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Novel Nematogenic Benzene Derivatives: *N,N'*-Dialkanoyl-2,5,6-trimethyl-4-alkanoyloxy-1,3-benzenediamines

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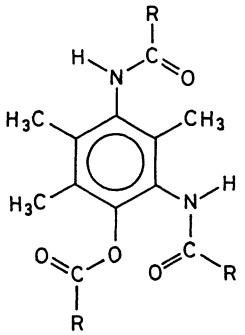
A series of *N,N'*-dialkanoyl-2,5,6-trimethyl-4-alkanoyloxy-1,3-benzenediamines has been synthesized. The mesophases appearing in the octanoyl to octadecanoyl derivatives adopt a schlieren texture and are transformed into isotropic liquids, with enthalpy changes as small as from 1 to 4 kJ mol^{-1}. Their X-ray diffraction patterns consist of only two diffuse peaks, fully confirming that the phases are nematic in type. The spacing deduced from the inner diffraction peak is markedly shorter than the molecular length and is similar to the spacings, d_{100}, found for the hexagonal disordered columnar phases exhibited by closely-related benzene derivatives. This is strong evidence for the alignment with their normals to the average molecular planes parallel. In other words, the mesophase is classified as discotic even though the molecular shape is far from disk-like. Another viscous birefringent phase is found below the nematic phase when the molecule carries octanoyl to hexadecanoyl groups.

As has been reported in our earlier papers, the $NHCOC_nH_{2n+1}$ substituents are efficient in promoting the thermal stability of discotic mesophases and are useful in designing mesogenic benzene derivatives.[1-3] For example, a hexagonal disordered columnar phase emerges upon the replacement of the two $OCOC_nH_{2n+1}$ groups in the 1 and 4 positions of hexakis(alkanoyloxy)benzenes with the above-mentioned groups, or it is markedly stabilized, if the hexaester itself is mesogenic.[4] Similarly, some members of the homologous series of *N,N'*-dialkanoyl-2,4-bis(alkanoyloxy)-1,3-benzenediamines, the molecule of which is half-disk-shaped, have been shown to be discogenic. Furthermore, we established that the enthalpy change at the transition into an isotropic liquid of *N,N'*-dialkanoyl-1,3-benzenediamines can be so much diminished by methyl substitution that various mesophases are obtainable by this approach. Thus, the 2-methyl compounds with decanoyl to octadecanoyl groups exhibit a hexagonal disordered columnar phase, and the 2,4,6-trimethyl compounds with octanoyl to octadecanoyl groups produce a nematic phase.

The employment of both $OCOC_nH_{2n+1}$ group(s) and methyl group(s) would be a feasible way of adjusting the intermolecular interaction to attain nematic phases. As a first attempt along this line, we decided to examine the thermal behavior of *N,N'*-dialkanoyl-2,5,6-trimethyl-4-alkanoyloxy-1,3-benzenediamines (**1**).



$R=C_nH_{2n+1}$ (**1**)

Experimental

Materials. 2,3,5-Trimethylphenol was dissolved in glacial acetic acid and then nitrated with fuming nitric acid dissolved in the same solvent, following the procedure of John and Rathmann.[5] The dinitrophenol was reduced with metallic tin and concentrated hydrochloric acid. The desired compounds were prepared by the reaction of the diamine hydrochloride dissolved in pyridine with appropriate alkanoyl chlorides keeping the reaction mixture below 40 °C except for the following two members; the tridecanoyl and pentadecanoyl derivatives were obtained by a reaction between the diamine and the alkanoic acids, following the method of Hassner and Alexanian.[6] Found: C, 73.71; H, 10.63; N, 4.79%. Calcd for $C_6(CH_3)_3(NHCOC_8H_{17})_2(OCOC_8H_{17})$: C, 73.68; H, 10.65; N, 4.77%.

Measurements. The calorimetric and X-ray diffraction measurements were carried out as has been described in a previous paper.[1]

Results and Discussion

The thermal properties of the eleven derivatives carrying heptanoyl to octadecanoyl groups are summarized in Table 1. Here, K, M_2, M_1, and I stand for the crystalline phase, mesophases appearing at lower and higher temperatures, and the isotropic phase respectively.

