transition temperatures which were taken as the maxima of the endothermic peaks. The heating rate was 10°C min^{-1}. A Leitz Laborlux 12 Pol polarizing optical microscope (POM) with a Leitz 350 heating stage was used for observing the thermal transitions and the mesomorphic textures. X-ray diffraction measurements were performed with a Philips PW-1700 powder diffractometer using CuK_α radiation. A combination of the results from the three techniques (DSC, POM, and X-ray) was used to confirm the existence of the liquid crystallinity.

3. Results and discussion

The structures of the compounds were confirmed, as exemplified in the synthesis of compound **2** in the previous section, by routine analyses including elemental analysis, mass spectrometry and ^{1}H NMR spectroscopy. Some of the results are collected in table 1.

The phase behaviour of each of the compounds **1**–**13** was assessed by DSC, POM and powder X-ray diffraction. The DSC and POM gave about the same results for the number of phase transitions, although the temperatures obtained from DSC were somewhat higher than those from polarizing optical microscopy. This difference stems from the fact that a higher heating rate (10°C per minute) was used in the DSC measurements and that the DSC transition temperatures were read at the maxima of the endothermic peaks. In the microscopic studies we had a better temperature control and were able to study the transitions carefully in repeated heating and cooling cycles of each sample. We believe that our data from the microscopic observations are closer to the equilibrium values than those from DSC. The results for the phase transitions are collected in table 2.

As noted in table 2, most of our aromatic amides (including the methoxy homologue) form one or two thermotropic liquid crystal phases. However, few other aromatic amides were previously known to form thermotropic liquid crystalline phases. The aromatic nature of the molecules and the strong hydrogen bonding formed among the amide groups usually give rise to a very high melting point. This is shown by comparison of the following two types of compound (the amides were also synthesized in this laboratory) that have similar structures except that the linking groups are different (figure 1). The ester does not need a long tail to show liquid crystallinity. The ester with methoxy as the two terminal groups already forms a nematic phase upon heating to above 213°C. The amide, on the other hand, has a much higher melting point than its ester counterpart. It does not form a liquid crystalline phase nor does the amide with $n=4$. A narrow thermotropic liquid crystal phase is observed only when the tails are sufficiently long ($n=10$), when the melting point is significantly lower.

The introduction of a bromine atom into the central phenylene ring enables the aromatic amides to form liquid crystalline phases. The lateral substitution on the mesogens brings about a decreased density of molecular packing and a weakened hydrogen bonding between amide groups. The melting temperatures of the aromatic amides are thus significantly depressed. For example,

Table 1. Analytical data for the compounds **A** and **B**. Compounds **11** and **12** are two unsymmetrically substituted members **B**: compound **11** is 2-bromo-4-(*p*-cyanobenzamido)-1-(*p*-ethoxybenzamido) benzene, compound **12** is 2-bromo-1-(*p*-cyanobenzamido)-4-(*p*-cyanobenzamido)-4-(*p*-(S)-2-methylbutyloxybenzamido) benzene.

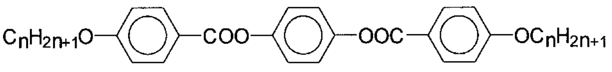
Compound	*R*	Formula	Mass	C/%	H/%	N/%
1	Methoxy	$C_{22}H_{19}O_4N_2Br$	455·31	58·07(58·04)[a]	4·37(4·21)	6·16(6·15)
2	Ethoxy	$C_{24}H_{23}O_4N_2Br$	483·36	59·79(59·64)	5·03(4·80)	5·70(5·80)
3	*n*-Propoxy	$C_{26}H_{27}O_4N_2Br$	511·39	61·27(61·06)	5·26(5·32)	5·33(5·48)
4	*n*-Butoxy	$C_{28}H_{31}O_4N_2Br$	539·47	62·28(62·34)	5·97(5·79)	5·06(5·19)
5	*n*-Pentyloxy	$C_{30}H_{35}O_4N_2Br$	567·49	63·49(63·49)	6·19(6·22)	4·69(4·94)
6	*n*-Hexyloxy	$C_{32}H_{39}O_4N_2Br$	595·54	64·22(64·53)	6·42(6·60)	4·61(4·70)
7	*n*-Heptyloxy	$C_{34}H_{43}O_4N_2Br$	623·60	65·58(65·48)	6·96(6·96)	4·22(4·49)
8	*n*-Octyloxy	$C_{36}H_{47}O_4N_2Br$	651·68	66·16(66·35)	7·37(7·27)	4·15(4·30)
9	Ethyl	$C_{24}H_{23}O_2N_2Br$	451·36	63·88(63·87)	5·15(5·14)	6·10(6·21)
10	*n*-Butyl	$C_{28}H_{31}O_2N_2Br$	507·47	66·43(66·27)	6·15(6·16)	5·40(5·52)
11	R_1: Ethoxy R_2: Cyano	$C_{23}H_{18}O_3N_3Br$	464·32	59·44(59·49)	3·84(3·91)	8·69(9·05)
12	R_1: Cyano R_2: (S)-2-methylbutoxy	$C_{26}H_{24}O_3N_3Br$	506·40	61·59(61·67)	4·81(4·78)	8·27(8·30)
13	Nitro	$C_{20}H_{13}O_6N_4Br$	485·24	49·01(49·51)	2·99(2·70)	12·10(11·55)

