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New Discogenic Compounds: *N,N'*-Dialkanoyl-2,3,5,6-tetrakis-(alkanoyloxy)-1,4-benzenediamines

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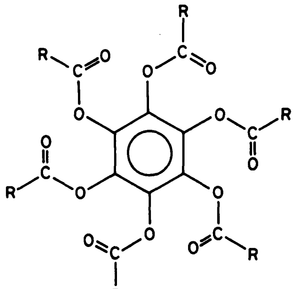
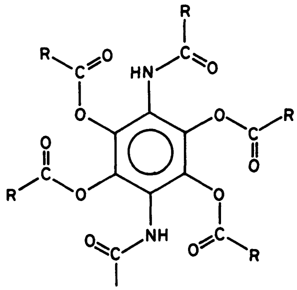
A series of *N,N'*-dialkanoyl-2,3,5,6-tetrakis(alkanoyloxy)-1,4-benzenediamines has been prepared and found to be mesogenic over a wide temperature range. The transformation into an isotropic liquid at a temperature between 189 and 209 °C is followed by thermal decomposition. The X-ray diffraction pattern of unoriented specimens in the mesophase consists of two sharp inner peaks and a broad outer one assignable to 100, 110, and 001 reflections respectively, indicating that the phase is hexagonal columnar.

A number of single compounds composed not only of elongated molecules but also of disk-like molecules are known to form stable or metastable thermotropic liquid crystals.[1,2] The first series of the latter group was discovered by Chandrasekhar et al. in 1977.[3,4] The compounds examined by them were hexakis(alkanoyloxy)benzenes (**1**), which were synthesized forty years earlier by Backer and van der Baan.[5] The discotic mesophase is observable only when n=6, 7, and 8. The temperature ranges are 5.8 and 3.6 °C in the first and the second members respectively. The mesophase appearing in the last member is metastable. In these mesophases, the disk-like molecules 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 the substituent $NHCOC_nH_{2n+1}$ is efficient to promote the thermal stability of nematic and smectic phases,[6,7] the partial replacement of $OCOC_nH_{2n+1}$ groups in the above-mentioned hexasubstituted benzenes by $NHCOC_nH_{2n+1}$ groups might also stabilize discotic phases. Therefore, we have undertaken a study of *N,N'*-dialkanoyl-2,3,5,6-tetrakis(alkanoyloxy)-1,4-benzenediamines (**2**). A discotic mesophase was found over temperature ranges as wide as 140 °C when n=4 to 15.





$R = C_nH_{2n+1}$

1 **2**

Experimental

Materials. The sodium salt of 2,5-dihydroxy-3,6-dinitro-*p*-benzoquinone prepared by starting from *p*-chloranil was reduced to 3,6-diamino-1,2,4,5-benzenetetrol according to Nietzki and Benckiser.[8] The acylation was carried out employing acyl chloride in the presence of pyridine. For example, Found: C, 68.09; H, 9.61; N, 3,31%. Calcd for $C_6(NHCOC_6H_{13})_2(OCOC_6H_{13})_4$: C, 68.21; H, 9.54; N, 3.31%. Found: C, 73.90; H, 11.24; N, 2.33%. Calcd for $C_6(NHCOC_{11}H_{23})_2(OCOC_{11}H_{23})_4$: C, 74.00; H, 11.15; N, 2.21%. Hexakis(heptanoyloxy)benzene to be used as a reference discogen was prepared by the reaction between heptanoic anhydride and benzenehexol.[5] The latter compound was derived from the diaminobenzenetetrol.[8]

