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Novel Nematogens Derived from *N,N'*-Dialkanoyl-4-alkanoyloxy-1,3-benzenediamines

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The mesomorphic properties of homologous series of *N,N'*-dialkanoyl-2,5-dimethyl-4-alkanoyloxy-1,3-benzenediamines and their 2-methyl-5-isopropyl and 2-methyl-5-*t*-butyl analogues have been studied. All the mesophases appearing in the nonanoyl to hexadecanoyl derivatives of the first series are metastable and nematic in type. By the replacement of the methyl group at the 5-position with an isopropyl or *t*-butyl group, nematic thermal stability is promoted. As a result, the nonanoyl to tetradecanoyl derivatives in the second series can exhibit a nematic phase with a temperature range of stable existence over 7 to 22°C. The 2-methyl-5-isopropyl compounds, in which the ester alkyl group is different from the other alkyl groups, were also synthesized. The broadest temperature range of stable existence of a nematic phase of 31°C is achieved when tridecyl groups are connected through the CONH groups and a octyl group through the COO group. The *t*-butyl group at the 5-position stabilizes not only the mesophase but also the crystalline phase; therefore, a nematic phase is detectable only for the undecanoyl to hexadecanoyl derivatives.

Keywords: nematic, benzene derivatives, isopropyl group, t-butyl group

INTRODUCTION

We have been engaged in a study of the mesomorphic behavior of benzene derivatives. The previous papers in this series dealt with *N,N'*-dialkanoyl-2,3,5,6-tetrakis(alkanoyloxy)-1,4-benzenediamines,[1] *N,N',N''*-trialkyl-1,3,5-benzenetricarboxamides,[2] *N,N',N''*-trialkanoyl-2,4,6-trimethyl-1,3,5-benzenetriamines,[3] *N,N'*-dialkanoyl-2,4,6-trimethyl-1,3-benzenediamines,[4] *N,N'*-dialkanoyl-2,4-bis(alkanoyloxy)-1,3-benzenediamines,[5] and *N,N'*-dialkanoyl-2,5,6-trimethyl-4-alkanoyloxy-1,3-benzenediamines.[6] The last-mentioned compounds are nematogenic when the alkanoyl group is octanoyl to octadecanoyl. Comparing the thermal behavior to that of the unmethylated compound, the function of the three methyl groups appeared to strengthen the intermolecular attraction by increasing the polarizability of the

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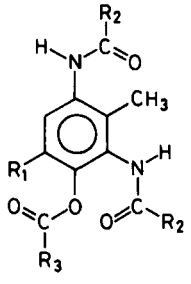
molecule, to an extent outweighing the intermolecular separation, and to convert an isotropic liquid into mesophases. Further comparison with *N,N'*-dialkanoyl-2,4,5,6-tetramethyl-1,3-benzenediamine disclosed that the replacement of a methyl group with an alkanoyl group results in the appearance of a nematic phase in the temperature range covered by a more-ordered mesophase, reducing the intermolecular attractive force.[4] Thus, the achievement of a nematic phase in the above-mentioned compounds was ascribed to the adjustment of intermolecular attraction by employing the opposing effects of methyl groups and of a long alkanoyloxy group.

It seemed to us to be desirable to examine the effects of some other alkyl groups. Accordingly, this paper describes studies on series of *N,N'*-dialkanoyl-2,5-dimethyl-4-alkanoyloxy-1,3-benzenediamines (1), the 2-methyl-5-isopropyl analogues (2), and the 2-methyl-5-*t*-butyl analogues (3). In the course of the preparation of series 2, it turned out that the amino groups in 2-methyl-5-isopropyl-4-hydroxy-1,3-benzenediamine (2,4-diaminothymol) are selectively acylated possibly because of the steric influence of the isopropyl group on neighboring hydroxyl group. This finding developed the way to synthesize a large number of the 2-methyl-5-isopropyl compounds where the ester alkyl groups, $R_3 = C_mH_{2m+1}$, is different from the other two alkyl groups, $R_2 = C_mH_{2n+1}$. To the authors' knowledge, the dissymmetric hexasubstituted triphenylenes reported by Nguyen *et al.* are the only compounds somehow related to the aspect of our present study.[7]



