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New Mesogenic Benzene Derivatives: N,N′,N′-Trialkanoyl-2-alkanoyloxy-1,3,5-benzenetriamines, N,N′,N″-Trialkanoyl-2,4-bis(alkanoyloxy)-1,3,5-benzenetriamines, and N,N′-Dialkanoyl-4,5,6-tris(alkanoyloxy)-1,3-benzenediamines

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New Mesogenic Benzene Derivatives: N,N′,N″-Trialkanoyl-2-alkanoyloxy-1,3,5-benzenetriamines, N,N′,N″-Trialkanoyl-2,4-bis(alkanoyloxy)-1,3,5-benzenetriamines, and N,N′-Dialkanoyl-4,5,6-tris(alkanoyloxy)-1,3-benzenediamines

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Three new series of mesogenic benzene derivatives have been synthesized. N,N′,N″-Trialkanoyl-2-alkanoyloxy-1,3,5-benzenetriamine exhibits a hexagonal disordered columnar phase when the alkanoyl group is valeryl or longer, the temperature range of stable existence of the mesophase being as wide as 78 to 118°C. The addition of a second $OCOC_nH_{2n+1}$ group to this compound does not affect appreciably the clearing point but depresses the melting point by 28 to 78°C. The enthalpies at the clearing point are anomalously large in this series; that is, 40 to 58 kJ mol^{-1}. Nevertheless, the second moments of the broad-line NMR spectra of the heptanoyl and hexadecanoyl derivatives are 0.1 G^2 or less in the mesophases in accordance with the hexagonal disordered columnar phase assigned on the basis of the X-ray diffraction patterns. The replacement of an $NHCOC_nH_{2n+1}$ group in the second compound by an $OCOC_nH_{2n+1}$ group resulted in lowering the clearing point by 21 to 45°C and raising the melting point by 12 to 37°C and the decrease of the enthalpy at the former transition by a factor of two or more.

Keywords: hexagonal disordered columnar phase, discotic, benzene derivatives

INTRODUCTION

In 1977, Chandrasekhar and his collaborators disclosed that some hexakis(alkanoyloxy)benzenes exhibit stable or metastable thermotropic liquid crystals.[1] The disk-like molecules in these mesophases are stacked one on top of the other in columns forming a hexagonal arrangement but the spacing between the molecules in each column is irregular. As we reported earlier,[2] the mesomorphic behavior can be considerably enhanced by the replacement of the two $OCOC_nH_{2n+1}$ groups at the

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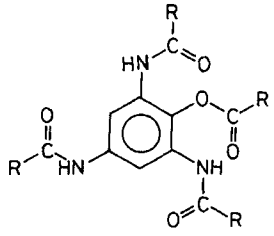
1 and 4 positions of hexakis(alkanoyloxy)benzenes by $NHCOC_nH_{2n+1}$ groups. Moreover, our study on N,N′-dialkanoyl-2,4-bis(alkanoyloxy)-1,3-benzenediamines revealed that even these half-disk-shaped molecules can form a hexagonal disordered columnar phase.[3] Thus, the $NHCOC_nH_{2n+1}$ groups appeared to be very efficient in promoting the thermal stability of discotic mesophases and are useful in designing mesogenic benzene derivatives.[4–6] With the hope of clarifying the effects of $OCOC_nH_{2n+1}$ and $NHCOC_nH_{2n+1}$ groups on mesomorphic behavior, we prepared three new series of compounds bearing only these two kinds of functional groups; namely, N,N′,N″-trialkanoyl-2-alkanoyloxy-1,3,5-benzenetriamines (1), N,N′,N″-trialkanoyl-2,4-bis(alkanoyloxy)-1,3,5-benzenetriamines (2), and N,N′-dialkanoyl-4,5,6-tris(alkanoyloxy)-1,3-benzenediamines (3) and compared their thermal properties and X-ray diffraction patterns with each other and also with those of N,N′-dialkanoyl-2,4-bis(alkanoyloxy)-1,3-benzenediamines (4).



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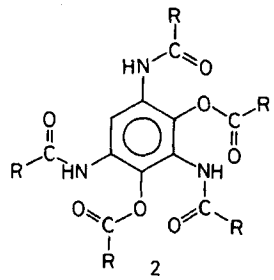

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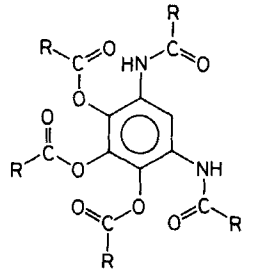

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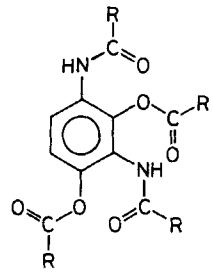

