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Mesomorphic behaviour of *N,N'*-dialkanoyl-3,4,5,6-tetramethylbenzene-1,2-diamines and related compounds

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DSC, X-ray, broad-line proton NMR, and microscopy studies on several series of *N,N'*-dialkanoylbenzene-1,2-diamines are presented. The melting point and associated enthalpy are not much affected by methylation of the aromatic nucleus. While the dimethyl compounds carrying heptanoyl-to-hexadecanoyl groups generate metastable mesophases below 111°C, the 3,4,5,6-tetramethyl compounds carrying propionyl-to-hexadecanoyl groups produce stable hexagonal columnar mesophases appearing mostly above 200°C. *N,N'*-dialkylbenzene-1,2-carboxamides are transformed into birefringent viscous fluids exhibiting a focal-conic texture at a temperature between 76 and 99°C when the alkyl groups are decyl, undecyl, dodecyl, and tetradecyl.

1. Introduction

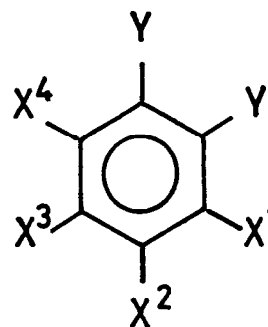
The enthalpy change at the isotropization of *N,N'*-dialkanoylbenzene-1,3- and -1,4-diamines has been found to be drastically diminished by methylation substitution of the aromatic nucleus, and various mesomorphic states can be generated by this approach [1–4]. In these two diamine series, the trimethyl compounds yield nematic phases when the alkanoyl group is long enough and the tetramethyl compounds produce more ordered viscous fluids. We will report here attempts to obtain mesomorphic compounds based on *N,N'*-dialkanoylbenzene-1,2-diamine by employing the same approach.

Furthermore, our earlier work revealed that *N,N',N''*-trialkylbenzene-1,3,5-tricarboxamides carrying pentyl or longer alkyl groups exhibit hexagonal disordered columnar mesophases, the temperature range of which extends over 100°C; but the 1,3- and 1,4-dicarboxamides are not mesogenic [5, 6]. In this paper, we will demonstrate that the 1,2-analogous show mesophases although the number of homologous members is limited and the temperature range is narrow.

The structures of the series of compounds studied are as follows:

- I $X^1 = X^2 = X^3 = X^4 = H$, $Y = \text{NHCOC}_n\text{H}_{2n+1}$
- II $X^2 = \text{CH}_3$, $X^1 = X^3 = X^4 = H$, $Y = \text{NHCOC}_n\text{H}_{2n+1}$
- III $X^2 = X^3 = \text{CH}_3$, $X^1 = X^4 = H$, $Y = \text{NHCOC}_n\text{H}_{2n+2}$
- IV $X^1 = X^2 = X^3 = X^4 = \text{CH}_3$, $Y = \text{NHCOC}_n\text{H}_{2n+1}$
- V $X^1 = X^2 = X^3 = X^4 = H$, $Y = \text{CONHC}_n\text{H}_{2n+1}$.

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2. Results and discussion

2.1. *N,N'*-Dialkanoylbenzene-1,2-diamines (I)

The thermal behaviour of the hexadecanoyl ($n = 15$) and octadecanoyl members ($n = 17$) given in table 1 differs markedly from that of the corresponding members of the 1,3- and 1,4-diamines. The melting points are lower than those of the 1,3-diamines (about 130°C) and also of those of the 1,4-diamines (about 180°C). The associated enthalpies are smaller by a factor of three to four than those of the structural isomers.

2.2. 4-Methyl derivatives (II)

The melting point is lowered a little by this structural modification. In contrast to the 1,3- and 1,4-diamines, the enthalpy of melting is unaffected by methylation of the aromatic nucleus. The high temperature phases of the unsubstituted and the methyl compounds produce bright birefringent films when a sample placed between two glass plates is strongly pressed and examined through crossed polarizers. No further examination was made on them and they are classified as solids in table 1.