(1) $R_1 = CH_3$

(2) $R_1 = CH(CH_3)_2$

(3) $R_1 = C(CH_3)_3$

$R_2 = C_nH_{2n+1}$

$R_3 = C_mH_{2m+1}$

EXPERIMENTAL

The nitration of 2,5-dimethylphenol and 2-isopropyl-5-methylphenol (thymol) dissolved in acetic acid was carried out by the procedure of Ganguly and Le Fèvre,[8] and that of 2-*t*-butyl-5-methylphenol dissolved in benzene by the procedure of Albert and Sears.[9] The dinitrophenols were reduced to diaminophenols with metallic tin and concentrated hydrochloric acid. The final products were obtained by the reaction of the diaminophenol hydrochlorides dissolved in pyridine with appropriate acyl chlorides. Found: C, 76.82; H, 11.63; N, 3.42%. Calcd for $C_6H(CH_3)$ (iso-C_3H_7) ($NHCOC_{13}H_{27}$)$_2$ ($OCOC_{13}H_{27}$): C, 76.98; H, 11.68; N, 3.45%. Found:

C, 77.16; H, 11.72; N, 3.38%. Calcd for $C_6H(CH_3)$ (t-C_4H_9) $(NHCOC_{13}H_{27})_2$ $(OCOC_{13}H_{27})$: C, 77.13; H, 11.72; N, 3.39%. The calorimetric and X-ray diffraction measurements were made as has been described in a previous paper.[1]

RESULTS AND DISCUSSION

N,N'-Dialkanoyl-2,5-dimethyl-4-alkanoyloxy-1,3-benzenediamines (1)

The transition temperatures and the associated enthalpies for the 2,5-dimethyl compounds are presented in Table I. The notations, K, N, and I refer to the crystalline, nematic, and isotropic phases, respectively. The compounds carrying nonanoyl ($n = m = 8$) or higher alkanoyl groups exhibit a metastable mesophase (see plot a in Figure 1). This phase is fluid and adopts a schlieren texture. The enthalpy associated with the transition into an isotropic liquid is small and decreases from 1.4 kJ mol^{-1} for the decanoyl derivative to 0.6 kJ mol^{-1} for the hexadecanoyl derivative. On the basis of these observations, one may safely conclude that the mesophase is nematic in type. The phase given by the nonanoyl derivative was microscopically observable but the associated enthalpy could not be determined because of rapid solidification. The clearing point is lower by 44 to 47°C than that of the 2,5,6-trimethyl compounds (see plot d in Figure 1). Thus, a methyl group at the 6-position of the latter compounds appears to be very efficient in promoting

TABLE I

Transition temperatures (t/°C) and associated enthalpies (ΔH/kJ mol^{-1})[a] of *N,N'*-dialkanoyl-2,5-dimethyl-4-alkanoyloxy-1,3-benzenediamines

n[b]	K_3	K_2	K_1	N	I
6	. 140 (6.6)		. 203 (48)		.
7	. 125 (5.2)		. 191 (47)		.
8	. 137 (12)	. 165[c]	. 180 (38)	[. 154 (---)][d]	.
9	. 121 (11)	. 161 (26)	. 171 (11)	[. 150 (1.4)][d]	.
10	. 111 (8.3)	. 149 (12)	. 164 (16)	[. 147 (1.2)][d]	.
11	. 102 (7.5)	. 150[c]	. 159 (30)	[. 143 (1.0)][d]	.
13	. 103 (13)	. 147[c]	. 151 (23)	[. 137 (0.8)][d]	.
15	. 101 (9.5)	. 141[c]	. 147 (26)	[. 127 (0.6)][d]	.

a. Values in parentheses.

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

c. The enthalpy is added to that of the next higher temperature transition.

d. Monotropic transition.

