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Mesomorphic behaviour of *N*,*N*′-dialkanoyl-2,3,5-trimethylbenzene-1,4-diamines and 2,3,5,6-tetramethylbenzene-1,4-diamines

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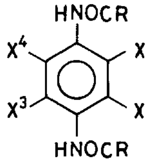
DSC and microscopic studies on several series of *N*,*N*′-dialkanoylbenzene-1,4-diamines are presented. The isotropization enthalpy is drastically reduced by the introduction of methyl groups into the aromatic nucleus. The trimethyl derivatives carrying octanoyl and nonanoyl groups generate metastable mesophases exhibiting a spherulitic texture; those carrying undecanoyl-to-octadecanoyl groups generate metastable or stable nematic phases exhibiting schlieren textures. The addition of the fourth methyl group to the nucleus results in an increase in the order of molecular arrangement and the enhancement of the thermal stability. A fingerprint texture is observed for many members of the tetramethyl derivatives and a transient schlieren texture for the octadecanoyl member.

1. Introduction

As reported in our previous papers, the enthalpy change at the transition into an isotropic liquid of *N*,*N*′-dialkanoylbenzene-1,3-diamine is considerably diminished by methyl substitution of the aromatic nucleus, and various mesomorphic states are produced by this approach [1, 2]. While the 2-methyl derivatives with decanoyl-to-octadecanoyl groups exhibit disordered hexagonal columnar phases, the 2,4,6-trimethyl derivatives with octanoyl-to-octadecanoyl groups yield nematic phases, and the 2,4,5,6-tetramethyl derivatives generate more ordered phases. X-ray diffraction studies on the trimethyl derivatives carried out by Malthête *et al.* revealed that the amide groups induce mesogenic infinite polymeric threads by hydrogen bonding; these, in turn, arrange in a nematic phase [3]. The presence of one substituent more bulky than a hydrogen, close to an amide group, was suggested to be the requirement for producing mesomorphic threads. Since then many more mesogenic compounds derived from *N*,*N*′-dialkanoylbenzene-1,3-diamines have been prepared [4–10]. In this paper, we describe efforts to obtain mesomorphic compounds based on *N*,*N*′-dialkanoylbenzene-1,4-diamines by the incorporation of methyl groups into the aromatic nucleus. We were particularly interested in finding out whether mesophases formed by these rod-shaped molecules are columnar or not.

The structures of the compounds investigated are given below.



$R = C_nH_{2n+1}$

I $X^1 = X^2 = X^3 = X^4 = H$

II $X^1 = CH_3, X^2 = X^3 = X^4 = H$

III $X^1 = X^4 = CH_3, X^2 = X^3 = H$

IV $X^1 = X^2 = X^3 = CH_3, X^4 = H$

V $X^1 = X^2 = X^3 = X^4 = CH_3$

2. Results and discussion

2.1. *Unsubstituted compounds* (*I*)

As summarized in table 1, the unsubstituted compounds exhibit two or three solid–solid transitions above 100°C and are transformed into isotropic liquids above 184°C. The enthalpy change upon melting ranges from 60 to 68 kJ mol^{-1}. The corresponding entropy changes are 127 to 146 J mol^{-1} K^{-1}. Hydrocarbons of the same chain length as the employed terminal alkyl groups are known to have the following entropies of melting: undecane, 90 J mol^{-1} K^{-1}; tridecane, 106 J mol^{-1} K^{-1}; pentadecane, 122 J mol^{-1} K^{-1}; heptadecane, 137 J mol^{-1} K^{-1} [11]. As the present compounds carry two alkyl groups, the conformational melting in the high temperature phases

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Table 1. Transition temperatures (T/°C) and associated enthalpies (ΔH/kJ mol^{-1}) for N,N'-dialkanoylbenzene-1,4-diamines. n is the number of carbon atoms in the alkyl group.