Table 1. Transition temperatures T ($^{\circ}\text{C}$) and associated enthalpies ΔH (kJ mol^{-1}) for N,N' -dialkanoylbenzene-1,2-diamines. n is the number of carbon atoms in the alkyl group.

n	Cr_3	Cr_2	Cr_1	M	I
<i>Unsubstituted compounds</i>					
15		• 94 (78)	• 115 (32)		•
17		• 103 (45)	• 112 (30)		•
<i>4-Methyl compounds</i>					
15		• 85 (50)	• 104 (29)		•
17		• 86 (41)	• 104 (30)		•
<i>4,5-Dimethyl compounds</i>					
5			• 140 (32)		•
6		• 128 (5)	• 134 (31)	[• 108 (16)] ^a	•
7			• 118 (29)	[• 108 (15)] ^a	•
8	• 59–82 (26)	• 110 (7)	• 117 (22)	[• 110 (21)] ^a	•
9	• 67–85 (17)		• 104 (34)	[• 99 (18)] ^a	•
10	• 63–72 (19)		• 114 (34)	[• 111 (17)] ^a	•
11	• 76–85 (37)		• 116 (38)	[• 111 (17)] ^a	•
13	• 70–84 (45)		• 116 (39)	[• 111 (18)] ^a	•
15	• 74–109 (49)		• 115 (33)	[• 110 (19)] ^a	•
17	• 89–102 (26)		• 113 (34)		•

^a Monotropic transition.

2.3. 4,5-Dimethyl derivatives (III)

The melting point and associated enthalpy remain essentially the same as those of the unsubstituted compound. Nevertheless, the heptanoyl ($n = 6$)-to-hexadecanoyl ($n = 15$) members exhibit metastable mesophases. The enthalpy of monotropic transition is about half that of melting. The nonanoyl member ($n = 8$) is exceptional: that is, the enthalpy of melting agrees with that of the monotropic transition. This agreement is not due to the delayed solidification of the melt because the X-ray diffraction patterns of these two phases are different.

The X-ray diffraction pattern of the high temperature phase is dominated by two sharp inner peaks and a broad outer peak. The longest spacing (d_1) in the higher temperature phase is approximated by $d_1/\text{nm} = 1.72 + 0.208n$ and the second-longest spacing (d_2) by $d_2/\text{nm} = 1.03 + 0.119n$, the ratio d_2/d_1 being 0.586 to 0.581. The broad outer peak gives a spacing of 0.45 nm and the overlapped sharp peak gives a spacing of 0.41 nm. These two spacings are independent of the alkyl chain length. The former peak suggests the configurational disorder of the alkyl chains and the latter indicates the regular stacking of the parallel molecules in a column.

The metastable phase gives only one sharp inner peak, the spacing (d'_1) of which is approximated by $d'_1/\text{nm} = 2.28 + 0.121n$. The decrease in the increment per methylene group may imply that the alkyl chains in the metastable phase are more conformationally disordered than those in the stable high temperature phase. The presence of a weak sharp peak assignable to the 1 1 0

reflection, and only one broad outer peak, suggests that the phase is of the hexagonal disordered columnar (Col_{hd}) type. The above-mentioned spacing (d'_1) is much longer than those found for disordered hexagonal mesophases given by any other benzene derivatives. The present results may be compared with those for N,N' -dialkanoyl-2-alkanoyloxy-5-methylbenzene-1,3-diamine *s* carrying three long alkyl chains, and with N,N' -dialkanoyl-2,4-bis(alkanoyloxy)benzene-1,3-diamine carrying four chains in consecutive positions [7, 8]. The Col_{hd} phases of these 1,3-diamine derivatives are known to give rather large spacings approximated by $d/\text{nm} = 1.97 + 0.108n$ and $1.33 + 0.110n$, respectively. These results indicate clearly that the rigid core size increases significantly with the decrease of the number of the attached alkyl chains but the increment per methylene group changes less.

The second moment $\langle \Delta H^2 \rangle$ of the broad-line proton NMR spectrum of the dodecanoyl member ($n = 11$) measured as a function of the temperature is presented in figure 1. The value is as large as 11 G^2 ($\text{G} = 10^{-4} \text{ T}$) at room temperature; it decreases suddenly to 5.4 G^2 by the lower transition ($76\text{--}85^{\circ}\text{C}$) then gradually to about 3 G^2 on approaching the melting point (116°C). The isotropic melt gives a value $< 0.01 \text{ G}^2$. The observed value for the high temperature phase is small enough to support the presence of some large molecular motion; therefore, the phase may be a disordered solid.

On cooling, second moments as small as $0.2\text{--}0.3 \text{ G}^2$ are recorded until 94°C where a sharp exothermic peak with an enthalpy change of 16 kJ mol^{-1} is located