Measurements. Calorimetric curves up to the transition to isotropic liquids were recorded on a Rigaku Thermoflex differential scanning calorimeter at a heating rate of 5 K min^{-1}. The enthalpy changes were estimated by comparing the peak areas with that due to the melting of indium, 3.26 kJ mol^{-1}. The phase diagram was determined by the calorimetric curves of mixtures at every ten mol%. X-Ray diffractions were measured with a Rigaku auto-diffractometer, model RAD IVB, using filtered copper radiation. Proton NMR spectra were recorded as the first derivatives at 40 MHz, 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 thermal properties of *N,N'*-dialkanoyl-2,3,5,6-tetrakis(alkanoyloxy)-1,4-benzenediamines are summarized in Table 1. Here, K, D, and I stand for crystalline, discotic, and isotropic phases respectively. No solid-solid transition is observed above room temperature for any member. The valeryl derivative (n=4)

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

n[b)]	K		D		I
3	.		219 (53)		.
4	.	134 (26)	.	208 (45)	.
5	.	71 (18)	.	209 (45)	.
6	.	64 (28)	.	208 (40)	.
7	.	75 (39)	.	205 (37)	.
8	.	77 (50)	.	200 (36)	.
9	.	77 (62)	.	199 (33)	.
10	.	81 (65)	.	198 (31)	.
11	.	89 (82)	.	197 (28)	.
13	.	92 (103)	.	189 (22)	.
15	.	94 (115)	.	190 (18)	.

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

forms a viscous birefringent fluid upon the transition located at 134 °C. All the higher homologous members melt below 100 °C. It is noted that the melting (K–D transition) points of the heptanoyl, octanoyl, and nonanoyl derivatives (n=6, 7, and 8) are not far from those of the compounds **1** with the same alkyl groups, 81, 80, and 80 °C respectively. On the other hand, the clearing (D–I transition) point is at a temperature higher than 200 °C in the case of the valeryl to nonanoyl derivatives and gradually lowers as the series is ascended. Thus, the temperature range of the mesophase is so expanded upwards by the replacement that the D–I transition of compound **2** is followed by thermal decomposition. The enthalpy of the D–I transition decreases with the increase of the alkyl chain length as is known for discotic hexasubstituted triphenylenes by the work of Destrade et al.[9] The same tendency may be noted also for the short series of compounds **1**. However, the value in the present compound is larger almost by a factor of two than that of the corresponding member in the series **1**. For example, 40 kJ mol^{-1} versus 22.2 kJ mol^{-1} when n=6.

The X-ray diffraction patterns of unoriented liquid crystals were measured at temperatures 10 to 15 °C below the clearing point. The major feature resembles that known for smectic A or C phase. The innermost peak is sharp and strong and is often accompanied by the second order reflection. An additional weak sharp peak is found in all the diffraction patterns. The spacing given by the former peak increases linearly within the limits of our experimental errors from 1.36 nm of the valeryl derivative to 2.37 nm of the hexadecanoyl derivative (n=15) and that given by the latter from 0.79 to 1.37 nm (see Fig. 1). These two spacings are in a ratio of about $1/\sqrt{3}$ characteristic of a hexagonal lattice. Therefore, the strong inner peak may be assigned to 100 reflection and the weak one to 110 reflection. This observation is interpreted by the presence of lamellar order with hexagonal symmetry in two dimensions in agreement with that reported for compounds **1**.[3,4] The diffuseness of the outer peak assignable to the 001 reflection must be evidence of the liquid-like disorder in the third dimension. The mean intermolecular spacing calculated using the formula $2d_{001}=\lambda/\sin\theta$ is 0.47 nm throughout the series **2** and essentially agrees with the values reported for compounds **1**, namely, 0.46 nm.