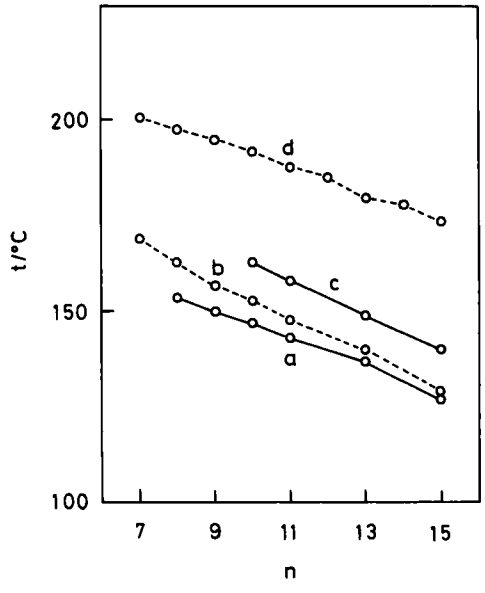


FIGURE 1 N—I transition temperature plotted against the number of carbon atoms in the alkyl group (n). a) *N,N'*-dialkanoyl-2,5-dimethyl-4-alkanoyloxy-1,3-benzenediamines, b) the 2-methyl-5-isopropyl analogues, c) the 2-methyl-5-*t*-butyl analogues, and d) the 2,5,6-trimethyl analogues.

nematic thermal stability. Since this methyl group is accommodated in the space produced between the NHCOR group at the 1-position and the methyl group at the 5-position, it may contribute to an increase in the cohesive forces due to the increased polarizability without affecting the intermolecular separation and/or may turn the NHCOR group at the 1-position out of the plane of the benzene ring, leading to more extensive hydrogen-bonded self-association, as proposed by Malthête *et al.*[10,11] The methyl group at either the 2- or 5-position would be found similarly efficient in promoting the mesophase stability if the behavior of the 5,6- or 2,5-dimethyl compound were compared with that of the 2,5,6-trimethyl compound. Therefore, we are only permitted to conclude that the contribution of two methyl groups to attractive forces is not enough to convert an isotropic liquid into a thermodynamically stable nematic phase.

The X-ray diffraction pattern of the mesophase consists of two diffuse peaks, supporting our conclusion that the phase is nematic in type. The spacing given by the inner broad peak is 1.80 nm for the undecanoyl derivative and increases linearly with the alkyl chain length up to 2.21 nm for the hexadecanoyl derivative. These values are shorter by a factor of about two than the lengths of the most extended molecular configuration but close to those recorded for the hexagonal disordered columnar phases and also those found for the nematic phases of the 2,5,6-trimethyl compounds.[1-6] Therefore, the present nematic phase is not a classical one. The outer broad peak gives invariably a spacing of 0.47 nm, indicating the liquid-like disorder.

Two solid-solid transitions are shown above 100°C by virgin samples of most of the homologous members. Only the transition at a higher temperature is detected

in the second heating though the enthalpy of the transition at a lower temperature is rather small; that is, 5 to 13 kJ mol^{-1}. The K_1 phase is not quite rigid but viscous. However, it must be noted that the monotropic N—I transition is located well below the K_2—K_1 transition in support of our classification. The longest spacing found in the X-ray diffraction pattern of the K_1 phase is 2.85 nm for the nonanoyl derivative and 4.41 nm for the hexadecanoyl derivative. They are a little longer than those of the so-called M_2 phases of the corresponding 2,5,6-trimethyl compounds.

