  Bull. Chem. Soc. Jpn., 61, 3083—3085 (1988)

New Mesomorphic Compounds: *N,N'*-Dialkanoyl-2,4-bis(alkanoyloxy)-1,3-benzenediamines

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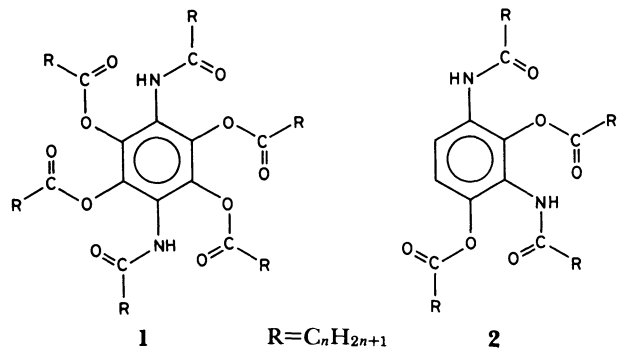
(Received March 31, 1988)

A series of *N,N'*-dialkanoyl-2,4-bis(alkanoyloxy)-1,3-benzenediamines has been synthesized. The high-temperature phases appearing in the heptanoyl to hexadecanoyl derivatives are viscous and are transformed into isotropic liquids with enthalpy changes of 20 kJ mol^{-1} or less. Their X-ray diffraction patterns are characteristic of the hexagonal disordered columnar phase. The second moment of the broad-line proton NMR spectrum measured in the mesophase region is 0.8 to 0.9 G^2 in the case of the octanoyl derivative and 0.04 G^2 in the case of the tetradecanoyl derivative, indicating the rather large difference in the motional behavior between these half-disk-shaped molecules.

As we reported earlier,[1] the mesomorphic behavior can be considerably enhanced by the replacement of the two $OCOC_nH_{2n+1}$ groups in the 1 and 4 positions of hexakis(alkanoyloxy)benzenes by $NHCOC_nH_{2n+1}$ groups; namely, the clearing point of discogenic *N,N'*-dialkanoyl-2,3,5,6-tetrakis(alkanoyloxy)-1,4-benzenediamine (**1**) is much higher than that of the corresponding hexakis(alkanoyloxy)benzene,[2,3] while the melting point of the former compound remains almost the same as that of the latter. These two compounds are composed of disk-like molecules in which the planar rigid core is densely surrounded by a planar ring of aliphatic chains. Although it is generally assumed that the distinctive feature common to all the mesomorphic compounds is the rod-like or disk-like shape of the molecule,[4-6] we have found that *N,N'*-dialkanoyl-2,4,6-trimethyl-1,3-benzenediamines are mesogenic.[7] These findings suggest that the presence of two $NHCOC_nH_{2n+1}$ groups per molecule is favorable to form stable mesophases and also that the molecule is not required to be rod-like or disk-like in order to form a mesophase. What is indispensable to the formation of mesophase is apparently the presence of a molecular core which keeps the molecules aligned up to relatively high temperatures and that of long flexible alkyl chains conformationally disordered at lower temperatures. Consequently, it seemed to us highly probable that *N,N'*-dialkanoyl-2,4-bis(alkanoyloxy)-1,3-benzenediamine (**2**), even though the molecule of which is half-disk-shaped, can produce some kind of mesophase.



1 R=C_nH_{2n+1} **2**

Experimental

Materials. 2,4-Dinitrosoresorcinol was prepared following the method described by Fitz,[8] but the addition of sodium nitrite at lower temperatures, −2 to −4 °C, was found to be recommendable. The wet product was added in small portions to tin(II) chloride dissolved in concentrated hydrochloric acid avoiding excessive raising of the temperature by the heat of the reaction. The warm solution was filtered and the amine was precipitated by the addition of concentrated hydrochloric acid. The acylation was carried out at room temperature by adding acyl chloride drop by drop to a pyridine solution of the diamine. The desired compounds were recrystallized from acetone or mixtures of benzene and diethyl ether. Found: C, 73.03; H, 10.65; N, 3.71%. Calcd for $C_6H_2(NHCOC_9H_{19})_2(OCOC_9H_{19})_2$: C, 72.97; H, 10.65; N, 3.70%. Found: C, 75.82; H, 11.49; N, 2.86%. Calcd for $C_6H_2(NHCOC_{13}H_{27})_2(OCOC_{13}H_{27})_2$: C, 75.87; H, 11.50; N, 2.85%.

Measurements. Calorimetric, X-ray, and NMR measurements were made mostly as described in our previous papers.[1,7] As the endothermic peaks due to melting and clearing are closely located in some derivatives, a rather slow rate of heating, 150 K h^{-1}, was employed throughout the present work in order to improve the separation between the peaks.