4

$R = C_nH_{2n+1}$

EXPERIMENTAL

2-Hyroxy-1,3,5-benzenetriamine and 2,4-dihydroxy-1,3,5-benzenetriamine hydrochlorides were prepared by reduction of 2,4,6-trinitrophenol and 2,4,6-trinitroresorcinol respectively with tin and hydrochloric acid. 4,6-Dinitro-1,2,3-hydroxybenzene was prepared by nitration of 1,2,3-triacetylpyrogallol following the procedure of Kehrmann and Poehl.[7] These hydrochlorides were acylated by refluxing in benzene with alkanoyl chloride and pyridine. The products were purified by recrystallizations from mixtures of benzene and ethanol. For example, Found: C, 75.74; H, 11.55; N, 4.02%. Calcd for C_6H_2 $(OCOC_{13}H_{27})$ $(NHCOC_{13}H_{27})_3$ (1): C, 76.02;

H, 11.52; N, 4.29%. Found: C, 75.46; H, 11.68; N, 3.38%. Calcd for $C_6H(OCOC_{13}H_{27})_2$ $(NHCOC_{13}H_{27})_3$ (2): C, 75.63; H, 11.61; N, 3.48%. Found: C, 73.41; H, 11.13; N, 2.90%. Calcd for $C_6H(OCOC_{10}H_{21})_3$ $(NHCOC_{10}H_{21})_2$ (3): C, 73.45; H, 10.91; N, 2.81%. The transition temperatures and associated 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 autodiffractometer, model RAD B, using filtered copper radiation. Proton NMR spectra were measured as the first derivative using a JEOL model JES-ME-3X spectrometer with a broad-line NMR attachment, model JES-BE-1, which employs a crossed-coil system.

RESULTS AND DISCUSSION

The calorimetric data of compound 1 are presented in Table I. Here, crystalline, hexagonal disordered columnar, and isotropic phases are denoted by K, D_{hd}, and I respectively. Figure 1 shows plots of the transition temperatures as a function of the number of carbon atoms (n) in the alkyl group. The temperature range of stable existence of the mesophase varies from 78°C in the valeryl (n = 4) derivative to 118°C in the dodecanoyl (n = 11) derivative. The enthalpies for the D_{hd}-I transition are in the range from 24 to 35 kJ mol^{-1} and comparable with those of N,N′-dialkanoyl-2-methyl-1,3-benzenediamines, the simplest among the molecules

TABLE I

Transition temperatures (°C) and associated enthalpies (kJ mol^{-1}) of compounds 1[a]

n[b]	K	D_{hd}	I
3	.	185 (34)	.
4	. 144 (30)	. 222 (28)	.
5	. 133 (35)	. 225 (28)	.
6	. 129 (40)	. 229 (31)	.
7	. 123 (48)	. 227 (31)	.
8	. 109 (47)	. 226 (33)	.
9	. 111 (56)	. 227 (35)	.
11	. 107 (65)	. 225 (29)	.
13	. 112 (76)	. 225 (28)	.
15	. 113 (86)	. 218 (24)	.

[a] The latter quantities are in parentheses.

[b] The number of carbon atoms in the alkyl group.

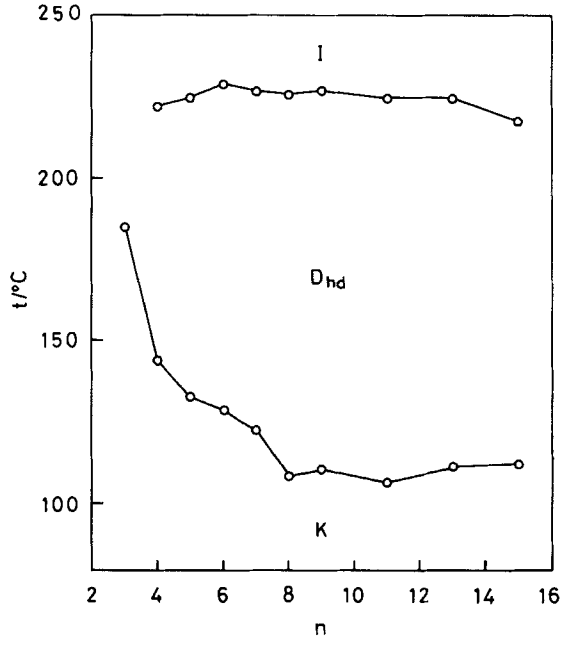

FIGURE 1 Plots of transition temperatures as a function of the number of carbon atoms (n) in the alkyl group for compound 1.

so far known to form a D_{hd} phase.[5] The clearing points in the present series are higher by about 20°C and the melting points are lower by 50 to 90°C than those for the corresponding members in the latter series.