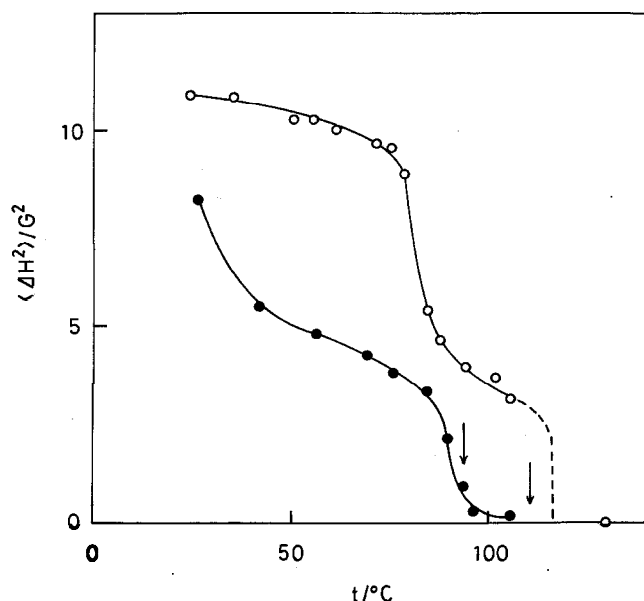


Figure 1. Second moment $\langle \Delta H^2 \rangle$ of the broad line NMR spectrum of the dodecanoyl ($n=11$) compound series of III. The vertical arrows indicate the transition temperatures (111 and 94°C) determined by calorimetry during cooling.

on the thermogram. The value found for the metastable phase agrees with the above phase assignment [8]. The phase appearing below 94°C may be the high temperature crystalline phase (Cr_1) judging from the magnitude of the second moments.

2.4. 3,4,5,6-Tetramethyl derivatives (IV)

The transition temperatures and associated enthalpies of these compounds are listed in table 2. The isotropization occurs above 200°C with an enthalpy change of 16–25 kJ mol⁻¹. The X-ray diffraction pattern of the highest temperature phase (M_1) consists of only a sharp inner peak and a broad outer one, suggesting

unstructured smectic phases. However, a hexagonal disordered columnar structure cannot be excluded because the 1 1 0 reflection is often too weak to be detected [5]. The spacing given by the inner peak is approximated by $d_1/nm = 0.858 + 0.066n$ when $2 \leq n \leq 6$ and $d_1/nm = 2.15 + 0.095n$ when $7 \leq n \leq 15$. It may be noted that the former relation is fairly close to $d/nm = 1.14 + 0.081n$ obtained for N,N' -dialkanoyl-4,5,6-trialkanoyloxybenzene-1,3-diamines and $d/nm = 1.04 + 0.090n$ for N,N',N'' -trialkanoyl-4,6-dialkanoyloxybenzene-1,3,5-triamines in the Col_{hd} phase [9]. The spacing given by the M_2 phase is longer and expressed by $d_2/nm = 1.99 + 0.133n$ throughout the whole series of compounds. Thus, the compounds are classified into two groups based on the spacing in the M_1 phase. The textures shown in figures 2(a) and 2(b) are given by the M_1 phases of the valeryl ($n=4$) and decanoyl members ($n=9$) respectively. They seem to be characteristic of hexagonal columnar phases. The enthalpy changes at the lower transitions are generally small, especially in the first group; therefore, it is difficult to decide whether a phase is crystalline or not. The classification proposed in table 2 is tentative and subject to further investigations.

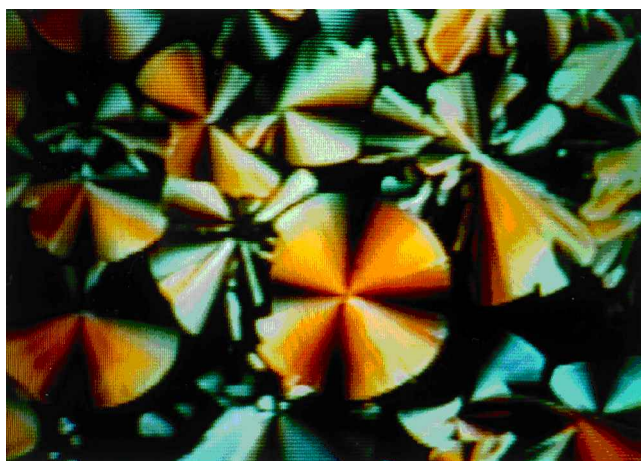
The second moment of the broad line proton NMR spectrum of the dodecanoyl member ($n=11$) was measured as a function of temperature. The moment is about 13 G² at room temperature and gradually decreases to about 5 G² a little below the transition temperature (128°C). After a drastic decrease to less than 1 G² at the phase transition the moment remains around 0.4 G² with no detectable change at the next transition temperature (187°C), in agreement with the above-mentioned assignment of the high temperature phases.