N,N'-Dialkanoyl-2-methyl-5-isopropyl-4-alkanoyloxy-1,3-benzenediamines (2)

Table II summarizes the thermodynamic data for the 2-methyl-5-isopropyl compounds. We will first consider only the compounds with $n = m$ in order to compare them with the 2,5-dimethyl compounds. Hereafter, the homologous members of this particular series will be denoted by (n, m). The N—I transition is raised by 2°C for (8, 8) to 9°C for (15, 15) by the replacement of the methyl group at the 5-position with an isopropyl group (compare plots a and b in Figure 1), whereas the K_1—N transition temperature is lowered by 18 to 36°C. The nematic phase is thermodynamically stable in (8, 8) and the higher homologous members, the broadest temperature range of stable existence being 22°C for (9, 9). The N—I transition temperature is depressed as the series is ascended and simultaneously the associated enthalpy is diminished. The latter quantity is approximately twice larger compared with that of the 2,5-dimethyl analogue; that is 3.0 versus 1.4 kJ mol^{-1} for the decanoyl derivative and 1.1 versus 0.6 kJ mol^{-1} for the hexadecanoyl derivative.

The X-ray diffraction pattern for the K_1 phase is dominated by a sharp inner peak and a broad outer one. The spacing given by the former peak increases linearly with the number of carbon atoms in the alkyl chain and that given by the latter is about 0.47 nm. The inner peak is accompanied by its second- and third-order reflections and the outer one is overlapped by two sharp peaks which give spacings of 0.44 and 0.46 nm, respectively. No peak assignable to 110 reflection which is crucial for the identification of hexagonal order is detected. The K_1 phase might be a sort of the lamello-columnar mesophase reported by Malthête *et al.*,[11] if it is not classified into a highly disordered solid.

In Figure 2, the compounds are arranged by placing n on the abscissa and m on the ordinate. The members exhibiting an enantiotropic N—I transition are represented by open circles which are found in a rectangular area confined by $n = 8$ to 13 and $m = 5$ to 15. Thus, the nematic stability is more sensitive to n than to m. Crosses represent the non-nematogenic members and are located on the periphery. Shaded circles are for the members exhibiting a monotropic N—I transition. The N—I transition for (9, 5), (13, 4), and (15, 15) are not distinguishable from the K_1—N transition by our calorimetric measurements; therefore, they are arbitrarily represented by shaded circles. As is shown in Figure 3, the N—I transition temperature does not depend much upon the alkyl chain length or decreases with increasing either n or m; therefore, the highest temperature is 170°C found for (8, 5) and the lowest is 129°C for (15, 15). The dashed curves in Figure 2 are isothermals drawn for intervals of every 10°C only as guides for the eyes.

As to the enthalpy at the N—I transition, the largest value (5.5 kJ mol^{-1}) is

TABLE II

Transition temperatures (t/°C) and associated enthalpies (ΔH/kJ mol^{-1})[a] of *N,N'*-dialkanoyl-2-methyl-5-isopropyl-4-alkanoyloxy-1,3-benzenediamines

n[b]	m[c]	K_2	K_1	N	I
5	5	. 138 (15)	. 178 (17)		.
6	6	. 124 (15)	. 177 (19)		.
6	11	. 114 (5.1)	. 158 (16)		.
6	15	. 118 (8.3)	. 148 (14)		.
7	7	. 126 (19)	. 171 (20)	[. 169 (---)][d]	.
7	9	. 160 (28)	. 167 (10)	[. 160 (---)][d]	.
7	11	. 129 (20)	. 157 (14)	[. 155 (---)][d]	.
7	13	. 118 (13)	. 151 (14)	[. 149 (---)][d]	.
7	15	. 129 (15)	. 147 (15)	[. 144 (---)][d]	.
8	4	. 177 (18)			.
8	5	. 163 (19)	. 165 (8.5)	. 170 (5.5)	.
8	6	. 151 (17)	. 159 (8.2)	. 169 (5.0)	.
8	7	. 107 (15)	. 154 (8.3)	. 167 (4.2)	.
8	8	. 120 (21)	. 156 (11)	. 163 (4.0)	.
8	9	. 140 (16)	. 149 (9.3)	. 161 (3.4)	.
8	11	. 143 (30)	. 148 (7.7)	. 154 (2.1)	.
8	13	. 117 (11)	. 141 (9.0)	. 149 (1.8)	.
8	15	. 127 (19)	. 137 (10)	. 143 (1.6)	.
9	5	. 155 (2.8)	. 162 (12)	[. 162 (3.2)][d]	.
9	6	. 138 (9.2)	. 144 (6.3)	. 164 (3.9)	.
9	9	. 124 (28)	. 135 (9.6)	. 157 (3.0)	.
9	15	. 127 (23)	. 129 (7.1)	. 144 (1.7)	.
10	10	. 129 (21)	. 135 (11)	. 153 (2.5)	.
11	4	. 92 (14)	. 152 (12)	[. 151 (---)][d]	.
11	5	. 78 (8.4)	. 146 (8.3)	. 152 (2.4)	.
11	6	. 74 (6.4)	. 128 (8.4)	. 154 (2.5)	.
11	8	. 127 (9.0)	. 144 (8.6)	. 153 (2.2)	.
11	11	. 128 (33)	. 131 (11)	. 148 (1.9)	.
11	13	. 135 (12)		. 144 (1.7)	.