[a] Calculated figures in parentheses.

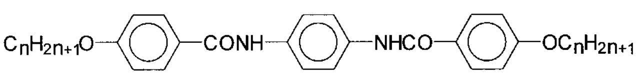
Table 2. Phase transitions of the compounds **A** and **B**. Cr: crystal; Sm: smectic; N: nematic; N*: cholesteric; I: isotropic; LC: liquid crystal.

		Phase transition data °C	
Compound	*R*	POM	DSC
1	Methoxy	Cr 246 LC 250 I	Cr_1 249 Cr_2 252 LC 255 I
2	Ethoxy	Cr 241 N 258 I	Cr 246 N 260 I
3	*n*-Propoxy	Cr 233 I (I 214 LC)[a]	Cr 239 I
4	*n*-Butoxy	Cr 227 I (I 217 LC)	Cr 230 I (I 219 LC 218C)
5	*n*-Pentyloxy	Cr 192 LC 202 I	Cr 197 LC 202 I
6	*n*-Hexyloxy	Cr 181 LC 202 I	Cr_1 169 Cr_2 186 LC 206 I
7	*n*-Heptyloxy	Cr 180 LC 187 N 198 I	Cr_1 155 Cr_2 186 LC 192 N 203 I
8	*n*-Octyloxy	Cr 167 LC 197 N 199 I	Cr_1 130 Cr_2 176 LC 202 N 203 I
9	Ethyl	Cr_1 183 Cr_2 213 I	Cr_1 190 Cr_2 221 I
10	*n*-Butyl	Cr 185-188 I	Cr_1 191 Cr_2 193 I
11	R_1: Ethoxy R_2: Cyano	Cr 242 SmA 280 I	Cr 249 SmA 289 I
12	R_1: Cyano R_2: (S)-2-methylbutoxy	Cr 207 N* 212 I	Cr 211 I
13	Nitro	Cr 334-337 I	Cr 360 I

[a] Data in parentheses were from cooling cycles.



Phase transitions of n=1: C 213 N 297 I [5]
n=4 C 156 N 253 I [6]
n=10: C 126·7 S 146·6 N 181·7 I [7]



Phase transitions of n=1: C 337 I
n=4 C 313 I
n=10: C 274 S 280 I

Figure 1. Comparison of aromatic amides and esters.

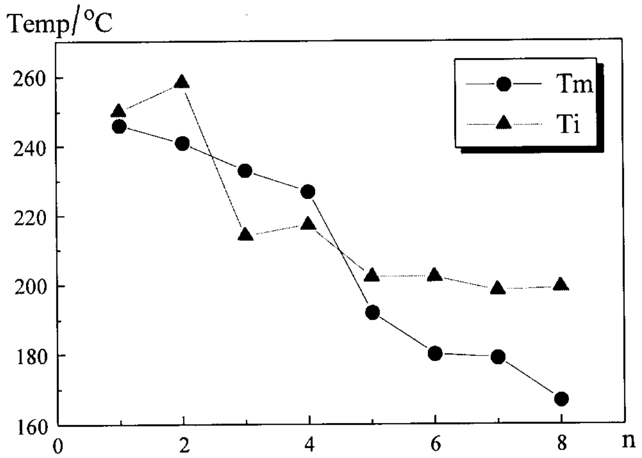


Figure 2. The melting and isotropization temperatures for the homologous compounds **1–8** (temperatures T_m and T_i, vs. number of carbon atoms, *n*, in the alkoxy tails).

