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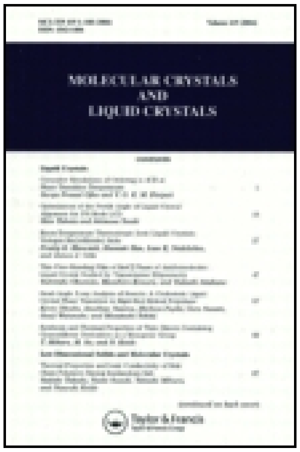

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Liquid Crystal Phases Exhibited by N,N′-Dialkanoyldiaminomesitylenes

Y. Matsunga [a] & M. Terada [a]

[a] Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, 060, Japan

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Liquid Crystal Phases Exhibited by N,N′-Dialkanoyldiaminomesitylenes

Y. MATSUNAGA and M. TERADA

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

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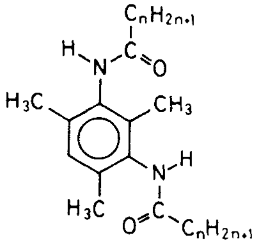
The enthalpy of melting of N,N′-dialkanoyl-1,3-diaminobenzene is drastically decreased by the introduction of lateral methyl groups and becomes so small that liquid crystal phases exhibiting schlieren textures emerge in the 2,4,6-trimethyl compounds carrying octanoyl to octadecanoyl groups. The X-ray diffraction patterns of unoriented specimens consisting of two diffuse peaks indicate that these phases are of the nematic type. Another high-temperature phase with both optical anisotropy and fluidity appears in the butyryl to dodecanoyl derivatives. The diffraction pattern is composed of a number of sharp peaks showing that this phase has a three-dimensional lattice.

Keywords: liquid crystals, nematic phases, smectic phases, 1,3-diaminobenzenes, lateral methyl groups, diaminomesitylenes

INTRODUCTION

As described in our paper on smectogenic N,N′,N″-trialkyl-1,3,5-benzenetricarboxamides, the substituent $C_nH_{2n+1}NHCO$ is very efficient to promote the thermal stability of liquid crystal phases.[1] The closely-related substituent $C_nH_{2n+1}CONH$ seemed to be equally useful for this purpose.[2] Therefore, we attempted to obtain mesomorphic compounds introducing some lateral substituents to the framework of N,N′-dialkanoyl-1,3-diaminobenzene. The enthalpy of melting is so much reduced by methyl groups that the N,N′-dialkanoyl-1,3-diamino-2,4,6-trimethylbenzene (diaminomesitylene) are nematogenic.



EXPERIMENTAL

The compounds were prepared by the condensation reaction between alkanoyl chloride and methylated 1,3-diaminobenzenes. Dinitromesitylene was obtained with good yield by adding drop by drop the hydrocarbon to fuming nitric acid cooled in an ice-water bath.[3] Tin and hydrochloric acid were used to prepare diaminomesitylene. Other diamines or the precursory dinitro compounds were commercially available. The results of elemental analysis were in accord with the composition of the desired compounds. For example, Found: C, 72.79; H, 9.85; N, 8.06%. Calcd. for $C_6H(CH_3)_3(NHCOC_5H_{11})_2$: C, 72.79; H, 9.89; N, 8.08%. Found: C, 78.39; H, 11.92; N, 4.50%. Calcd. for $C_6H(CH_3)_3(NHCOC_{15}H_{31})_2$: C, 78.53; H, 11.89; N, 4.47%. The transition temperatures and enthalpies were determined by a Rigaku Thermoflex differential scanning calorimeter at a heating rate of 5 K min^{-1}. The X-ray diffraction patterns were recorded on a Rigaku auto-diffractometer, model RAD IVB, using filtered copper radiation. Proton NMR spectra were measured using a JEOL model JES-ME-3X spectrometer with a broad-line NMR attachment, model JES-BE-1.

