New Mesomorphic Compounds: *N,N′,N″*-Trialkanoyl-2,4,6-trimethyl-1,3,5-benzenetriamines

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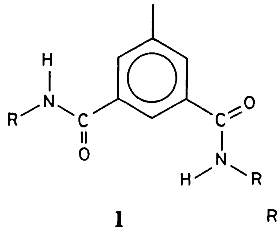
The homologous series of *N,N′,N″*-trialkanoyl-2,4,6-trimethyl-1,3,5-benzenetriamines has been prepared. The viscous birefringent melts are given by the butyryl to hexadecanoyl derivatives. The X-ray diffraction pattern recorded for the octanoyl derivative and the higher homologous members consists of two sharp inner peaks and a broad outer one assignable to the 100, 110, and 001 reflections respectively, indicating that the phase is hexagonal disordered columnar (D_{hd}). A more-structured high-temperature phase is displayed at lower temperatures by the nonanoyl to hexadecanoyl derivatives.

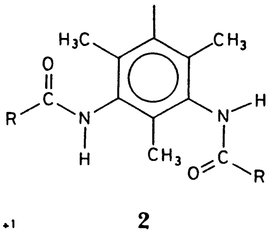
A number of single compounds composed of disk-like molecules are known to form stable or metastable mesophases. The first series, reported by Chandrasekhar et al. in 1977, consists of three homologous members of hexakis(alkanoyloxy)benzenes.[1] The hexaalkoxytriphenylenes, discovered by Billard et al., constitute the second series.[2] These disk-like molecules are made of a planar rigid core fully surrounded by a planar ring of paraffinic chains. Nevertheless, our earlier study revealed that *N,N′,N″*-trialkyl-1,3,5-benzenetricarboxamides (**1**), the molecule of which has only three long alkyl groups and is far from the shapes of discogens discovered to date, can exhibit hexagonal disordered columnar (D_{hd}) mesophases.[3]

In this paper, we wish to describe a new series of mesomorphic compounds designed on the basis of their isomers: *N,N′,N″*-trialkanoyl-1,3,5-benzenetriamines. Since the enthalpy change upon melting of *N,N′*-dioctadecanoyl-1,3-benzenediamine, 81 kJ mol^{-1}, is larger by about 70% than that of *N,N′*-dioctadecyl-1,3-benzenedicarboxamide,[4] the appearance of a mesophase in the above-mentioned isomeric compounds does not seem highly probable. However, the enthalpy change upon a transformation into an isotropic liquid can be considerably reduced by methyl substitution, as disclosed also by the same work. For example, *N,N′*-dioctadecanoyl-2-methyl-1,3-benzenediamine is transformed into an isotropic liquid with an enthalpy change of 26 kJ mol^{-1} and the corresponding 2,4,6-trimethyl compound with 0.7 kJ mol^{-1}. Consequently, *N,N′,N″*-trialkanoyl-2,4,6-trimethyl-1,3,5-benzenetriamines (**2**) seemed to be good candidates for new mesomorphic compounds.



1

R = C_nH_{2n+1}



2

Experimental

Materials. Trinitromesitylene was prepared by the nitration of mesitylene with a mixture of concentrated sulfuric acid and fuming nitric acid.[5] The product was reduced with metallic tin and concentrated hydrochloric acid. The reaction between 2,4,6-trimethyl-1,3,5-benzenetriamine and acyl chloride was carried out in benzene by the addition of pyridine. The compounds were purified by repeated recrystallization from appropriate solvents: methanol for the propanoyl to octanoyl derivatives, ethanol for the nonanoyl to dodecanoyl derivatives, and mixtures of benzene and ethanol for the remaining two. The results of elemental analysis are in good agreement with the composition of the desired compounds. For example, Found: C, 71.79; H, 10.19; N, 8.33%. Calcd for $C_6(CH_3)_3(NHCOC_6H_{13})_3$: C, 71.81; H, 10.24; N, 8.37%.

Measurements. Calorimetric, X-ray, and NMR measurements were made as reported in our previous work.[4]

Results and Discussion

The compounds prepared for this investigation are listed in Table 1 along with their transition temperatures and the associated enthalpy changes. By an examination using a polarizing microscope the appearance of viscous birefringent melts was noted with the butyryl to hexadecanoyl derivatives. In addition,

