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Design of Novel Mesomorphic Compounds: *N,N′,N″*-Trialkyl-1,3,5-benzenetricarboxamides

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N,N′-Dialkyl-1,4-benzenedicarboxamides melt with anomalously small enthalpy changes. The 1,3-analogs behave similarly but at lower temperatures. These observations provide a clue to design novel mesomorphic compounds; *N,N′,N″*-trialkyl-1,3,5-benzenetricarboxamides. The compounds carrying pentyl to octadecyl groups melt at temperatures between 49 and 119 °C depending upon the alkyl chain length. The clearing points are located above 200 °C. The unoriented liquid crystals show X-ray diffraction patterns consisting of two major peaks. The inner sharp peak gives a spacing, which increases as the series is ascended, from 1.40 to 2.26 nm. The outer one is sharp in the pentyl and hexyl derivatives but diffuse in the higher homologous members. The second moments of the broad-line proton NMR spectra measured above the melting points are as small as a few hundredths G^2 and firmly establish the liquid-like characteristics of the alkyl chains.

Our earlier study on the phase diagrams of a number of binary systems composed of *N*-(4-propoxybenzylidene)-4-hexylaniline and *N*-alkyl-4-nitrobenzamide or *N*-(4-nitrophenyl)alkanamide revealed that these *p*-disubstituted benzenes would form smectic liquid crystals near room temperature if the melts were sufficiently supercooled.[1] Thus, the substituents $CONHC_nH_{2n+1}$ and $NHCOC_nH_{2n+1}$ appeared to be outstandingly efficient to promote the thermal stability of liquid crystals. This conclusion is in accordance with the placement of the $NHCOCH_3$ group by Gray at the top of the order of efficiency in promoting both nematic and smectic liquid crystals.[2] He suggested that hydrogen bonding is possibly of importance in this case in retaining the molecular order in the mesophases. Therefore, we have looked into the thermal properties of benzene derivatives carrying two or more $CONHC_nH_{2n+1}$ or $NHCOC_nH_{2n+1}$ groups with the hope of finding new ways to design mesomorphic compounds.[3,4] The present paper records details of our work on *N,N′*-dialkyl-1,4- and 1,3-benzenedicarboxamides and *N,N′,N″*-trialkyl-1,3,5-benzenetricarboxamides.

Experimental

Materials. The isophthaloyl dichloride, terephthaloyl dichloride, 1,3,5-benzenetricarbonyl trichloride, and alkylamines were obtained from commercial sources. The condensation reaction between the acyl chloride and the amine was carried out in boiling benzene by the addition of pyridine. The products were purified by repeated recrystallizations from appropriate solvents and were carefully dried. For example, Found: C, 68.91; H, 9.43; N, 10.08%. Calcd for $C_6H_3(CONHC_5H_{11})_3$: C, 69.03; H, 9.41; N, 10.06%. Found: C, 77.43; H, 11.93; N, 5.10%. Calcd for $C_6H_3(CONHC_{15}H_{31})_3$: C, 77.36; H, 11.90; N, 5.01%.

Measurements. Calorimetric, X-ray, and NMR measurements were made as described in our previous papers.[3—5]

Results and Discussion

Thermal Properties of *N,N′*-Dialkylbenzenedicarboxamides. As ordinary liquid crystals are known to be formed by elongated molecules, the compounds initially examined by us were *N,N′*-dialkyl-1,4-benzenedicarboxamides (**1**). Their transition temperatures and associated enthalpies are presented in Table 1. It must be noted that the enthalpy of melting decreases as the series is ascended and also that the values are rather small. For comparison, dioctadecyl terephthalate, which is closely-related in molecular structure to the octadecyl derivative, melts at 86 °C with an enthalpy change of 136 kJ mol^{-1}. This value is 2.2 times the corresponding one of octadecane, 62 kJ mol^{-1}. These observations imply that the *N,N′*-dialkyl-1,4-benzenedicarboxamide crystal is considerably disordered just below the melting point. In other words, the high-temperature form is in a stage

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

n[b)]	Solid–solid	Solid–liquid
12	121 (33)	187 (69)
	173 (9)	
14	116 (10)	179 (62)
	123 (17)	
	160 (16)	
16	117 (14)	164 (48)
	124 (26)	
	136 (2)	
	155 (42)	
18	105 (3)	171 (45)
	129 (15)	
	151 (10)	
	157 (7)	