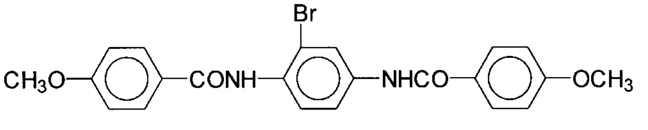
while the melting point of *N*,*N*′-bis(*p*-methoxybenzoyl)-phenylene-1,4-diamine (figure 1, $n=1$) is 337°C, the melting point of its laterally brominated counterpart (compound **1**, table 1) is only 246°C. Substituents other than bromine (e.g. nitro) have been tested and also proved applicable in generating liquid crystallinity in aromatic amides.

The compounds in table 2 can be divided into four categories according to their end groups. Those in the first group have alkoxy as molecular tails and form at very least metastable monotropic liquid crystals (compounds **1–8**). Figure 2 shows the variations of both the melting and the isotropization temperatures with increasing length of the alkoxy tails. All the compounds with alkoxy tails form enantiotropic phases except two which form only monotropic phases. The molecules in the second group have alkyl tails and do not form liquid crystals (compounds **9** and **10**; however, we have not synthesized and studied the homologues with longer alkyl tails). This behaviour is well known [1] because the alkoxy groups have a higher polarizability than alkyl groups. The third group with different tails at the two ends also form liquid crystalline phases (compounds **11** and **12**). The fourth group has nitro as the terminal groups and no liquid crystalline phase was observed above the melting point at 360°C (compound **13**).

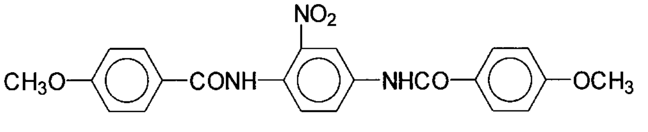
It is clear, therefore, that rod-like molecules with an aromatic amide core structure do have the potential to form thermotropic liquid crystals. However, it is necessary to have in the molecules appropriate terminal and lateral substitutions in order to realize this potential. Aromatic amides have a rod-like shape and significant polarizability as found in common liquid crystalline compounds. The factor hindering formation of a stable thermotropic liquid crystalline phase by amides is the strong tendency to hydrogen bond. The melting temperature (if it does melt) is much higher than in the case of common liquid crystalline compounds. Lateral substitution by a bulky atom (e.g. Br) or group (e.g. NO_2) separates the molecules from each other, resulting in a less dense packing and a lowered degree of hydrogen bonding. The melting point can in this way be depressed to such an extent that a stable mesophase is formed upon melting. The terminal substitution plays a similar role to the lateral substitution, but is probably less effective in separating the molecules.

In order to understand further the subtle effect of the lateral substituent on the formation of a thermotropic liquid crystalline phase, we also synthesized a few analogues that have the same methoxy end groups, but different lateral substituents, as shown in figure 3.

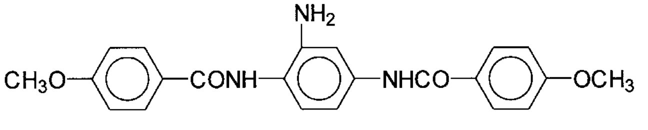
Compound **1** forms a smectic C phase in the temperature range of 246–250°C. When the bromine atom is replaced by a nitro group, compound **15** (figure 2) is obtained which forms a wider range smectic phase in the temperature range of 259–275°C. However, if the bromine atom is substituted by an amino group (compound **16**), the melting point (282–285°C) seems to be still too high for formation of a liquid crystalline phase. This is conceivable if the clearing temperatures (250°C and 275°C, respectively; both are below 280°C) of the liquid crystalline phases of the bromo- and the nitro-substituted compounds are considered. The amino group has two contradictory roles. It separates the molecular cores on the one hand, but on the other can play an active role in hydrogen bonding. The latter role would impair the effectiveness of the lateral substitution in depressing the melting point.