n	Cr_4		Cr_3		Cr_2		Cr_1		M		I
Unsubstituted compounds											
11			•	108(16)	•	172(6)	•	199(60)			•
13			•	123(23)	•	161(6)	•	193(68)			•
15			•	114(21)	•	159(8)	•	187(64)			•
17	•	102(20)	•	139(6)	•	172(6)	•	184(61)			•
2-Methyl compounds											
11					•	120(18)	•	153(30)			•
13					•	118(22)	•	148(31)			•
15			•	120(13)	•	127(15)	•	145(27)			•
17					•	95(30)	•	142(33)			•
2,6-Dimethyl compounds											
11							•	116(47)	•	128(13)	•
13							•	113(47)	•	121(12)	•
15							•	117(82)			•
17							•	114(62)			•

is supposed to be appreciable. Consequently, N,N'-dialkanoylbenzene-1,4-diamines would seem to be potential parent compounds for mesogenic derivatives.

2.2. *2-Methyl derivatives (**II**)*

The thermal properties of four 2-methyl derivatives are presented in table 1. The effect of a lateral methyl group on the phase behaviour is very striking. The substituent causes the lowering of the melting point by 40°C or more relative to the unsubstituted compound. The change may be an indication that the molecular long axes are forced apart by the methyl group reducing the intermolecular forces of attraction. The associated enthalpy change is diminished by a factor of about two.

2.3. *2,6-Dimethyl derivatives (**III**)*

The transition temperatures and associated enthalpy changes of the 2,6-dimethyl derivatives are also listed in table 1. While the introduction of the second methyl group lowers further the isotropization temperature, the effect on the enthalpy change is not straightforward. The enthalpy is decreased again by a factor of about two for the dodecanoyl and tetradecanoyl members (n = 11, and 13) but is markedly increased for the hexadecanoyl and octadecanoyl members (n = 15 and 17). The high temperature phases appearing in the former compounds produce bright birefringent films when a sample placed between two glass plates is pressed and examined through crossed polarizers. On cooling the isotropic melt, a spherulitic texture develops gradually from the homeotropic regions. These high temperature phases are tentatively considered to be mesomorphic but their nature is subject to further investigation. The melt of the hexadecanoyl member could be supercooled and the emergence of another phase with an enthalpy change of 12 kJ mol^{-1} was observed around 100°C; no metastable mesophase was detected for the octadecanoyl member.

2.4. *Trimethyl derivatives (**IV**)*

The thermal properties of the trimethyl derivatives are recorded in table 2. Both the enthalpy change at the isotropization and the fluidity of the high temperature phase are similar to those of the dodecanoyl and tetradecanoyl members (n = 11 and 13) of the dimethyl derivatives. Therefore, the lower transition temperature in the present series may be regarded as a melting point and the higher one as a clearing point. If this assignment is correct, the clearing point is greatly raised by the addition of the third methyl group, whereas the melting

Table 2. Transition temperatures (T/°C) and associated enthalpies (ΔH/kJ mol^{-1}) for N,N'-dialkanoyl-2,3,5-trimethylbenzene-1,4-diamines. n is the number of carbon atoms in the alkyl group.

n	Cr		M		N		I
5	•	259(33)					•
6	•	180(14)	•	239(24)			•
7	•	126(23)	•	227(20)			•
8	•	137(31)	•	214(19)			•
9	•	121(30)	•	204(17)			•
10	•	125(38)	•	194(17)	[•	*c.* 192]^{ab}	•
11	•	124(39)	•	189(15)	[•	184(1.0)]^{a}	•
13	•	126(50)	•	174(17)	•	174(0.6)	•
15	•	127(61)	•	162(18)	•	163(0.6)	•
17	•	122(60)	•	153(17)	•	154(0.5)	•

[a] Monotropic transition.
[b] Microscopic observation.

point is only slightly affected. On the basis of the thermal behaviour observed in the process of cooling, the homologous members may be classified into the following three groups.

2.4.1. *n* = *5 to 8*

The hexanoyl to nonanoyl members ($n = 5$ to 8) exhibit metastable mesophases, the associated enthalpy change being about a half that of the stable high temperature phase. For example, the heptanoyl member ($n = 6$) gives two exothermic peaks on cooling:

$$\mathrm{M}_2' \xleftarrow{221(10)} \mathrm{M}_1' \xleftarrow{237(11)} \mathrm{I}. \quad (^\circ\mathrm{C})$$

A rod-shaped texture develops with the coexistence of small spherulites from the isotropic melt. On further cooling, the former texture turns irreversibly into a striped rod-shaped texture.