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

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

n[b)]	Solid–solid	Solid–liquid
12	101 (37)	129 (36)
	123 (15)	
14	89 (4)	128 (43)
	101 (31)	
	123 (10)	
16	57 (1)	129 (48)
	96 (5)	
	112 (44)	
	124 (18)	
18	69 (2)	128 (54)
	102 (5)	
	112 (50)	
	124 (20)	

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

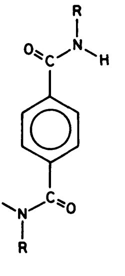
Table 3. Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of Compounds **3**[a)]

n[b)]	K_2		K_1		M		I
4	·	98 (8)	·	226 (17)			·
5	·	75 (6)	·	119 (10)	·	206 (6)	·
6			·	99 (12)	·	205 (22)	·
7			·	116 (16)	·	208 (12)	·
8			·	102 (19)	·	204 (17)	·
9			·	65 (17)	·	215 (15)	·
10			·	49 (47)	·	208 (20)	·
11			·	72 (32)	·	216 (15)	·
12	·	21 (11)	·	88 (36)	·	212 (16)	·
13	·	32 (7)	·	81 (27)	·	216 (13)	·
14			·	61 (59)	·	209 (15)	·
15			·	88 (56)	·	214 (14)	·
16	·	73 (68)			·	205 (12)	·
17			·	87 (66)	·	211 (9)	·
18			·	78 (68)	·	206 (12)	·

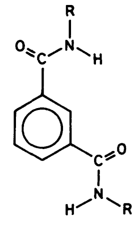
a) The latter quantities are in parentheses. b) The number of carbon atoms in the alkyl group.

intermediate between the isotropic liquid and the well-organized solid state. The compound is not very soluble in most organic solvents. Moreover, the endothermic peaks are broadened in a second and subsequent heatings indicating that the compound is prone to thermal decomposition.

We extended our examination to *N,N'*-dialkyl-1,3-benzenedicarboxamides (**2**) expecting depression of melting points and also improved solubilities. These compounds are polymorphic (see Table 2). The enthalpies of melting are as small as those of the 1,4-analogs; however, the value increases with the increase of alkyl chain length in contrast to the aforementioned series. The compounds dissolve well in benzene and are easily recrystallized from mixtures of benzene and ethanol. Thus, both compounds **1** and **2** are promising as starting materials to obtain mesomorphic compounds but the latter are easiler to handle. Our next step to approach the emergence of liquid crystals was the introduction of an extra $CONHC_nH_{2n+1}$ group into the *N,N'*-dialkyl-1,3-benzenedicarboxamide molecule. As will be described in the following paragraphs, *N,N',N''*-trialkyl-1,3,5-benzenetricarboxamides (**3**) are truly mesomorphic.

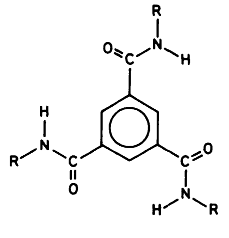


1



R = C_nH_{2n+1}

2



3

Thermal Properties of *N,N',N''*-Trialkyl-1,3,5-benzenetricarboxamides. The thermal properties are summarized in Table 3. Here, K, M, and I stand for crystal, mesophase, and isotropic liquid respectively. The stable form of the hexadecyl derivative melts at about 90 °C. As this form is always contaminated by the metastable form melting at 73 °C which is easily crystallized from the melt, the data for the latter are presented in this table. Most of the compounds exhibit two transitions above room temperature. The pentyl derivative and higher homologs form viscous birefringent fluids upon the transition located between 49 and 119 °C. The enthalpy change associated with the transition increases on ascending the series. The presence of a large difference between the nonyl and decyl derivatives must be noted. The mesophase covers a wide temperature range and the transformation into an isotropic liquid occurs above 200 °C in all cases. The transition is accompanied by enthalpy changes from 6 to 22 kJ mol^{-1}. The supercooling of the isotropic liquid is not detectable at a cooling rate of 5 K s^{-1}. The odd-even alternation of clearing point is found in the whole series and is particularly remarkable when the alkyl group is octyl or longer.

The butyl derivative shows a solid–solid transition in the temperature range where the higher homologs are transformed into liquid crystals and melts at a temperature higher than the clearing points of any other members. It may be added that trioctadecyl 1,3,5-benzenetricarboxylate melts at 79 °C with an enthalpy change of 133 kJ mol^{-1}. Therefore, the mesophase of the octadecyl derivative appears in the temperature range where the corresponding ester is liquid.