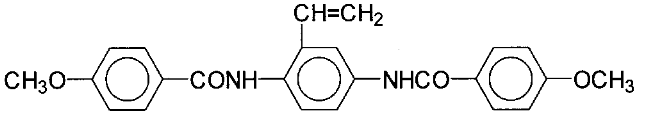
compound **1**: m.p.:246°C; smectic C; T_c: 250°C



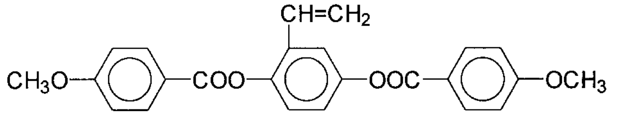
compound **15**: m.p.:259°C; smectic C; T_c: 275°C



compound **16**: m.p.:282-285°C; not liquid crystalline



compound **17**: m.p.:220°C; not liquid crystalline

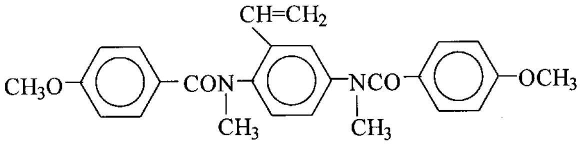


compound **18**: m.p.:184°C; nematic; T_c: 195°C

Figure 3. Several compounds related in molecular structure.

Gray [8] has emphasized the fact that, to cite him, 'although the molecule must contain groups which will give rise to suitably high intermolecular attractions, the basic requirement that the molecule should be essentially linear must not be sacrificed to any great extent. An increase in molecular breadth reduces the length-to-breadth ratio, and the rod-like molecule has moved at least some way towards becoming a spherical system which is structurally unsuitable for liquid crystalline behaviour.' 'The thermal stabilities of the mesophases of a liquid crystalline compound are likely to be high if dipolar or polarizable groups occur terminally or centrally in the rod-like molecules, but to be low if these occur along the side of the molecule and lead to any significant increase in the molecular breadth.' This structural effect was nicely demonstrated by 4-decyloxybenzoic acid and its 3-halogen-substituted analogues. The thermal stability measured by the temperature of the smectic-to-nematic (T_{SN}) transition, as well as the clearing temperature of the nematic phase (T_{NI}) was found to decrease with increase in size of the halogen. While the parent acid and its fluoro- and chloro-analogues are all liquid crystalline with, respectively, 122, 112 and 86°C as T_{SN} and 142, 116·5 and 90·5°C as T_{NI}, the most bulkily substituted bromo compound showed no sign of a mesophase. Another experiment showed that while the compound 4-(4″-hexadecyloxyphenyl)benzoic acid has T_{SI} 241·5°C, the T_{SI} of the 3′-chloro-, the 3′-bromo-, and the 3′-nitro-substituted analogues are, respectively 211, 202, and 198·5°C (ref [8], p. 154). With these examples one sees that the introduction of a lateral substituent generally decreases the thermal stability of a mesophase.

These principles should also apply to our system of aromatic amides. In fact, compound **17**, which has a bulky vinyl group as the lateral substituent, does not form a liquid crystalline phase upon melting. However, if one notes the liquid crystalline behaviour of 2,5-bis(4-methoxybenzoyloxy)styrene (compound **18**, nematic from 184–195°C), one can conclude that the non-mesomorphic behviour of compound **17** is simply a result of its very high melting point. The two compounds are very similar in structure. They are both aromatic with a rod-like shape. The length-to-breadth ratios of the two are also the same. The only difference is that in compound **18**, the ester linkage is used rather than the amide linkage which is found in compound **17**. This structural difference allows the ester to melt at a much lower temperature (184 compared with 220°C). Therefore, we believe compound **17** has potential to form a mesophase. The question thus arises: should compound **19** (structure below) be liquid crystalline?



There is no amide hydrogen to give hydrogen bonding in this compound. This compound has not yet been synthesized, and the *N*-methyl groups may of course prevent liquid crystalline behaviour through steric effects.

Returning to comparison of the bromo- and nitro-substituted compounds **1** and **15**, while the mesophase of the nitro-compound of Gray (cited above) has a lower thermal stability than that of the bromo-compound, the mesophase of our nitro compound **15** is higher than that of our bromo compound **1**. Our result cannot be reconciled with the size effect, because a nitro group is larger than a bromine atom. We tend to believe that in compound **15**, there exists some intramolecular hydrogen bonding as shown below.

Because rotation about the aromatic-N bond is now restricted, the molecules are expected to be much stiffer. The higher melting and clearing temperatures of the nitro substituted compound may thus be explained.