The next two homologous members ($n = 7$ and 8) give well developed spherulitic textures on cooling, as exemplified by the octanoyl member ($n = 7$).

$$\mathrm{M}_2' \xleftarrow{215(10)} \mathrm{M}_1' \xleftarrow{226(9)} \mathrm{I}. \quad (^\circ\mathrm{C})$$

The texture of the M_1' phase changes during the M_1'–M_2' transition into concentric rings, see figures 1 (*a*) and 1 (*b*). Such textures are known to be characteristic of either rectangular or oblique columnar phases [12, 13].

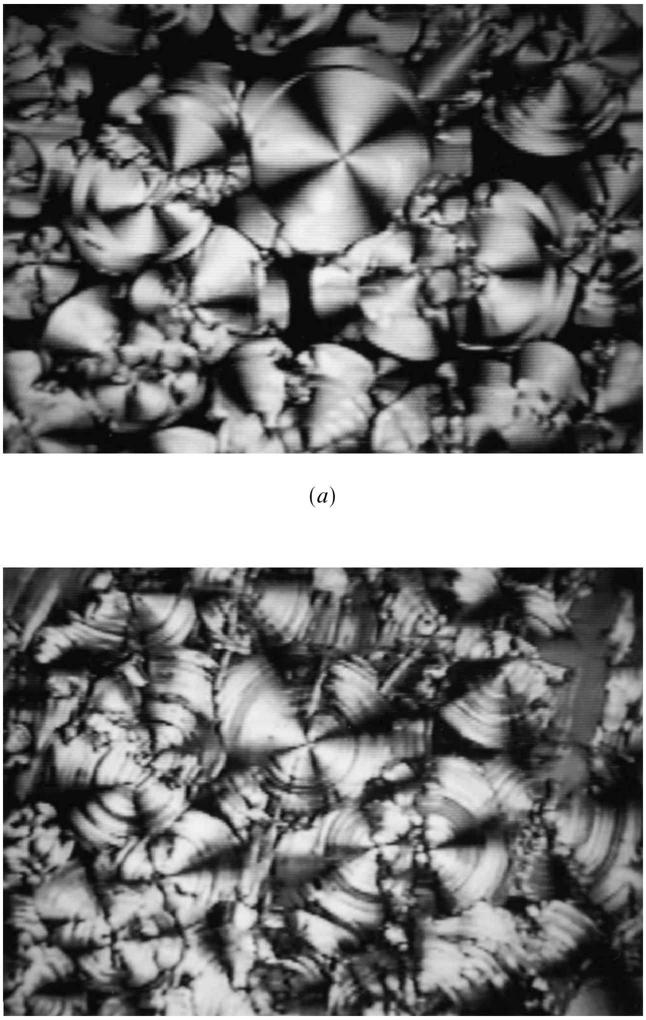
2.4.2. *n* = *9,10*

On the thermogram, nothing new could be detected on cooling isotropic melts of the decanoyl and undecanoyl members ($n = 9$ and 10), although supercooling by as much as 6–7°C occurs. However, the latter compound exhibits a metastable nematic phase with a schlieren texture which is so unstable that it could be observed visually only when the isotropic melt was cooled quickly.

2.4.3. *n* = *11 to 17*

The nematic–isotropic transition given by the dodecanoyl and higher homologous members ($n = 11$ to 17) were recorded by a differential scanning calorimeter at a cooling rate of $5\,\mathrm{K\,min^{-1}}$. The phase assignment is supported by enthalpy changes as small as 0.5–$1.0\,\mathrm{kJ\,mol^{-1}}$. The phase appearing below the nematic phase of these four members may be the thermodynamically stable one, judging from the magnitude of the enthalpy changes.