Table 1. Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of Compounds **2**[a)]

n[b)]	K		M$_2$		M$_1$		I
2	·	421(45)					·
3	·	380(4)			·	410(35)	·
4	·	315(16)			·	380(34)	·
5	·	300(22)			·	357(30)	·
6	·	257(28)			·	357(16)	·
7	·	239(30)			·	346(15)	·
8	·	200(8)	·	222(19)	·	340(15)	·
9	·	189(5)	·	206(16)	·	342(15)	·
10	·	185(15)	·	191(15)	·	338(9)	·
11	·	183(14)	·	189(7)	·	342(11)	·
13	·	118(16)	·	182(19)	·	338(9)	·
15	·	120(28)	·	175(12)	·	328(9)	·

a) The latter quantities are in parentheses. b) The number of carbon atoms in the alkyl group.

another high-temperature phase, tentatively called a mesophase because of low rigidity, was observed at lower temperatures for the nonanoyl to hexadecanoyl derivatives. In this table, K, M_1, M_2, and I stand for crystalline, mesophases appearing at higher and lower temperatures, and isotropic phase respectively.

The mesophases (M_1) of the present series are thermally much more stable than those of the previously studied isomeric series **1**, the difference in the transition temperature between the corresponding members being greater than 100 °C. This stability enhancement may be ascribed to an increase in the intermolecular interaction by the substituents $NHCOC_nH_{2n+1}$ outweighing the decrease by three methyl groups. The steady and rather drastic falling of melting point (K-M_1 or K-M_2 transition temperature) is noted as the series is ascended. Nonetheless, its lowest temperature is comparable with the highest melting point observed for series **1**. The clearing point (M_1-I transition temperature) is also lowered by the increase of alkyl chain length, up to the octanoyl derivative, but no consistent variation has been found for the higher homologous members. Because of the high clearing point, compounds **2** are not stable above this temperature and the reversible transition cannot be recorded by calorimetry. The focal conic texture may be observed when the M_1 phase, heated to relatively high temperatures, is cooled. Finally, it may be added that the enthalpy change at the clearing point is much larger than that given by the corresponding *N,N'*-dialkanoyl-2,4,6-trimethyl-1,3-benzenediamine, reflecting the intermolecular interaction strengthened by the introduction of an extra $NHCOC_nH_{2n+1}$ group to the molecule.

Since the high-temperature phases of the lower homologous members are located at temperature ranges too high to carry out X-ray measurements, the diffraction patterns were recorded for the octanoyl to hexadecanoyl derivatives. The patterns observed with the unoriented M_1 phases are similar to those reported for compounds **1**.[3] The sharp innermost peak is strong and is accompanied by a weak peak, the spacing of which is about $1/\sqrt{3}$ times that given by the innermost peak. This ratio is characteristic of a hexagonal lattice. Such a symmetry may be achieved by the rotation of the molecular core around the columnar axis, even if the molecule has only three alkyl groups. The innermost peak may be assigned to the 100 reflection and the other one to the 110 reflection. The two spacings defined by these peaks are independent of the temperature. They increase linearly with the alkyl chain length. The spacing d_{100} given by the octanoyl derivative is 1.48 nm and that given by the hexadecanoyl derivative is 1.93 nm. A broad peak located at a large Bragg angle gives a spacing of about 0.46 nm throughout the series. This spacing is characteristic of the melted state of the paraffinic moieties in mesophases and gives the average stacking distance between the molecular planes irregularly spaced in a column. Thus, the observed feature is of the hexagonal disordered columnar (D_{hd}) structure. The M_1 phase, given by the heptanoyl derivative, is probably of the same nature; however, those exhibited by the butyryl to hexanoyl derivatives may be more-structured because of about twice larger enthalpy changes upon the transformation into an isotropic liquid.

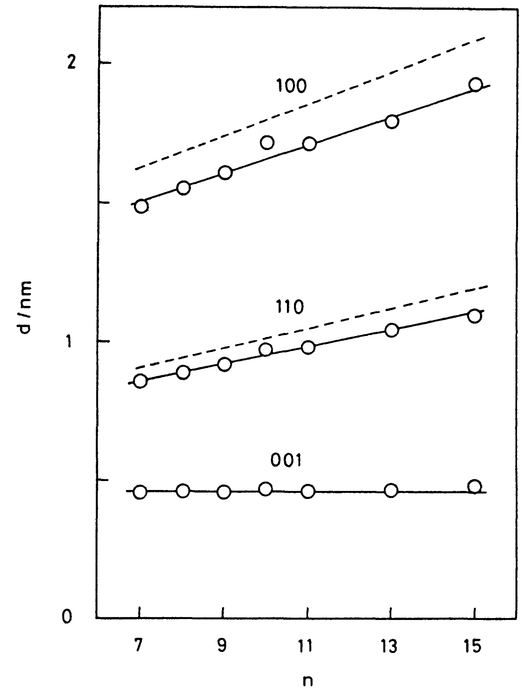


Fig. 1. Plots of spacings measured in M_1 phases against the number of carbon atoms in the alkyl group for compounds **2**. Broken lines indicate the corresponding spacings of compounds **1**.