The identification of the mesophase is supported by an uninterrupted miscibility between the phases of compounds **1** and **2**. Figure 2 presents the diagram of the binary system composed of *N,N′*-dinonanoyl-2,3,5,6-tetrakis(nonanoyloxy)-1,4-benzenediamine (n=8) and hexakis(heptanoyloxy)benzene (n=6) as the reference discogenic compound. The open and shaded circles on the reference compound-rich side (the right-hand side) show the transitions recorded on the calorimetric curves during the processes of heating and cooling respectively, while recording during cooling on the other side was not made because of the thermal instability of compound **2** at high temperatures. The D–I transition does not occur sharply and the curve exhibits a minimum around 72.5 °C and 60 mol% of the reference compound. The destabilization of the mesophase by mixing may account for the differences in the geometrical, chemical, and mechanical properties of the component molecules. The estimated ratio of spacings is about 1.3. Such a value is known to be large

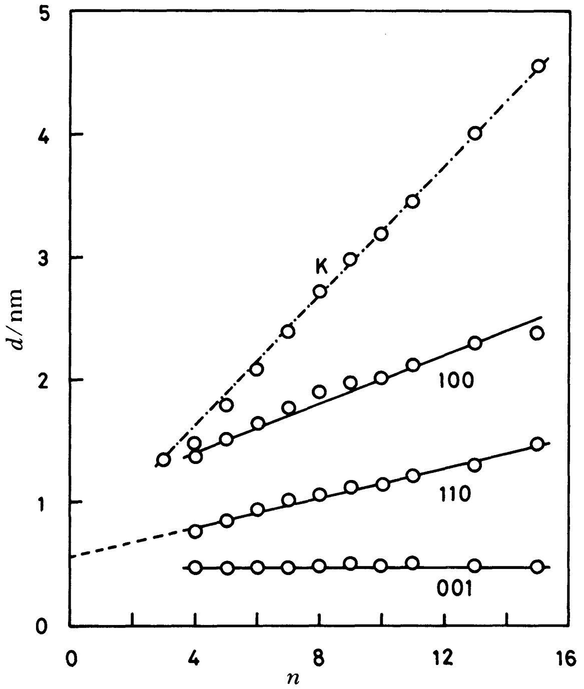


Fig. 1. Plot of spacings against the number of carbon atoms in the alkyl group for compounds **2**.

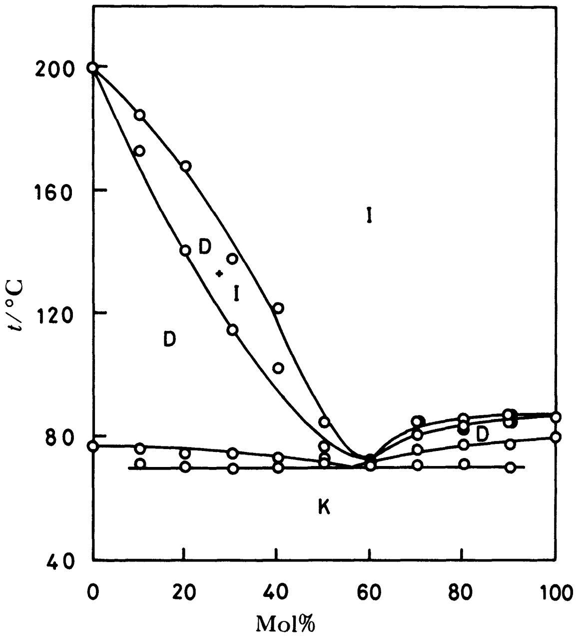


Fig. 2. Phase diagram of the compound **2** (n=8)–compound **1** (n=6) system. The former compound is located on the left-hand side.

enough to produce a marked deviation from a straight line even when the monomolecular smectic A phases of two homologous members are mixed.[10] Although this minimum lies close to the eutectic point, these two are readily distinguished from each other in the process of cooling because the I-D transition is never delayed but the discotic phase is markedly supercooled.