No identifiable texture is shown by the liquid crystals when the crystals melt. However, the texture observed for liquid crystals of low homologous members appearing by slow cooling of the isotropic liquid is likely to be fan or broken fan shaped.

X-Ray Diffraction. Figure 1 presents plots of spacings against the number of carbon atoms in an alkyl group, *n*. The longest spacing given by the butyl derivative is 1.20 nm at room temperature. No abrupt change is found at the solid–solid transition located at 98 °C. The spacing increases gradually upon further heating and reaches 1.26 nm at 150 °C. The higher members in the crystalline state can be classified into three groups by the alkyl chain length dependence. The pentyl and hexyl derivatives give nearly the same values, 1.67 and 1.68 nm. From the heptyl to decyl derivatives, the spacing increases by 0.17 nm per methylene group. There is an abrupt increase between the decyl and undecyl derivatives. Then, the spacing changes again linearly with *n* by as much as 0.20 nm per methylene group. The tetradecyl derivative is the only exception to this group.

The diffraction patterns recorded at 150±10 °C for the "unoriented" liquid crystals consist of two major peaks. In fact, the specimen spread in the form of a thin film over an aluminum holder cannot be free from orientation; therefore, "unoriented" here means not intentionally oriented. The inner peak is sharp and strong and gives a spacing of 1.63 nm for the heptyl derivative and 2.26 nm for the octadecyl derivative. The outer peak is diffuse in these homologous members. The maximum remains at the same Bragg angle throughout the series as shown in Fig. 1. This feature is consistent with not only a nonordered smectic phase but also a hexagonal disordered columnar structure. The enthalpy changes at the clearing points, 6 to 22 kJ mol^{-1}, are in the range of values for the nonordered smectic-isotropic transitions collected by Demus et al.[6] They are also comparable with the enthalpy changes given at the hexagonal disordered columnar-isotropic transitions of hexakis(alkanoyloxy)benzenes but appreciably smaller than the corresponding values of *N,N′*-dialkanoyl-2,3,5,6-tetrakis(alkanoyloxy)-1,4-benzenediamines.[5,7,8]

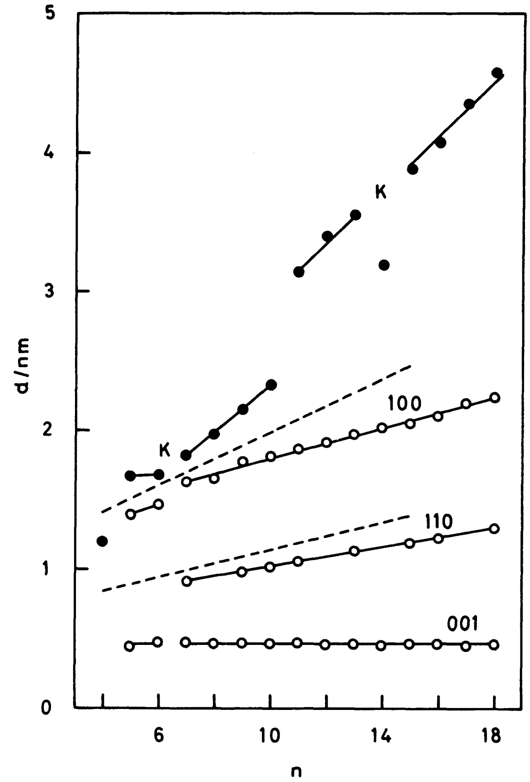


Fig. 1. Plots of spacings against the number of carbon atoms in the alkyl group of compounds **3**. The open circles show the spacings measured in mesophases. Broken lines indicate the corresponding spacings of *N,N′*-dialkanoyl-2,3,5,6-tetrakis(alkanoyloxy)-1,4-benzenediamines in the hexagonal disordered columnar phase.