Results and Discussion

The thermal properties of the eight derivatives carrying heptanoyl to hexadecanoyl groups are summarized in Table 1. Here, crystalline, discotic, and isotropic phases are denoted by K, D, and I respectively. No solid-solid transition is found above room temperature for any homologous member. It may be noted that the temperature range of the mesophase is narrowed as the series is ascended. The mesophase appears over 35 °C range in the case of the heptanoyl and octanoyl derivatives but only over 11 °C in the case of the hexadecanoyl derivative. Compared with the corresponding homologous member in the series **1**, the present compounds melt at higher temperatures and are transformed into isotropic liquids at much lower temperatures. While the enthalpy change at the clearing point (D–I transition temperature) is in a narrow range

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

n[b]	K		D		I
6	·	89(9)	·	124(19)	·
7	·	87(10)	·	122(18)	·
8	·	90(16)	·	121(18)	·
9	·	93(18)	·	122(17)	·
10	·	95(23)	·	120(16)	·
11	·	97(26)	·	117(15)	·
13	·	101(41)	·	114(13)	·
15	·	103(60)	·	114(16)	·

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

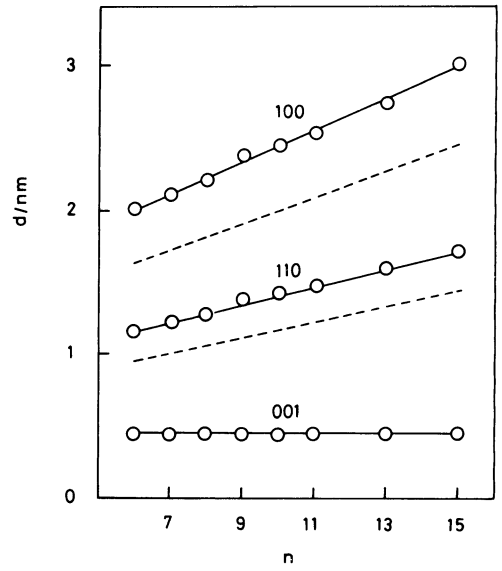


Fig. 1. Plots of spacings measured in the mesophases against the number of carbon atoms in the alkyl group for compounds **2**. Broken lines indicate the corresponding spacings of compounds **1**.

from 13 to 19 kJ mol^{-1}, that at the melting point (K–D transition temperature) increases rapidly with the increase of the alkyl chain length, from 9 to 60 kJ mol^{-1}. The entropy change at the clearing point is 83 J mol^{-1} K^{-1} for the heptanoyl derivative of the series **1** and 48 J mol^{-1} K^{-1} for the corresponding member of the series **2**. The value becomes smaller as both the series are ascended and 39 and 41 J mol^{-1} K^{-1} are obtained for the hexadecanoyl derivatives of the series **1** and **2** respectively. Thus, the entropy change in the present series is less dependent on the alkyl chain length than that in the hexasubstituted benzene series.

The isotropic liquid of all the derivatives may be supercooled as much as 20 °C. The mesophase of the heptanoyl to undecanoyl derivatives can be cooled to room temperature. No crystallization was observed even when the specimen was annealed at 5 °C below the melting point for four hours. On the other hand, three exothermic peaks are detected in the process of cooling for the dodecanoyl to hexadecanoyl derivatives. These metastable solid phases are easily transformed into the stable ones.

The X-ray diffraction pattern of the mesophase is essentially of the hexagonal disordered columnar structure; that is, there are two sharp inner peaks giving spacings in the ratio of $1:1/\sqrt{3}$ and one broad peak giving a spacing of 0.46 nm throughout the series. They may be assigned to 100, 110, and 001 reflections respectively. The innermost peak is accompanied in most cases by a weak peak assignable to the second order reflection. In addition, two weak extra peaks are detectable in the patterns given by the dodecanoyl derivative and the lower homologous members in the region between the sharp peaks and the broad one, indicating the appearance of some regularity in the molecular arrangement. The spacings d_{100} and d_{110} increase linearly with the alkyl chain length as shown in Fig. 1. For example, the heptanoyl derivative gives a d_{100} of 1.99 nm and the hexadecanoyl derivative 2.98 nm. They are much longer than those of the corresponding members in the series **1** represented by broken lines in the same figure. This suggests that the alkyl chains in compounds **2** are more extended and/or less interdigitated. In the mesophases formed by disk-like molecules, rotation of the whole molecule about the normal to the molecular plane and fluctuations of this axis around the preferred aromatic director are conceivable.[9] In order to achieve the hexagonal symmetry, the present half-disk-shaped molecule must be effectively disk-like in the mesophase. In other words, the molecules in a column must be oriented in various directions and rotating more freely than disk-like molecules do. Therefore, the interlocking of the alkyl chains must be less pronounced than that in the mesophase of compounds **1**. The supercooling of the mesophases of the heptanoyl to undecanoyl derivatives was confirmed by the X-ray measurements. The diffraction pattern recorded at room temperature for the once melted specimen is the same as that recorded in the temperature range of the stable existence.