Table II (*Continued*)

n[b]	m[c]	K_2	K_1	N	I
11	15	. 129 (33)	. 132 (8.7)	. 140 (1.4)	.
13	4	. 122 (4.3)	. 141 (7.7)	[. 141 (1.4)][d]	.
13	5	. 89 (13)	. 134 (6.9)	. 143 (1.7)	.
13	6	. 76 (12)	. 125 (12)	. 144 (1.6)	.
13	7	. 77 (11)	. 121 (11)	. 144 (1.7)	.
13	8	. 83 (26)	. 113 (9.5)	. 144 (1.6)	.
13	11	. 108[e]	. 117 (39)	. 143 (1.5)	.
13	13	. 124[e]	. 129 (51)	. 140 (1.4)	.
13	15	. 149[e]	. 152 (91)	[. 136 (1.2)][d]	.
15	5	. 100 (6.8)	. 149 (23)		.
15	8	. 153 (18)	. 161 (15)		.
15	11	. 148[e]	. 153 (22)		.
15	13	. 144[e]	. 152 (9.0)		.
15	15	. 123[e]	. 129 (63)	[. 129 (1.1)][d]	.

a. Values in parentheses.

b. The number of carbon atoms in alkyl group R_2.

c. The number of carbon atoms in alkyl group R_3.

d. Monotropic transition.

e. The enthalpy is added to that of the next higher temperature transition.

found for (8, 5) and the second largest (5.0 kJ mol^{-1}) for (8, 6). As the value is decreased by an increase of n and/or m, the contour lines constructed for the enthalpy resemble the isothermals for the N—I transition temperature (Figure 2).

The K_1—N transition temperature dependence upon n and m is more complicated. When n = 9 and 15, the temperature is generally high. In the former region, it decreases monotonously by an increase of m but such a tendency is not observed in the latter. When n = 13, the temperature gives a broad minimum around m = 8. Consequently, the temperature range of stable existence of the nematic phase tends to be wide for the members located around (11, 8). For this particular member the range is merely 9°C. The ranges wider than 20°C are given by the following members; 31°C by (13, 8), 26°C by (13, 11), 23°C by (13, 7), and 22°C by (9, 9).

For compounds (7, 7–15) and also (11, 4), the monotropic N—I transition was microscopically determined. Measurements of the associated enthalpies were ham-