Levelut has assumed that a disk-like molecule must be made of a planar rigid core surrounded by a more or less planar ring of aliphatic chains.[9] According to this view, the paraffinic crown of the *N,N′,N″*-trialkyl-1,3,5-benzenetricarboxamide molecule cannot be considered to be dense enough to form columnar liquid crystals. However, a careful examination of many diffraction patterns revealed the presence of a peak, although not in all the cases, the spacing of which is about $1/\sqrt{3}$ times the longest one. The peak is very weak possibly due to the unfavorable orientation of the liquid crystals. This ratio is characteristic of a hexagonal columnar structure. The longest spacing may be assigned to the first order 100 reflection and the other one to 110 reflection. In Fig. 1, broken lines show the spacings d_{100} and d_{110} in the mesophase of *N,N′*-dialkanoyl-2,3,5,6-tetrakis(alkanoyloxy)-1,4-benzenediamines taken from our previous work.[5] Compared with them, not only the spacings themselves but also the increments per methylene group of compound **3** are shorter suggesting that the alkyl chains are more liquid-like and/or more interdigitated. Because the molecule carries only three alkyl groups, the chains attached to neighboring molecules must be differently oriented in order to achieve hexagonal packing of the columns. The molecules in each column are irregularly spaced. The average distance 0.47 nm agrees well with the values estimated for the above-mentioned hexasubstituted benzenes.[5,7,8]

While the d_{100} value in the heptyl to octadecyl derivatives varies linearly with *n*, the longest spacings exhibited by the pentyl and hexyl derivatives are smaller by about 0.1 nm than those expected by a linear relationship. The two compounds give sharp outer peaks and the whole diffraction patterns bear strong resemblances to those reported for smectic B phase. The intermolecular distance (d) is estimated to be 0.47 nm by Bragg's formula and 0.54 nm when one employs the formula $2d \sin\theta = 1.1547\lambda$ proposed by de Vries specifically for smectic B phase.[10] The latter value is slightly longer than those reported for ordinary smectic B liquid crystals. If this identification is accepted, the longer spacing is assigned to the 001 reflection and the shorter one to the overlap of the 110 and 200 reflections. The molecules must be in a high degree of rotational disorder around the axis in the plane of the benzene ring and are in hexagonal packing within the layers. Such a motion may be possible only when the alkyl chains are not long. One might assume that the mesophases exhibited by these two are also hexagonal columnar. As the outer peak is sharp, the molecules in each column are equally spaced. It must be noted that the observed distance between parallel molecules, 0.47 nm, is unusually large compared with those known for some ordered columnar phases; namely, 0.36 nm of hexaalkoxytriphenylenes and hexaalkoxytruxenes.[11,12] Evidently, further studies are required to yield precise information regarding the molecular arrangement in these mesophases.

NMR Spectra. The liquid-like characteristics of alkyl chains in the mesophases are well demonstrated by small second moments of broad-line proton NMR spectrum (the mean-square width of the resonance line), $\langle \Delta H^2 \rangle$, above the melting point. Values of the order of 0.01 G^2 ($G=10^{-4}$ T) for the mesophases of the octyl and hexadecyl derivatives are almost indistinguishable from those of isotropic liquids because of the resolution limit of our spectrometer. The increase in the enthalpy change of melting with the increase of alkyl chain length is clearly manifested by the magnitude of the second moment decrease at the transition temperature; that is, about 2 G^2 at 116 °C and about 6 G^2 at 90 °C. The depression of the moment by about 2 G^2 in the non-mesogenic butyl derivative occurs in a temperature range higher by 10 to 20 °C than the calorimetric transition point located at 98 °C, indicating that the chains are not moving fast enough on an NMR time scale at the transition temperature. Moreover, the moment remains at about 3 G^2 in the high-temperature form.

The molecules examined in the present work are neither rod-like nor disk-like; nevertheless, the behavior reported above fully confirms the formation of liquid crystals. The primary requirement for the appearance of liquid crystals is not the specific geometrical anisotropy of the molecules but the anisotropy of the intermolecular forces maintaining order in the crystal and liquid crystals. The interaction between the benzenetricarboxamide units keeps the molecules in columns or layers up to relatively high temperatures. The N–H stretching vibrational band is shifted by 15 to 35 cm^{-1} to the lower wavenumber by melting and the C=O band slightly to the opposite direction, suggesting that the hydrogen bonding is strengthened upon the transition. On the other hand, the long flexible alkyl chains are conformationally disordered at lower temperatures. This molecular feature seems sufficient to fulfill the above-mentioned requirement.

Finally, it must be added that mesomorphic 1,3,5-trisubstituted benzenes are not entirely new. However, the compounds so far reported carry substituents such as cholesteryloxycarbonyloxy groups or 4-alkyl- and 4-alkoxybenzoyl groups.[13–15] They are not as simple as the present compounds and may be classified into different families of liquid crystal materials.

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