As the series is ascended, both the M_2-M_1 and M_1-I transition temperatures are progressively lowered. The former transition is accompanied by an enthalpy change of about 21 kJ mol^{-1} up to the tetradecanoyl derivative and by one of 2 to 4 kJ mol^{-1} for the next two members. No M_2 phase is found for the octadecanoyl derivative. While the M_2 phase of the lower homologous members tends to be strongly supercooled, a metastable crystalline phase appears in the higher members. As for the tridecanoyl and tetradecanoyl derivatives, the thermal behavior in the

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

n[b]	K	M_2	M_1	I
6	·	211(36)		·
7	·	130(8) · 186(20)	· 201(4)	·
8	·	126(14) · 169(21)	· 198(4)	·
9	·	108(19) · 159(21)	· 195(3)	·
10	·	123(25) · 152(21)	· 192(3)	·
11	·	111(32) · 143(20)	· 188(2)	·
12	·	117(—) · 137(21)	· 185(2)	·
13	·	110(—) · 128(22)	· 180(2)	·
14	·	108(49) · 126(4)	· 178(2)	·
15	·	109(54) · 122(2)	· 174(2)	·
17	·	104(80)	· 165(1)	·

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

temperature range around the melting point is not very reproducible. Therefore, the enthalpy change was not determined for the K-M_2 transition in these two members. The enthalpy change at the M_1-I transition decreases monotonously from 4 kJ mol^{-1} of the octanoyl derivative to 1 kJ mol^{-1} of the octadecanoyl derivative. Not only the magnitude but also the relationship with the number of carbon atoms in the alkyl group are in qualitative agreement with those observed for the N-I transition of *N,N'*-dialkanoyl-2,4,6-trimethyl-1,3-benzenediamines; namely, from the 3 kJ mol^{-1} of the octanoyl derivative to the 0.7 kJ mol^{-1} of the octadecanoyl derivative. Moreover, the N-I transition temperatures are fairly close to each other: 201 °C vs. 223 °C for the shortest alkanoyl group and 165 °C vs. 168 °C for the longest group. The nematic phases in these series formed in the process of cooling from the isotropic melts adopt well-developed schlieren textures. The continuous miscibility between the two nematic phases was firmly established by the phase diagram of a binary system employing the undecanoyl derivatives. The N-I transition temperature is lowered, is slightly broadened by mixing, and exhibits a minimum around 177 °C and 60 mol% of the component compound prepared in the present work.

The X-ray diffraction pattern of the M_1 phase spread in the form of a thin film over an aluminum holder consists of two diffuse peaks, providing evidence that the phase is nematic in type. The spacing given by the inner peak is 1.51 nm for the octanoyl derivative, and it increases linearly with the alkyl-chain length up to 2.16 nm for the octadecanoyl derivative. The finding that the spacing is much shorter than the molecular length is in sharp contrast with what is known for the classical nematic phases given by rod-like molecules. In the cases so far examined, the spacings are in the order of the length estimated for the most extended molecular configuration. In some cases, the spacing seems to be in good agreement with the molecular length, but in the other cases the value is shorter by about 10 %.[7] The present values are similar to, or shorter than, the d_{100} values found for a variety of hexagonal disordered columnar phases previously measured by the present authors.[1-3,8,9] For example, the spacing for the hexadecanoyl derivative, 2.08 nm, is close to those of the corresponding members in the following series: *N,N',N''*-trialkanoyl-2,4,6-trimethyl-1,3,5-benzenetriamine (1.93 nm) and *N,N',N''*-trialkyl-1,3,5-benzenetricarboxamide (2.06 nm).[8,9] This observation led us to conclude that the M_1 phase bears the character of a discotic phase, in which the short axes (normals to the average molecular planes) are aligned parallel. The spacings calculated from the positions of the outer peak with the formula $2d\sin\theta=\lambda$ are 0.47±0.01 nm throughout the series. This value agrees well with the d_{001} spacing found in the above-mentioned hexagonal disordered columnar phases.

The M_2 phase gives a common X-ray diffraction pattern composed of five sharp peaks and one diffuse one. The sharp peak at the lowest Bragg angle is accompanied by its second- and third-order reflections. As is shown in Fig. 1, the spacing is markedly longer than that found for the M_1 phase of the same compound, but still shorter than the length of the most extended molecular configuration, which is represented by a broken line. The observed value is 2.36 nm for the octanoyl derivative and 4.20 nm for the hexadecanoyl derivative. The slope is 0.235 nm per

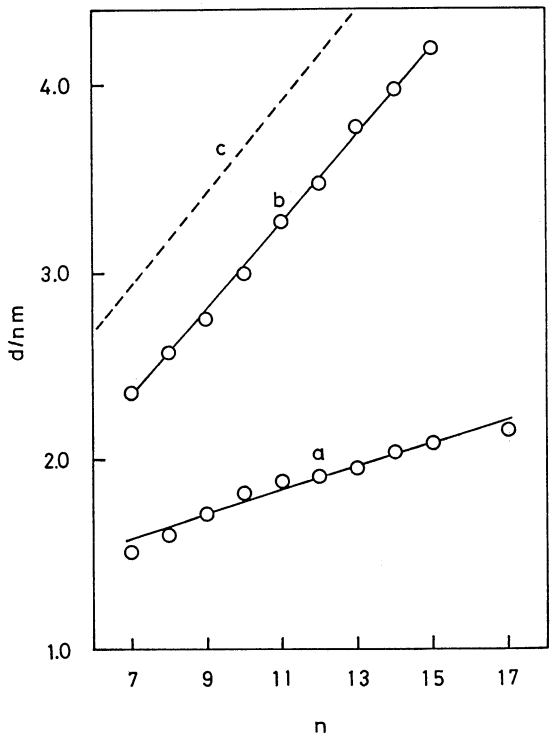


Fig. 1. Plots of the longest spacings in a) the M_1 phase, b) the M_2 phase, and c) the calculated molecular length against the number of carbon atoms in the alkyl group (n).