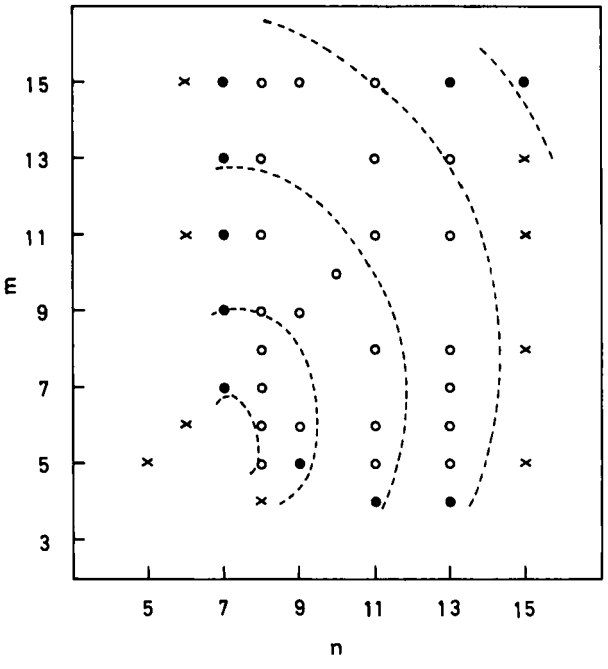


FIGURE 2 N—I transition temperature of *N,N'*-dialkanoyl-2-methyl-5-isopropyl-4-alkanoyloxy-1,3-benzenediamines plotted against the numbers of carbon atoms in alkyl groups R_2 (n) and R_3 (m). As to R_2 and R_3, see the structural formula.

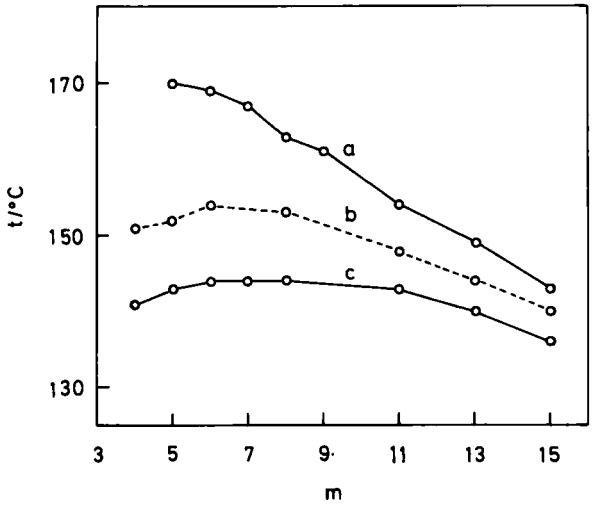


FIGURE 3 N—I transition temperature of *N,N'*-dialkanoyl-2-methyl-5-isopropyl-4-alkanoyloxy-1,3-benzenediamines plotted against the number of carbon atoms in ester alkyl group R_3 (m). a) $n = 8$, b) $n = 11$, and c) $n = 13$, where n is the number of carbon atoms in amide alkyl group R_2.

pered by rapid transformation from a nematic phase into a crystalline phase although the N—I transition is located at a temperature lower only by a few degrees, at most 7°C, than the K_1—N transition. In sharp contrast to these cases, both the isotropic and nematic phases of (13, 15) could be supercooled below the K_2—K_1 transition temperature.

Nguyen *et al.* studied the thermal stability of the mesophase exhibited by dissymmetric 2,3,6,7,10,11-hexaalkoxytriphenylenes.[7] The hexagonal ordered columnar phases given by the symmetrical and dissymmetrical derivatives were totally miscible. Both the dissymmetrical derivatives carrying four long and two short alkyl chains and also those carrying two long and four short alkyl chains exhibited D_{ho}—I transition temperatures lower than those of the derivatives carrying either six long or six short alkyl chains. Our compounds do not show such a tendency at all. The fact that long and short alkyl chains in our compounds connected through different functional groups to the molecular core may account for this behavior. The N—I transition temperatures are in the following order; $(n, n) > (n, n') > (n', n')$ if $n < n'$.