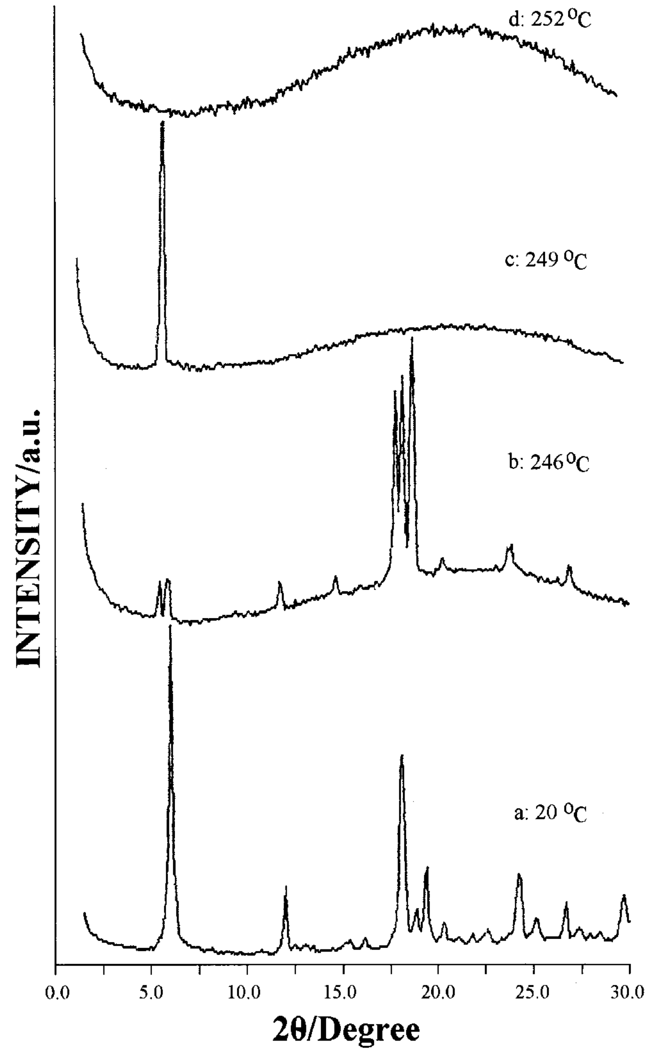


Figure 5. X-ray powder diffraction pattern of compound **1**.

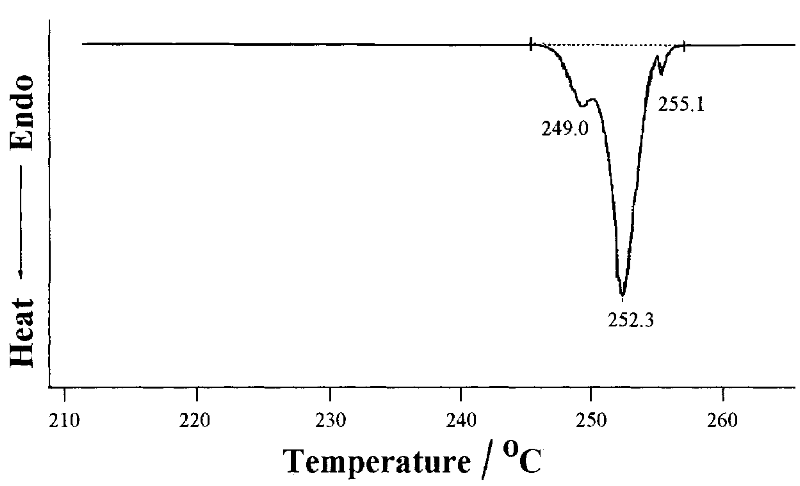
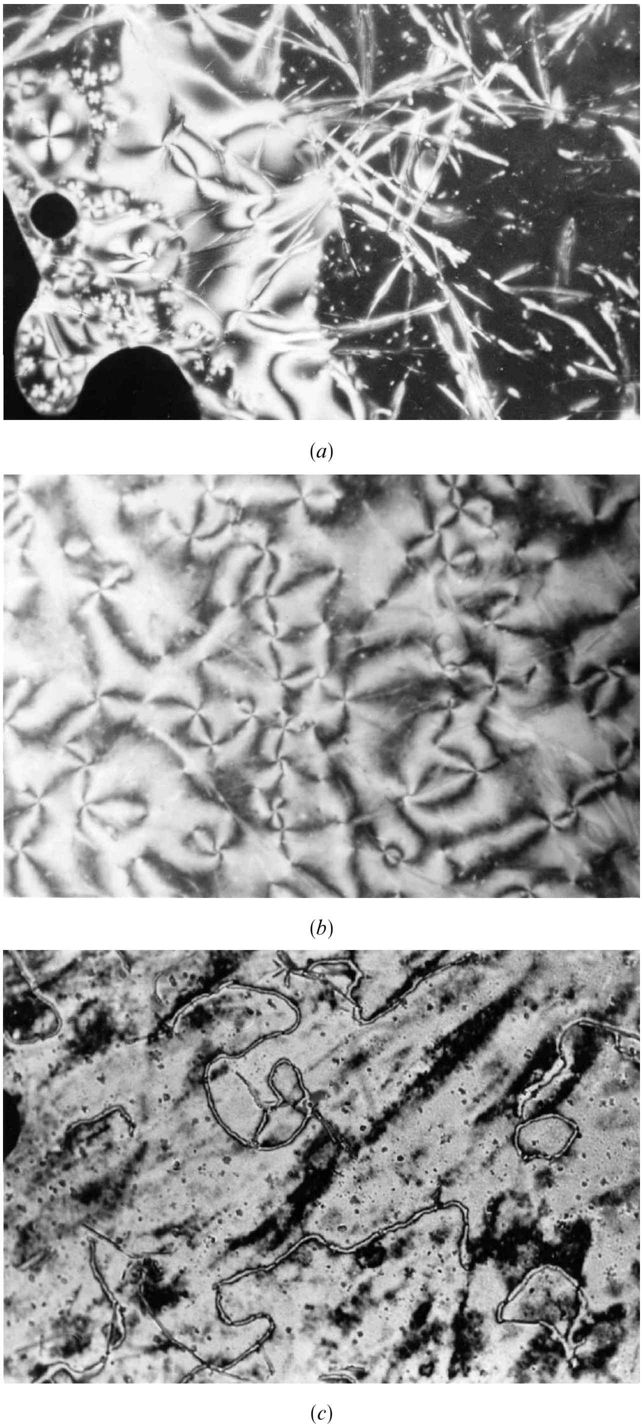