The X-ray diffraction pattern of the tetradecanoyl (n = 13) derivative in the unoriented mesophase shows three sharp peaks assignable to the 100, 110, and 200 reflections. The value of d_{100} is 2.14 nm and that of d_{110} is 1.24 nm, the ratio of about $1/\sqrt{3}$ being characteristic of a hexagonal columnar structure. The diffuseness of the outer peak assignable to the 001 reflection is evidence of the liquid-like disorder in the third dimension and the value of 0.46 nm is in good agreement with those known for the D_{hd} phases of hexakis(alkanoyloxy)benzenes.[1]

The addition of a second $OCOC_nH_{2n+1}$ group to the 4-position of compound 1 yields compound 2. As is summarized in Table II, the change in clearing point by this structural modification is merely −1 to 19°C, but the enthalpy is markedly increased and ranges from 40 to 58 kJ mol^{-1}. On the other hand, the modification depresses appreciably the melting point; 28°C in the tetradecanoyl (n = 13) derivative and 78°C in the hexanoyl (n = 5) derivative. As a result, the temperature range of stable existence of the mesophase is as wide as 140 to 193°C in compound 2.

Alternatively, one may regard compound 2 as derived from compound 4, which exhibits also a D_{hd} phase, by the introduction of a third $NHCOC_nH_{2n+1}$ group to the 5-position. By this modification, the melting point is lowered by 25 to 30°C and the clearing point is raised by 110 to 120°C. The effects of these substituents may be summarized as follows; the introduction of an $OCOC_nH_{2n+1}$ group de-

TABLE II

Transition temperatures (°C) and associated enthalpies (kJ mol^{-1}) of compounds 2[a]

n[b]	K	D_{hd}	I
3	.	231 (71)	.
4	. 100 (16)	. 241 (53)	.
5	. 55 (19)	. 238 (50)	.
6	. 63 (30)	. 241 (45)	.
7	. 49 (19)	. 242 (45)	.
8	. 73 (42)	. 227 (40)	.
9	. 65 (39)	. 225 (47)	.
11	. 78 (56)	. 224 (58)	.
13	. 84 (82)	. 224 (52)	.
15	. 66 (63)	. 225 (50)	.

[a] The latter quantities are in parentheses.

[b] The number of carbon atoms in the alkyl group.

stabilizes, to some extent, the crystalline phase without affecting the mesophase much, whereas that of an $NHCOC_nH_{2n+1}$ group destabilizes, to some extent, the crystalline phase and stabilizes greatly the mesophase. The enhanced hydrogen-bonded self-association of the molecules by the additional $NHCOC_nH_{2n+1}$ group may account for the promotion of the mesophase,[8] and also the increase of the enthalpy for the D_{hd}-I transition.

Although the enthalpies for the D_{hd}-I transition are relatively large in compounds 2, the X-ray diffraction measurements revealed that the mesophase is of the same type. In Figure 2 the spacings d_{100} and d_{110} measured for the D_{hd} phases are plotted against the number of carbon atoms in the alkyl group. For example, the tetradecanoyl (n = 13) derivatives gives a d_{100} of 2.16 nm and a d_{110} of 1.24 nm. These values are almost the same as those given by the corresponding member of compound 1.

The liquid-like characteristics of alkyl chains in the mesophase are clearly demonstrated by the small second moments of the broad-line proton NMR spectrum (the mean-square width of the resonance line), $\langle \Delta H^2 \rangle$, measured above the melting point. The moment given by the heptanoyl (n = 6) derivative below the melting point is about 5 G^2 (G = 10^{-4} T) and decreases abruptly to 0.1 G^2 near the melting point and then gradually to 0.02 G^2 by 140°C. The hexadecanoyl (n = 15) derivative yields moments similar to the afore-mentioned; namely, about 0.1 G^2 near the melting point and 0.03 G^2 around 140°C.

Table III presents the thermal behavior of compound 3. The replacement of the

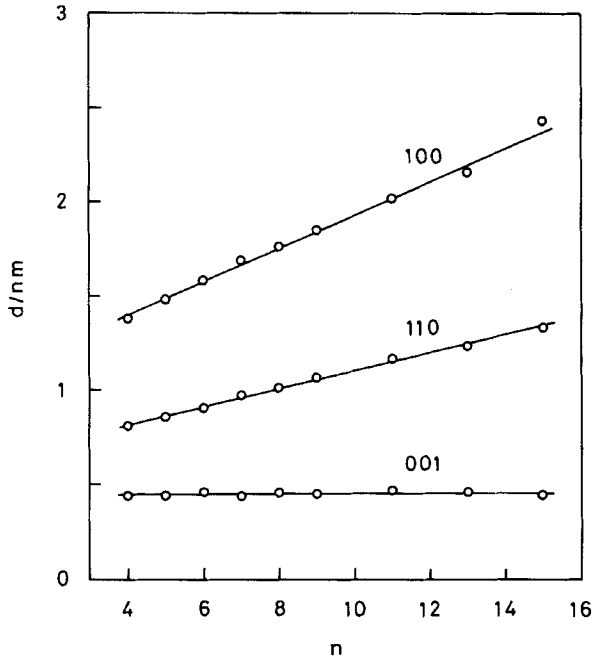

FIGURE 2 Plots of spacings d_{100}, d_{110}, and d_{001} in the D_{hd} phase against the number of carbon atoms (n) in the alkyl group for compound 2.