RESULTS AND DISCUSSION

N,N′-Bis(octadecanoyl)-1,3-diaminobenzene has a solid-solid transition at 100°C with an enthalpy change of 21 kJ mol^{-1} and melts at 130°C with an enthalpy change of 81 kJ mol^{-1}. The latter value is appreciably larger than the corresponding value of N,N′-bis(octadecyl)-1,3-benzenedicarboxamide, 48 kJ mol^{-1}. From this point of view, the diaminobenzene seems to be less suitable as a framework of mesogenic compounds than the benzenedicarboxamide. However, we explored the effects of methyl groups on the thermal properties of N,N′-dialkanoyl-1,3-diaminobenzene as this compound has an ad-

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vantage of easy introduction of lateral substituents which are the only structural parameters allowed for this simple molecule. Fortunately, a methyl group introduced to the 2- or 4-position can reduce drastically the enthalpy of transition to an isotropic liquid. The 2-methyl compound melts at 199°C with an enthalpy change of 26 kJ mol^{-1} and the 4-methyl compound at 144°C with 32 kJ mol^{-1}. These values may be small enough to call the high-temperature phases of these two "smectic liquid crystals."[4] The decrease by the second methyl group is relatively small but still significant; that is, the 2,4-dimethyl compound gives 25 kJ mol^{-1} at 149°C and the 4,6-dimethyl compound gives 14 kJ mol^{-1} at 130°C. The addition of one more methyl group to these dimethyl compounds gives rise to the emergence of nematic liquid crystals.

The calorimetric data of N,N'-dialkanoyldiaminomesitylenes are tabulated in Table I. Here, crystalline, smectic, nematic, isotropic phases are denoted by K, S, N, and I respectively. In the four cases including the octanoyl and octadecanoyl derivatives, the endothermic peak due to fusion is hardly separable from rather broad peak(s) due to solid-solid transition(s); therefore, the whole temperature range and the total enthalpy change are presented. The N—I transition is reversible at a cooling rate of 5 K min^{-1}, while the S—N transition shows detectable, often considerable supercooling. Schlieren texture

TABLE I

Transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) of N,N'-dialkanoyldiaminomesitylenes. The latter quantities are in parentheses.

n[a]	K		S		N		I
2	·					295 (38)	·
3	·	249 (17)	·			255 (14)	·
4	·	214 (17)	·			247 (17)	·
5	·	158-174 (15)	·			240 (15)	·
6	·	152-168 (21)	·			232 (13)	·
7	·	127-158 (22)	·	215 (7.9)	·	223 (3.1)	·
8	·	136 (31)	·	188 (5.4)	·	217 (2.4)	·
9	·	126 (33)	·	168 (5.1)	·	211 (2.2)	·
10	·	130 (40)	·	148 (4.8)	·	203 (1.7)	·
11	·	121 (40)	·	139 (4.5)	·	199 (1.5)	·
13	·			108 (73)	·	187 (1.1)	·
15	·			109 (79)	·	176 (0.9)	·
17	·			113-129 (45)	·	168 (0.7)	·

[a]Alkyl chain length in the alkanoyl group.

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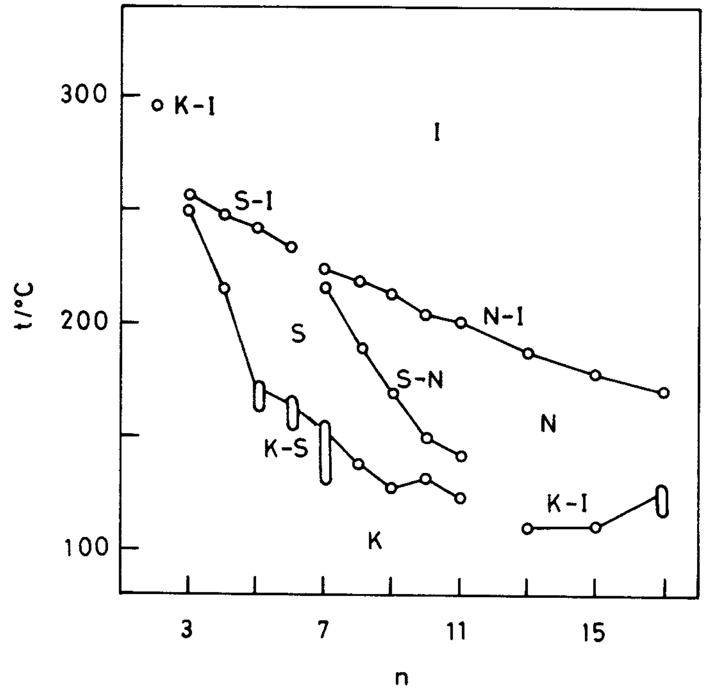

FIGURE 1 Plot of transition temperatures as a function of alkyl chain length in the alkanoyl group.

is adopted by the nematic phase. Figure 1 is a plot of the transition temperatures as a function of alkyl chain length in the alkanoyl group. The plot exhibits quite unusual feature; namely, the smectic phase appears in the lower members of the series and the nematic phase only in the higher members. This is just opposite to the general tendency known for liquid crystals that purely nematic behavior gives way to predominantly or purely smectic behavior in the higher homologs. This striking behavior may imply that the cohesion between the central units, which retains the molecules in the parallel orientation is rather strong and that the loss of alignment of the ends of the molecules required for the appearance of nematic phase can be achieved only when the extensive conformational disorder of long alkyl chains occurs. This explanation seems to be consistent with the steady falling of S—N and N—I transition temperatures as the series is ascended.