In Fig. 1, the broken lines represent the spacings d_{100} and d_{110} plotted against the number of carbon atoms in the alkyl group measured for the mesophases of compounds **1**.[3] The spacings in the present series are consistently shorter than those of series **1**. For example, the spacing d_{100} of the octanoyl derivative ($n=7$) is 1.48 nm and that of the heptyl derivative in series **1** is 1.63 nm. The former value is essentially the same as that found for hexakis(octanoyloxy)benzene, 1.50 nm, reported by Chandrasekhar et al.[1] On the basis of these differences in the spacing, one might suggest that the alkyl chains in the present series of compounds are conformationally more disordered than those in series **1**. The enthalpy changes at the clearing point are 15 kJ mol^{-1} for the present compound, 12 kJ mol^{-1} for the corresponding compound **1**,[3] and 19 kJ mol^{-1} for the hexasubstituted compound.[1] It must be noted that the clearing point of the present compound, 328 °C, is appreciably higher than that of the previously studied one, 214 °C, and also that of the compound reported by Chandrasekhar et al., 83.4 °C. Therefore, the entropy changes at the clearing point in the former two are actually close to each other but are smaller by a factor of two than that for hexakis(octanoyloxy)benzene. Three long alkyl groups carried by the molecules in our two series appear to be disordered nearly to the same extent in the mesophases; therefore, the shorter spacing may imply that the alkyl groups in series **2** are more interdigitated than those in series **1**.

The diffraction pattern recorded for the M_2 phase of the hexadecanoyl derivative shows four sharp peaks and two relatively broad ones. The sharp peak at the lowest Bragg angle is accompanied by its second and third order reflections. The spacing is markedly longer than that shown by the corresponding M_1 phase, namely 4.25 versus 1.93 nm. There are three peaks at relatively high Bragg angles giving spacings of 0.42, 0.46, and 0.55 nm respectively. The second one is sharp and the other two are rather broad. The shortest and the second shortest spacings are common to all the diffraction patterns of the M_2 phases. The spacing given by the innermost peak decreases almost linearly by the decrease in the alkyl chain length and 2.73 nm is obtained for the nonanoyl derivative. The diffraction pattern becomes more complicated as the series is descended. A few extra weak peaks appear in the intermediate Bragg angles. The phase is viscous but may have a three-dimensional lattice.[7] The innermost peak in the diffraction pattern recorded for the crystalline phases gives a spacing a little longer than that of the M_2 phase of the same compound; for example, 2.78 versus 2.73 nm for the nonanoyl derivative and 4.02 versus 3.81 nm for the tetradecanoyl derivative.

The conformational melting of the alkyl chains in the M_1 and M_2 phases is firmly supported by the small second moments of the broad-line proton NMR spectra (the mean-square widths of the resonance line), $<\Delta H^2>$, recorded above the melting point. The tetradecanoyl derivative gives a moment of about 12 G^2 ($1\ G=10^{-4}\ T$) at room temperature. The value decreases continuously to about 3 G^2 by the melting point and then rather abruptly to 0.5 G^2 of the M_2 phase. The moment remains at this value up to the M_2–M_1 transition temperature. The value as small as 0.03 G^2 observed for the M_1 phase is close to those observed for the mesophases of *N,N′,N″*-trioctyl- and *N,N′,N″*-trihexadecyl-1,3,5-benzenetricarboxamides and also *N,N′*-dihexadecanoyl-2,3,5,6-tetrakis(hexadecanoyloxy)-1,4-benzenediamine.[3,6] Their X-ray diffraction patterns are essentially the same and are attributable to the hexagonal disordered columnar structure.

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References

1) S. Chandrasekhar, B. K. Sadashiva, and K. A. Suresh, *Pramana,* **9**, 471 (1977).

2) J. Billard, J. C. Dubois, Nguyen Huu Tinh, and A. Zann, *Nouv. J. Chim.*, **2**, 535 (1978).

3) Y. Matsunaga, N. Miyajima, Y. Nakayasu, S. Sakai, and M. Yonenaga, *Bull. Chem. Soc. Jpn.*, **61**, 207 (1988).

4) Y. Matsunaga and M. Terada, *Mol. Cryst. Liq. Cryst.*, **141**, 321 (1986).

5) R. Fittig, *Justus Liebigs Ann. Chem.*, **141**, 133 (1867).

6) Y. Kobayashi and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **60**, 3515 (1987).

7) A. de Vries, *Mol. Cryst. Liq. Cryst.*, **63**, 215 (1981).