$NHCOC_nH_{2n+1}$ group at the 3-position of compound 2 by an $OCOC_nH_{2n+1}$ group leads to compound 3. On passing from compound 2 to compound 3 the melting point is raised by 12 to 37°C and the clearing point is lowered by 21 to 45°C. The latter result is in conformity with the effects of $OCOC_nH_{2n+1}$ and $NHCOC_nH_{2n+1}$ groups individually introduced but the former is not to be expected, indicating that the effects of the substituents on the melting point are more complex and may depend upon the molecular shape. From this point of view, it is interesting to point out that both the melting and clearing points of compound 3 are close to those of the corresponding N,N′-dialkanoyl-2,3,5,6-tetrakis(alkanoyloxy)-1,4-benzenediamine. This resemblance may be ascribed to the fact that the molecules of compounds 2 and 3 are sufficiently disk-shaped and that the former molecule carries three $NHCOC_nH_{2n+1}$ groups but the latter carries just two. The enthalpy for the D_{hd}-I transition is significantly diminished by the replacement of an $NHCOC_nH_{2n+1}$ group by an $OCOC_nH_{2n+1}$ group and tends to decrease as the series is ascended. The same trend is noted for the series of hexakis(alkanoyloxy)benzenes,[1] N,N′-dialkanoyl-2,3,5,6-tetrakis(alkanoyloxy)-1,4-benzenediamines,[2] and others.[4]

The mesophase of compound 3 was also identified by the X-ray diffraction measurements as a D_{hd} phase. Not only the spacings d_{100} and d_{110} but also the second moments of broadline NMR spectra measured for the heptanoyl (n = 6) and hexadecanoyl (n = 15) derivatives in the mesophases are very similar to those of compound 2.

The largest enthalpy observed for the D_{hd}-I transition is 58 kJ mol^{-1} of the dodecanoyl (n = 11) derivative in series 2 and the smallest is 11 kJ mol^{-1} of the

TABLE III

Transition temperatures (°C) and associated enthalpies (kJ mol^{-1}) of compounds 3[a]

n[b]	K	D_{hd}	I
3	.	213 (48)	.
4	. 113 (20)	. 196 (21)	.
5	. 67 (23)	. 208 (21)	.
6	. 88 (37)	. 208 (19)	.
7	. 77 (35)	. 208 (17)	.
8	. 93 (52)	. 206 (15)	.
9	. 92 (57)	. 203 (13)	.
10	. 96 (66)	. 202 (12)	.
11	. 101 (66)	. 203 (14)	.
13	. 103 (94)	. 198 (12)	.
15	. 103 (108)	. 193 (11)	.

[a] The latter quantities are in parentheses.

[b] The number of carbon atoms in the alkyl group.

hexadecanoyl (n = 15) derivative in series 3. According to Demus *et al.*,[10] the enthalpies for the non-ordered smectic-isotropic transition spread over 2.93 to 42.7 kJ mol^{-1}; therefore, our results would not be surprising at all. There are many benzene derivatives which exhibit mesophases more ordered than a D_{hd} phase or no mesophase but the enthalpy for the transition into an isotropic liquid is in the range covered by the above-mentioned extremes.[5,9] Apparently, the enthalpy alone does not provide a reliable means to identify a D_{hd} phase.

References

1. S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, *Pramana*, **9**, 471 (1977).
2. Y. Kobayashi and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **60**, 3515 (1987).
3. H. Kawada and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **61**, 3083 (1988).
4. Y. Harada and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **61**, 2739 (1988).
5. H. Kawada, Y. Matsunaga, T. Takamura and M. Terada, *Can. J. Chem.*, **66**, 1867 (1988).
6. H. Kawada and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **63**, 1961 (1990).
7. F. Kehrmann and N. Poehl, *Helv. Chim. Acta*, **9**, 485 (1926).
8. J. Malthete, A. M. Levelut and L. Liebert, *Adv. Mater.*, **4**, 37 (1992).
9. Y. Matsunaga, N. Miyajima, Y. Nakayasu, S. Sakai and M. Yonenaga, *Bull. Chem. Soc. Jpn.*, **61**, 207 (1988).
10. D. Demus, S. Diele, S. Grande and H. Sackmann, *Advances in Liquid Crystals*, Vol. 6, edited by G. H. Brown, Academic Press, New York (1983), p. 65.