carbon atom in the alkyl group. The remaining two sharp peaks are at 0.94 nm and 0.44 nm, regardless of the alkyl chain length. The latter peak overlaps with the diffuse one having a maximum at 0.47±0.01 nm. These features bear some resemblance to those reported by Levelut for the hexagonal ordered columnar phase of hexakis(pentyloxy)triphenylene.[10] Therefore, the following assignments are conceivable: the shortest spacing, to the relatively well-defined distance between the parallel molecules in a column; the second shortest, which agrees with that found in the M_1 phase, to the mean distance between the alkyl chains in the liquid-like order, and the spacing of 0.94 nm, to the pitch of the helicoidal stacking of the molecular cores, which is approximately twice the shortest spacing, postulating the extensive formation of the dimer with a center of symmetry. It must be added that neither the discontinuity in the linear relationship between the spacing and the number of carbon atoms in the alkyl group nor the change in the diffraction pattern could be detected between the pentadecanoyl derivative and the lower homologous members, though the enthalpy change at the M_2–M_1 transiton in the former compound is much less than those in the latter (see Table 1).

The thermal behavior of the unmethylated *N,N'*-bis(tetradecanoyl)-4-tetradecanoyloxy-1,3-benzenediamine was examined with the aim of clarifying the effects of methyl groups. The compound has a solid-solid transition at 90 °C with an enthalpy change of 17 kJ mol^{-1} and a melting point at 119 °C with a change of 70 kJ mol^{-1}. Thus, the presence of methyl groups is proved to be essential for the appearance of the M_1 and M_2 phases. The temperature range covered by these mesophases is located almost entirely above the melting point of the unmethylated compound. In other words, the function of the three methyl groups is to strenghten the intermolecular attraction by increasing the polarizability of the molecule, to an extent outweighing the decrease in the cohesive forces by increasing the intermolecular separation, and to convert an isotropic liquid into mesophases.

The difference in the effects on mesomorphic properties between a methyl group and a tetradecanoyl group may be demonstrated by comparison with *N,N'*-bis(tetradecanoyl)-2,4,5,6-tetramethyl-1,3-benzenediamine. As was reported in our earlier paper,[3] the reference compound yields a viscous phase at 122 °C and an isotropic liquid at 216 °C. The associated enthalpy changes are 18 and 25 kJ mol^{-1} respectively. The X-ray diffraction pattern of this viscous phase indicates that the phase is similar in nature to the M_2 phase in the present series. Consequently, the replacement of a methyl group with a tetradecanoyloxy group results in the appearance of the M_1 phase in the temperature range originally covered by the M_2 phase, reducing the intermolecular attractive force. This conclusion seems to be in accordance with the lowering of the clearing point as much as 36 °C by the replacement. The achievement of a nematic phase in the present series may be ascribed, to some extent, to the adjustment of intermolecular attraction by employing the opposing effects of three methyl groups and of a long alkanoyloxy group.

The classification of the mesophases into classic and discotic has been made intuitively on the basis of the molecular shape: rod-like or disk-like. Takenaka et al. have found that some 1,2,4-trisubstituted benzenes such as 4-alkoxyphenyl 3,4-bis(4-alkoxybenzoyloxy)benzoates exhibit the smetic A and nematic phases.[11,12] According to their proposition, the most important factor distinguishing the two classes is the molecular geometry; that is, the molecular length-to-breadth ratio of 1 : 1 is the most suitable condition for producing discotic properties. Therefore, it is particularly emphasized that the molecules studied here are aligned with their short axes parellel to each other, even though their molecular shape is far from disk-like. This situation encourages the assumption that the classification on the basis of the axes, with which the molecules are aligned in a common direction, is more general. Because of the existence of high degrees of thermal motion around the director, one may suggest that the mesophase is discotic if the molecular motion around the short axis is more readily accomplished than that around the long molecular axis. The reason why the present molecules are uniquely aligned with their short axes parallel to each other is not yet clear; nonetheless, one might speculate that the intermolecular hydrogen bonding due to the -NHCO- groups plays some role in the appearance of discotic properties. Such chemical aspects, which are undoubtedly important in determining the magnitude of the anisotropic intermolecular forces, have been entirely ignored in the above discussion.

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