Figure 2 illustrates the relationship between the enthalpy changes by the transitions and the alkyl chain length. It may be noted that

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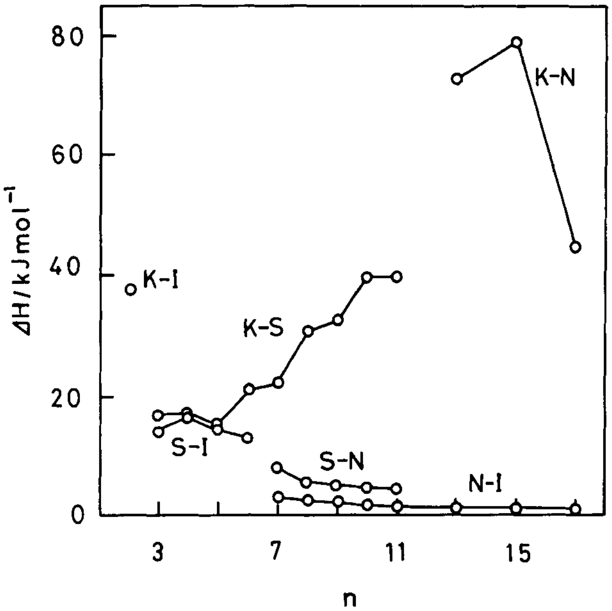

FIGURE 2 Plot of enthalpy changes by the transitions against the alkyl chain length in the alkanoyl group.

the enthalpies of S—N and N—I transitions decrease with increasing chain length rather than increase as is usually found. This behavior also suggests that the conformational melting in the liquid crystal phases is more extensive as the alkyl chain lengthens. The enthalpy changes by the N—I transition, 0.7 to 3.1 kJ mol^{-1}, are in the range of the corresponding values collected by Demus et al. and those by the S—N transition, 4.5 to 7.9 kJ mol^{-1}, do not exceed the largest value reported for ordered smectic phase-nematic phase transitions.[4]

The emergence of nematic phases in the octanoyl to octadecanoyl derivatives is firmly established by the X-ray diffraction. The pattern given by unoriented specimens consists of two diffuse peaks; one near 2° Bragg angle and the other near 9° Bragg angle. The phase denoted by S in Table I is birefringent and more viscous than the nematic phase. The diffraction pattern is composed of a number of sharp peaks. Undoubtedly, the phase has a three-dimensional lattice because the peaks appearing near 5° Bragg angle cannot be assigned to 00*l* and *hk*0 reflections.[5] The delay of S—N transition as much as 19° C observed with the dodecanoyl derivative by a cooling rate of 5 K min^{-1} may be also an evidence that this phase is highly structured.[6] The longest spacing in the smectic phase is 1.44 nm in the

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butyryl derivative and increases almost linearly up to 2.85 nm in the dodecanoyl derivative.

The second moment of broad-line proton NMR spectrum of the purely nematogenic hexadecanoyl derivative decreases suddenly at the K—N transition temperature. The values measured with the nematic phase is as small as 0.01 G^2, confirming the conformational melting of alkyl chains. In the case of the dodecanoyl derivative, the moment changes from about 7 G^2 to 1.5 G^2 upon the K—S transition and then remains at the latter value up to the S—N transition temperature. The nematic phase of this compound shows also moments of about 0.01 G^2.

In conclusion, N,N'-dialkanoyl-1,3-diaminobenzene can be mesogenic if the cohesion operating between the central units is adjusted, of course in relation to the conformational melting of alkyl chains, by the number and the positions of lateral methyl groups. Our work, we believe, proved that liquid crystal formation is possible even if the molecular shape is virtually of *m*-disubstituted benzene. The thermal properties of the series of the mono-, di-, and tetramethyl compounds will be reported elsewhere.

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