The spacing d_{100} in the mesophase of compound **1** reported by Chandrasekhar et al. is 1.50 nm for the octanoyl derivative and 1.59 nm for the nonanoyl derivative. The corresponding values for compounds **2** are appreciably longer; that is, 1.77 and 1.89 nm. The paraffinic chains in the present compounds are apparently more stretched and conformationally less disordered than those in compounds **1**. Such a dissimilarity is well indicated by the much larger enthalpy and entropy changes at the clearing point shown by compounds **2**. As is seen in Fig. 1, a linear relationship is found between n and the longest spacing in the crystalline phase, suggesting that the crystal structure is similar throughout this homologous series. The spacing shrinks only slightly upon melting when n=4 but by a factor of more than two when n=15. This behavior is not contradictory to the thermal data since the enthalpy change at the melting point increases remarkably with the increase of the alkyl chain length; for example 18 kJ mol^{-1} in the hexanoyl derivative and 115 kJ mol^{-1} in the hexadecanoyl derivative.

It may be added that the d_{110} value obtained by the extrapolation to n=0, 0.55 nm, is in good agreement with the radius estimated for the core structure, $C_6(NHCHO)_2(OCHO)_4$. Although rotation of the whole molecule about the normal to the molecular plane and the fluctuations of this axis around the preferred aromatic director are conceivable in the discotic phase,[11] the coincidence may be considered as an indication that the disk planes are, on an average, perpendicular to the columns in which the molecules are stacked.

The increment of spacing d_{110} per methylene group in the mesophase is merely 0.05 nm and is much shorter than that expected for the all-trans configuration of alkyl chains, 0.128 nm. Therefore, the longer the alkyl groups the faster on the NMR time scale, conformational changes of the alkyl groups are more extensive, resulting in more significant softening of the paraffinic crown. This proposition is in accordance with the considerable decrease of enthalpy change upon the D-I transition as the series is ascended. The change in the extent of liquid-like characteristic in the mesophase by the alkyl chain length is also manifested by the following proton second moments (the mean-square widths of the resonance lines), $\langle \Delta H^2 \rangle$, above the melting point; 0.3 G^2 (G=10^{-4} T) in the case of the octanoyl derivative and 0.03 G^2 in the case of the hexadecanoyl derivative. As is shown in Fig. 3, the moment measured at room temperature is as large as about 7 G^2 for the former compound and about 9 G^2 for the latter. It decreases gradually as the temperature is raised and then sharply near the transition temperature. The vertical arrows in this figure indicate the transition points determined by calorimetry.

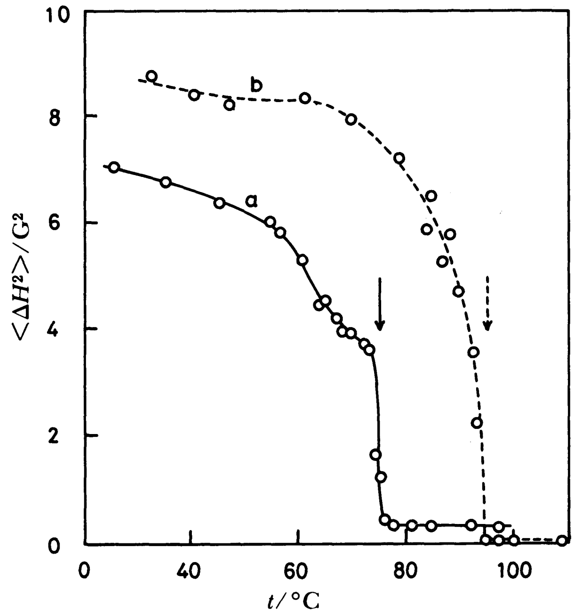


Fig. 3. Second moments of the broad-line proton NMR spectrum of compound **2**, (a) n=7 and (b) n=15. The vertical arrow indicates the melting point determined by calorimetry.

In conclusion, the substituent $NHCOC_nH_{2n+1}$ is an efficient group to promote the thermal stability of hexagonal columnar mesophase. As noted by Gray in his reasoning why the nematic and smectic efficiencies of $NHCOCH_3$ group are high,[12] the polarizable substituent employed by us has a strong dipole and can form hydrogen bonds. The dipole-dipole interaction and intermolecular hydrogen bonding operating across the molecular plane appear to contribute greatly to the enhancement of thermal stability of the discotic mesophase.

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