Figure 4. The DSC curve of compound **1**.

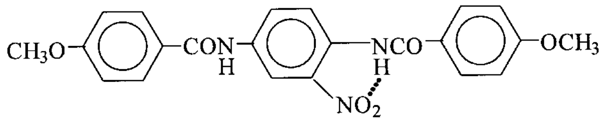


(*a*)

(*b*)

(*c*)

Figure 6. Microscopic textures of compound **1** (crossed polarities), (*a*) at 247°C, coexistence of the homeotropic and schlieren textures; (*b*) at 246°C, the schlieren texture; (*c*) at 236°C, the inversion wall texture.



It is interesting to note that many of the aromatic amides form a mesophase which is rather peculiar and is denoted simply by LC in table 2. As an example, figure 4 shows the DSC heating curve of compound **1** with three transition endotherms as noted in table 2. The first is the solid-to-solid transition, the second is the transition of the crystal to the LC phase which gives an X-ray diffraction pattern similar to a normal SmC phase (figure 5). The molecules form a layered structure with a tilt angle as large as 41·9°. However, when examined by polarizing optical microscopy this mesophase shows the textures usually observed in nematics. As an example, the mesophase of compound **1** gives not only a homeotropic texture, but also inversion walls and schlieren with singularities $s = \pm 1/2$ (figure 6). The full characterization of these mesophases of these new compounds will be published separately. As to why the ethoxy compound **2** does not have this SmC ordering and gives a simple nematic phase, we are not able to give an answer at present.

This work was supported by the National Natural Science Foundation of China.

References

[1] Kelker, H., and Hatz, R., 1980, *Handbook of Liquid Crystals* (Weinheim: Verlag Chemie), Chap. 2.

[2] Furniss, B. S., Hannaford, A. J., Smith, P. W. G., and Tatchell, A. R., 1989, *Vogel's Textbook of Practical Organic Chemistry*, 5th Edn. (Longman Scientific & Technical), p. 886.

[3] Nicolet, B. H., and Ray, W. L., 1927, *J. Am. chem. Soc.*, **49,** 1801.

[4] Wu, G. C., Tanaka, H., Sanui, K., and Ogata, N., 1982, *J. Polym.*, **14,** 571; **14,** 797.

[5] Dewar, M. J. S., and Goodberg, R. S., 1970, *J. org. Chem.*, **35,** 2711.

[6] Dewar, M. J. S., and Schroeder, J. P., 1965, *J. org. Chem.*, **30,** 2298.

[7] Arora, S. L., Fergason, J. L., and Taylor, T. R., 1970, *J. org. Chem.*, **35,** 4055.

[8] Gray, G. W., 1962, *Molecular Structure and the Properties of Liquid Crystals* (Academic Press), pp. 151–152.