The nematic phase of the hexadecanoyl member ($n = 15$) of the present compound was proved to be miscible with the nematic phase of the corresponding member of the 1,3-diamine analogue, employing contact preparations. Although the mesophase of the reference compound is stable between 109 and 176°C [1, 2], the mixed region is dark when the 1,4-diamine derivative begins to show a schlieren texture around 163°C. These two mesophases merged when the specimen was cooled to about 155°C. We deduce that the nematic phase generated by linear 1,4-diamine molecules is of the same kind as that generated by bent 1,3-diamine molecules, i.e. the phase is discotic in type and is formed by hydrogen-bonded polymeric threads. In the mixed region, a thread might be composed of both the 1,3- and 1,4-diamine molecules.



(*a*)

(*b*)

Figure 1. Microscopic textures observed for (*a*) the M_1' phase of the octanoyl derivative ($n = 7$) of the trimethyl compound at 218°C; (*b*) the M_2' phase at 215°C

2.5. *Tetramethyl derivatives* (**V**)

The thermal properties of the tetramethyl derivatives listed in table 3 demonstrate the significant effects of the number of lateral methyl groups on phase behaviour. The isotropization temperature is as high as 312°C for

Table 3. Transition temperatures (T/°C) and associated enthalpies (ΔH/kJ mol^{-1}) for N,N'-dialkanoyl-2,3,5,6-tetramethylbenzene-1,4-diamines. n is the number of carbon atoms in the alkyl group.

n	Cr_2		Cr_1		M_2		M_1		I
5			•	312(35)					•
6			•	297(20)			•	309(25)	•
7	•	135(6)	•	256(16)	•	265(7)	•	300(23)	•
8	•	152(15)	•	218(12)	•	254(10)	•	295(23)	•
9	•	148(22)	•	213(15)	•	249(10)	•	287(22)	•
10			•	152(41)	•	242(11)	•	275(17)	•
11			•	144(40)	•	237(11)	•	263(16)	•
13			•	141(52)	•	235(11)	•	241(12)	•
15			•	139(59)			•	225(22)	•
17			•	113(21)			•	216(24)	•

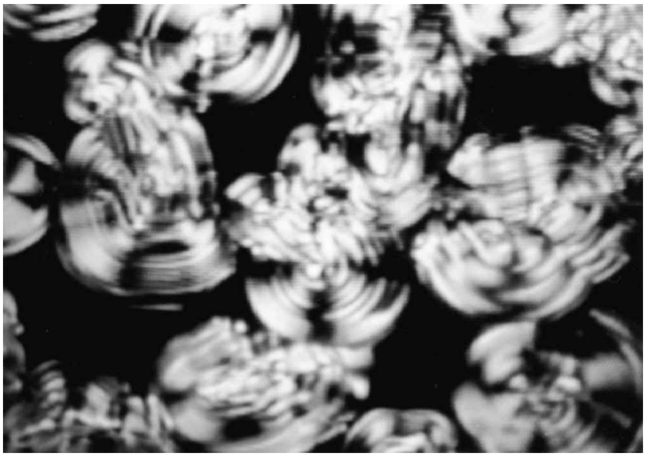


Figure 2. Microscopic texture observed for the M_1 phase of the undecanoyl derivative ($n = 10$) of the tetramethyl compound at 267°C.

the heptanoyl member ($n = 6$) and decreases gradually to 216°C for the octadecanoyl member ($n = 17$). A great enhancement of lateral intermolecular interaction, by the introduction of the fourth methyl group into the aromatic nucleus, may be primarily attributed to increased polarizability and uniform molecular thickness, both of which may help more regular stacking. The incidence of polymorphism above room temperature is high in these compounds; that is, the undecanoyl, dodecanoyl and tetradecanoyl members ($n = 10$, 11, and 13) are trimorphic, and the octanoyl to decanoyl members are tetramorphic ($n = 7$ to 9).

These phases appear at such high temperatures that no detailed work on them was possible. The second moment of the broad-line proton NMR spectrum measured at 195°C, the highest temperature attainable with our instrument, is of the order of $0.1\ G^2$ for the dodecanoyl, tetradecanoyl, and hexadecanoyl members ($n = 11$, 13, and 15). This is of the same order of magnitude as that given by the disordered hexagonal columnar phase of N,N'-dioctanoyl-2,3,5,6-tetrakis (octanoyloxy)benzene-1,4-diamine [14]; therefore, these highest and second highest temperature phases may be classified as mesophases.