2.5. N,N' -Dialkylbenzene-1,2-dicarboxamides (V)

The transition temperatures and associated enthalpies of these compounds are listed in table 3. Stable viscous

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

n	Cr_1	M_3	M_2	M_1	I
1			•	330 (48)	•
2		•	•	270 (8)	•
3		•	•	226 (6)	•
4	•	128 (8)	•	210 (5)	•
5	•	114 (10)	•	207 (6)	•
6		•	•	219 (6)	•
7	•	118 (8)	•	220 (2)	•
8	•	123 (11)	•	210 (2)	•
9	•	122 (15)	•	203 (2)	•
10	•	125 (17)	•	194 (2)	•
11	•	128 (18)	•	187 (1)	•
13	•	123 (18)	•	168 (1)	•
15		•	125 (43)	•	147 (1)



(a)



(b)

Figure 2. Microscopic textures observed for the M_1 phase of (a) the vareryl member ($n=4$) at 221°C and (b) the decanoyl member ($n=9$) at 228°C of series IV.

Table 3. Transition temperatures T ($^\circ\text{C}$) and associated enthalpies ΔH (kJ mol^{-1}) for N,N' -dialkylbenzene-1,2-dicarboxamides. n is the number of carbon atoms in the alkyl group.

n	Cr		M		I
9	•	120 (29)			•
10	•	76 (39)	•	100 (11)	•
11	•	82 (49)	•	100 (11)	•
12	•	91 (53)	•	99 (12)	•
14	•	99 (84)	•	100 (12)	•
16	•	115 (101)	[•	99 (12)] ^a	•

^a Monotropic transition.

fluids are observed for the decyl, undecyl, dodecyl, and tetradecyl members. While the isotropization temperature remains essentially at 100°C , the melting point rises through the series. Consequently, the range of stable existence of the mesophase decreases from 24°C for the

decyl member to merely 1°C for the tetradecyl member. The hexadecyl member melts at a further high temperature and the mesophase is metastable. The enthalpy change associated with isotropization is independent of the alkyl chain length; that is, 11 to 12 kJ mol^{-1} , the smallest among the compounds reported in this paper. The X-ray diffraction pattern of the mesophase of the hexadecanoyl member consists of one strong and one weak inner peak, assignable to the 1 0 0 and 1 1 0 reflections, respectively, and one broad outer peak, indicating that the phase is hexagonal disordered columnar. The 1 0 0 spacing of 3.29 nm is shorter than that of the hexadecanoyl member of series IV in the M_1 phase (3.51 nm) but much longer than that of N,N',N'' -tris(hexadecyl)benzene-1,3,5-tricarboxamide in the Col_{hd} phase (2.14 nm), and also that of N,N' -bis(hexadecanoyl)-2,3,5,6-tetrakis-(hexadecanoyloxy)benzene-1,4-diamine in the same phase (2.46 nm) [6, 10]. The texture observed for the 1,2-dicarboxamides is common to all the members and is exemplified by that of the dodecyl member (see figure 3).

3. Conclusions

Hexagonal disordered columnar phases are generated monotropically by N,N' -dialkanoyl-4,5-dimethylbenzene-1,2-diamines, and enantiotropically by N,N' -dialkanoyl-3,4,5,6-tetramethylbenzene-1,2-diamines and N,N' -dialkylbenzene-1,2-dicarboxamides. The spacings given by the 1 0 0 reflection of the tetramethylbenzene-1,2-diamines with $2 \leq n \leq 6$ are close to those known for some 1,3-diamine compounds but those of others are appreciably longer, suggesting that the alkyl chains are less conformationally disordered and/or less interdigitated.

4. Experimental

2,4,5,6-Tetramethylbenzene was nitrated following the procedure reported by Smith [11] and reduced to the



Figure 3. Microscopic texture observed for the M phase of the dodecyl member ($n=12$) of series V at 94°C .

1,2-diamine with iron powder by the method proposed by Mahood and Schaffner [12]. The reaction of the benzene-1,2-diamines with alkanoyl chloride and that of phthaloyl chloride with alkylamine in a mol ratio of 1:2 in benzene in the presence of pyridine produced the desired compounds. Elemental analysis: calc. for $C_6H_2(CH_3)_2(NHC_{15}H_{31})_2$, C 78.37, H 11.84, N 4.57; found, C 78.22, H 11.92, N 4.53%. Calc. for $C_6(CH_3)_4(NHCOC_{10}H_{21})_2$, C 76.75, H 11.27, N 5.59; found, C 76.80, H 11.32, N 5.46%.

Microscopic observation and calorimetric and magnetic resonance measurements were carried out as described in a previous paper [4]. X-ray diffraction patterns of 'unoriented' liquid crystal films spread on an aluminum plate were recorded with a Rigaku autodiffractometer, Model RADI VB, using filtered copper radiation. The temperature of the sample holder was regulated with the aid of a Chino temperature indicating controller, Model E 500.

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