The longest spacing in the crystalline phase is longer than that in the mesophase, d_{100} and changes linearly with the number of carbon atoms in the alkyl group; namely, 2.20 nm in the heptanoyl derivative and 4.70 nm in the hexadecanoyl derivative. The shrinkage at the melting point is only 0.21 nm in the former derivative and as much as 1.72 nm in the latter. This behavior is consistent with the remarkable increase in the enthalpy change as the series is ascended. The hexanoyl derivative is expected not to be mesomorphic because the shrinkage estimated by the linear relationship is nearly zero.

The liquid-like characteristics of alkyl chains in the mesophase are demonstrated by the small second moments of the broad-line proton NMR spectrum (the

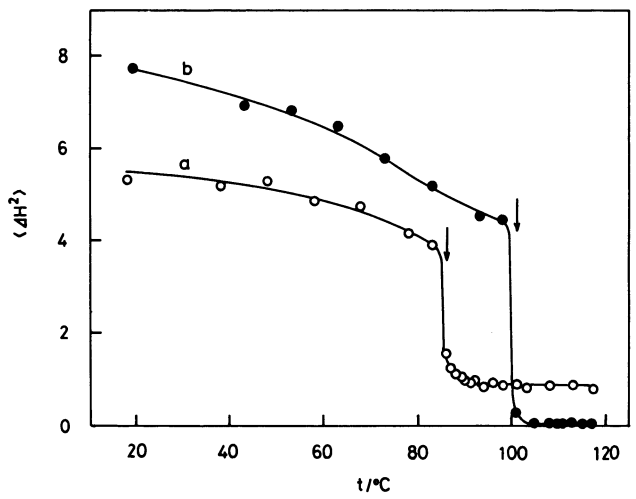


Fig. 2. Second moments of the broad-line proton NMR spectrum of compounds **2**, (a) n=7 and (b) n=13. The vertical arrows indicate the melting points determined by calorimetry.

mean-square width of the resonance line), $\langle \Delta H^2 \rangle$, measured above the melting point. As is shown in Fig. 2, the moment given by the octanoyl derivative is about 5.5 G^2 (1 G=10^{-4} T) at room temperature and about 4 G^2 just below the melting point which is indicated by a vertical arrow. An abrupt decrease of the moment occurs at the melting point and moments between 0.9 and 0.8 G^2 are shown by the mesophase. On the other hand, the tetradecanoyl derivative gives a moment of about 7.8 G^2 at room temperature and that of about 4.5 G^2 near the melting point. The moment observed above this temperature is only 0.04 G^2. Thus, the motional behavior in the hexagonal disordered columnar phase depends appreciably on the alkyl chain length. The similar but less pronounced tendency has been noted with compounds **1**; namely, the second moment observed for the mesophase of the octanoyl derivative was 0.3 G^2 and that of the hexadecanoyl derivative 0.03 G^2.[1] Judging from these values of the second moment, one may conclude that the alkyl chains in the lower homologous members are moving more slowly, in the time scale of NMR, than those in the higher members in both the series **1** and **2**. This conclusion is not incompatible with the entropy changes at the clearing point mentioned above.

According to the rule of selected miscibility of Sackmann and Demus,[10] an uninterrupted series of binary mixtures should be obtainable if the mesophases are of the same structural type. However, Dabrowski et al., employing a homologous series as one of the components, have shown that the smectic A phase in binary mixtures is more and more depressed and, in some extreme cases, separated by a gap as the layer spacing ratio is increased.[11,12] The mesophases given by the tetradecanoyl derivatives of series **1** and **2** were found not to be completely miscible by the contact method.[13] The d_{100} ratio of these two compounds is approximately 1.2. We also examined the combination of the hexadecanoyl derivative of series **1** and the decanoyl derivative of the series **2**. These two give the spacings similar to each other (see Fig. 1). In this combination too, the mesophases are not miscible. The results are apparently in contradiction to the above-mentioned rule and may be ascribed to the distinct difference in the shape of the molecules involved, disk-like and half-disk-like. We have examined the miscibility between the members in the present series. The mesophase of the tetradecanoyl derivative was found to be miscible in any ratio with those of the hexadecanoyl and dodecanoyl derivatives but not with those of undecanoyl derivative and the lower homologous members. The complete miscibility among the lower members is more severely restricted; that is, only the nearest neighboring members are miscible with each other. It may be too early to be certain of the situation, but these observations may imply that the similarity in the motional behavior is also of importance to provide complete miscibility.

The present work was supported by a Grant-in-Aid for Scientific Research No. 60470001 from the Ministry of Education, Science and Culture.

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