On cooling the isotropic melt of the octanoyl member ($n = 7$), a rod-shaped texture similar to that given by the heptanoyl member of the trimethyl derivatives with a coexisting focal conic texture was observed. The highest temperature phase given by the decanoyl to tetradecanoyl members ($n = 9$ to 13) may be rectangular or oblique because they produce a finger-print texture (see figure 2). In addition, when the isotropic melt of the octadecanoyl member ($n = 17$) is rapidly cooled, the appearance of a transient schlieren texture was observed.

3. Conclusions

Mesogenic benzene-1,4-diamine derivatives can be obtained by the introduction of methyl groups into the aromatic nucleus. A schlieren texture is exhibited by the trimethyl derivatives of N,N'-dialkanoylbenzene-1,4-diamime when the alkanoyl groups are sufficiently long, and also by the tetramethyl derivative carrying octadecanoyl groups. As the phase is miscible with the nematic phase given by the 1,3-diamine analogue described earlier, it must be formed by hydrogen-bonded polymeric threads and be discotic in type. However, the temperature range of stability is much narrower than for the 1,3-diamine analogues. The more ordered mesophases produced by the other members show striped rod-shape, concentric ring, or finger-print textures, suggesting that they are either rectangular or oblique columnar. Apparently, the present rod-shaped molecules are unfavourable to the formation of a highly symmetric mesophase.

4. Experimental

Alkanoyl chlorides, benzene-1,4-diamine, 2-methylbenzene-1,4-diamine, durenediamine, 1,5-dimethylphenol, and 1,2,5-trimethylphenol were commercially available.

An aqueous sodium nitrite solution was added dropwise to 0.1 mol of 1,2,5-trimethylphenol dissolved in a warm mixture of ethanol and equal volume of concentrated hydrochloric acid. 2,3,6-Benzoquinoneoxime was deposited as yellow crystals after standing for a few hours. The mono-oxime was dissolved in a mixture of ethanol and pyridine and then heated under reflux with hydroxylamine for 3 h, following the procedure of Bachmann and Boatner [15]. The dioxime thus prepared was reduced to 2,3,5-trimethylbenzene-1,4-diamine with iron powder in boiling aqueous ethanol by dropwise addition of hydrochloric acid, as described by Mahood and Schaffner [16]. 2,6-Dimethylbenzene-1,4-diamine was prepared similarly. The reaction of benzene-1,4-diamine or its methyl derivative with the appropriate alkanoyl chloride in a mol ratio of 1:2 in benzene in the presence of pyridine produced the desired *N*,*N*′-dialkanoylbenzene-1,4-diamine. Elemental analysis: calc. for $C_6H_4(NHCOC_{17}H_{35})_2$, C 78.69, H 11.95, N 4.37; found, C 78.68, H 11.92, N 4.51%: calc. for $C_6H_3(CH_3)(NHCOH_7H_{15})_2$, C 73.75, H 10.23, N 7.48; found, C 73.75, H 10.37, N 7.44%: calc. for $C_6H_2(CH_3)_2(NHCOC_9H_{19})_2$, C 75.63, H 10.88, N 6.30; found, C 75.77, H 10.99, N 6.24%: calc. for $C_6H(CH_3)_3(NHCOC_{11}H_{23})_2$, C 76.99, H 11.99, N 5.44; found, C 76.90, H 11.44, N 5.48%: calc. for $C_6(CH_3)_4(NHCOC_9H_{19})_2$, C 76.22, H 11.09, N 5.93; found, C 76.17, H 11.20, N 6.08%.

Mesomorphic behaviour was examined visually with a Yanaco melting point apparatus, model PV-500V, with the aid of a polarizing microscope (magnification 60×) combined with a video recorder for recording monotropic phase transitions and metastable phases. The transition temperatures and associated enthalpies were determined by a Rigaku Thermoflex differential scanning calorimeter at heating and cooling rates of 5 K min^{-1}. Proton NMR spectra were measured using a JEOL model JES-ME-3X spectrometer with a broad-line NMR attachment, model JES-BE-1.

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