N,N'-Dialkanoyl-2-methyl-5-*t*-butyl-4-alkanoyloxy-1,3-benzenediamines (3)

As is shown in Table III, all the observed N—I transition temperatures are higher than those in the previously-mentioned two series and are enantiotropic (see plot c in Figure 1). The K_1—N transition temperature of the lower homologous members is particularly high and the temperature decreases sharply as the series is ascended; therefore, the temperature range of stable existence of the nematic phase is merely 1°C for the undecanoyl derivative but is broadened to 18 and 16°C for the tetradecanoyl and hexadecanoyl derivatives, respectively. The enthalpy at the N—I transition is further increased by the replacement of the isopropyl group at the 5-position with a *t*-butyl group. For example, the enthalpy of the undecanoyl derivative is 1.2 kJ mol^{-1} for the 2,5-dimethyl compounds, 2.5 kJ mol^{-1} for the

TABLE III

Transition temperatures (t/°C) and associated enthalpies (ΔH/kJ mol^{-1})[a] of *N,N'*-dialkanoyl-2-methyl-5-*t*-butyl-4-alkanoyloxy-1,3-benzenediamines

n[b]	K_2	K_1	N	I
9	. 103 (25)	. 174 (22)		.
10	. 98 (29)	. 162 (19)	. 163 (4.0)	.
11	. 102 (34)	. 151 (12)	. 158 (3.0)	.
13	. 98 (45)	. 131 (10)	. 149 (2.0)	.
15	. 100 (48)	. 124 (9.0)	. 140 (2.0)	.

a. Values in parentheses.

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

2-methyl-5-isopropyl compound, and 4.0 kJ mol^{-1} for the 2-methyl-5-*t*-butyl compound. Since the N—I transition entropy increases in this order, the orientational ordering in the nematic phase must be enhanced by increasing the bulkiness of the alkyl group at the 5-position.

Recently, Malthête *et al.* disclosed the nematic behavior of *N,N'*-bis(dodecanoyl)- and *N,N'*-bis(hexadecanoyl)-2-methyl-5-*t*-butyl-1,3-benzenediamines.[11] Comparison of their data with ours indicates that the effects of the long alkanoyloxy group at the 4-position in our compounds on the transition temperatures are not large. While the melting and clearing points of our dodecanoyl derivative are lower, by 3°C and 9°C respectively, than those of theirs, those of the hexadecanoyl derivative are almost identical.

The X-ray diffraction pattern of the K_1 phase is essentially the same as that of the 2-methyl-5-isopropyl compounds. The spacing given by the inner broad peak of the pattern characteristic of a nematic phase is also similar to those given by the other two series.

Although the nematic thermal stability of the compounds studied here is markedly lower than that of the 2,4,6-trimethyl compounds (see plot d in Figure 1), the promotion of the clearing point by replacing the methyl group at the 5-position with an isopropyl group or a *t*-butyl group is worth mentioning. According to the work by Collard and Lillya, the methyl-branching at the 2-positions of the alkyl chains in hexakis (octanoyloxy)benzene and -cyclohexane destabilizes the columnar phase relative to the straight-chain analogues.[12] Therefore, our results may be rather unexpected. Concerning classical mesophases, a bulky *t*-butyl group has been known to be markedly unfavorable to mesophase formation as exemplified by the N—I transition temperature of 2-*t*-butyl-1,4-phenylene bis(4-methoxybenzoate), which is lower by as much as 191°C than that of the unsubstituted one.[13,14] However, our study of the effects of methyl-branching of the terminal ester alkyl group on the mesomorphic properties of some three-ring systems revealed that the second or the third methyl group introduced to the ester propyl group may raise or lower the N—I transition temperature, depending upon the kind of other terminal substituents.[15,16] In other words, the nature of the terminal substituent exerts significant effects on the local molecular ordering adopted in the nematic phase, resulting in quite different effects of chain branching of the ester alkyl group on the mesomorphic properties.

Naturally, the local molecular ordering in the present nematic phase is anticipated to be very different from that known for most classical mesophases. Malthête *et al.* performed X-ray diffraction measurements on the nematic phases exhibited by their own compounds and also by *N,N'*-dialkanoyl-2,4,6-trimethyl-1,3-benzenediamines. They proposed that these two-chain diamide molecules are in supramolecular hydrogen-bonded self-association in which the flat aromatic nuclei are regularly stacked. Then, the stacks are organized in a liquid array, leading to a "boiled-spaghetti-like" nematic phase. The non-classical nematic phases exhibited by the present compounds are highly likely to be of a similar character.

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