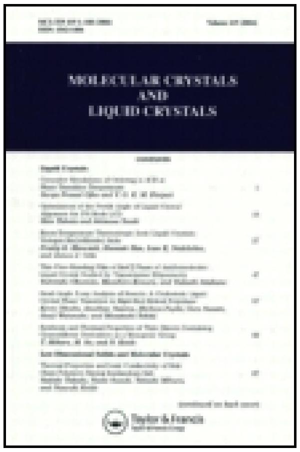

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Liquid Crystal Phases Exhibited by N,N′,N″-Trialkyl-1,3,5-Benzenetricaboxamides

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Liquid Crystal Phases Exhibited by N,N′,N″-Trialkyl-1,3,5-Benzenetricarboxamides

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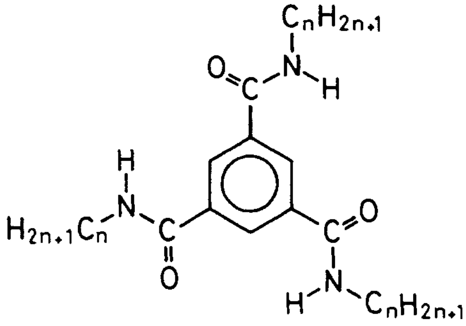
When crystals of N,N′,N″-trialkyl-1,3,5-benzenetricarboxamides with alkyl groups from pentyl to octadecyl are heated, viscous birefringent fluids are produced at temperatures between 40 and 120°C depending upon the alkyl chain length and they are transformed into optically isotropic liquids above 200°C. Transition to a liquid crystal phase is accompanied by an enthalpy change of 10 to 68 kJ mol^{-1} and that to an isotropic liquid by that of 6 to 22 kJ mol^{-1}. The X-ray diffraction pattern of the unoriented liquid crystal resembles that known for smectic A or B phase. A layer thickness given by a sharp inner peak is 1.40 nm for the pentyl derivative and increases up to 2.26 nm for the octadecyl derivative. The second moment of the broad-line proton NMR spectrum shows an abrupt decrease at the melting point from several G^2 to a few hundredths G^2.

Keywords: liquid crystals, smectic phases, benzenedicarboxamides, 1,3,5-benzenetricarboxamides, x-ray diffraction, broad-line NMR

INTRODUCTION

We studied earlier the phase diagrams of a number of binary systems consisting of N-(4-propoxybenzylidene)-4-hexylaniline and N-alkyl-4-nitrobenzamide or N-(4-nitrophenyl)alkanamide in order to demonstrate the potential liquid crystalline properties of these *p*-disubstituted benzenes.[1] The results clearly indicated that they would form smectic liquid crystals near room temperature if the melts were sufficiently supercooled. This conclusion may not be unreasonable as CH_3CONH group is placed by Gray at the top of orders of terminal group efficiency in promoting both nematic and smectic liquid crystals.[2] Therefore, it seemed interesting to look into the thermal behavior of benzene derivatives carrying $C_nH_{2n+1}NHCO$ or $C_nH_{2n+1}CONH$ groups. This paper reports the liquid crystal phases exhibited by N,N',N''-trialkyl-1,3,5-benzenetricarboxamides.



EXPERIMENTAL

The compounds were prepared by the condensation reaction between appropriate acyl chloride and alkylamine. The products were purified by repeated recrystallization and were carefully dried. The results of elemental analysis were in good agreement with the composition of the desired carboxamides. For example, Found: C, 73.02; H, 10.58; N, 7.75%. Calcd. for $C_6H_3(C_8H_{17}NHCO)_3$: C, 72.88; H, 10.56; N, 7.73%. Found: C, 78.53; H, 12.15; N, 4.23%. Calcd. for $C_6H_3(C_{18}H_{37}NHCO)_3$: C, 78.44; H, 12.22; N, 4.36%. 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}. X-Ray diffractions were measured with a Rigaku autodiffractometer, 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

N,N'-Bis(octadecyl)-1,4-benzenedicarboxamide exhibits solid-solid transitions at 117, 131, and 157°C with enthalpy changes of 8, 25, and

28 kJ mol^{-1} respectively. The melting occurs at 173°C with an enthalpy change of 44 kJ mol^{-1}. The last value is anomalously small compared with the enthaply of melting of a structurally similar compound, bis(octadecyl) terephthalate, 136 kJ mol^{-1} at 86°C. As the 1,4-benzenedicarboxamide is not very soluble in most of organic solvents and is prone to thermal decomposition, we extended our examination to the 1,3-analog. Solid-solid transitions at 57, 96, 112, and 124°C with enthalpy changes of 1, 5, 44, and 18 kJ mol^{-1} respectively are observed with the N,N'-bis-(octadecyl)-1,3-benzenedicarboxamide. The enthalpy change at the melting point of 129°C is 48 kJ mol^{-1}. These results strongly suggest that novel mesomorphic compounds might be obtained by suitable positioning of further substituents. Indeed, the introduction of one more $C_nH_{2n+1}NHCO$ group to the 5-position of N,N'-dialkyl-1,3-benzenedicarboxamide molecule led to the appearance of liquid crystal phases.

The thermal properties of the benzene-1,3,5-tricarboxamides are summarized in Table I. Here, K, S, and I stand for crystalline, smectic, and isotropic phases respectively. 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 40 and 120°C. The butyl derivative shows a solid-solid transition in this temperature range and melts at a temperature higher than the clearing points of the homologous members. A plot

TABLE I

Transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) of N,N'.N"-trialkyl-1,3,5-benzenetricarboxamides. The latter quantities are in parentheses.

n[a]	K_2		K_1		S		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 number of carbon atoms in an alkyl group.

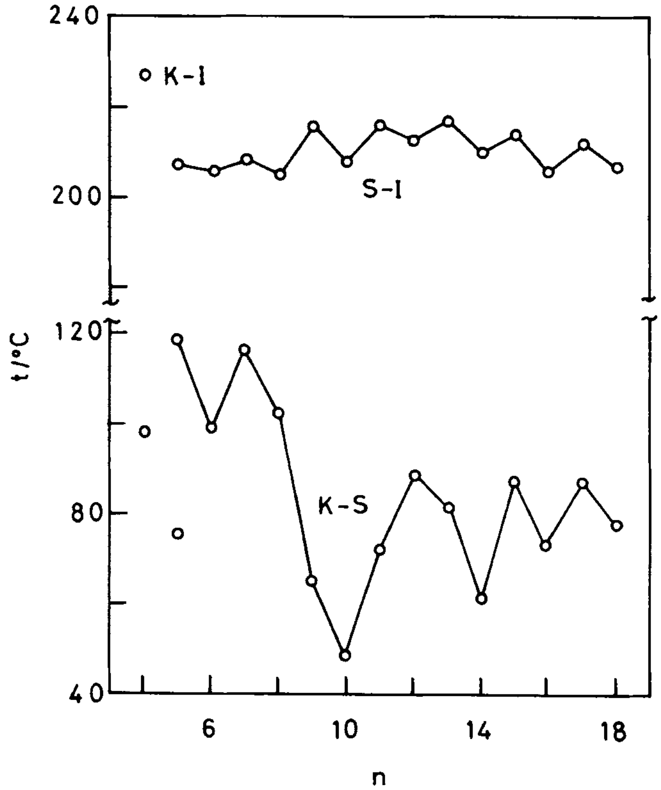


FIGURE 1 Plot of transition temperatures against the number of carbon atoms in the alkyl group for N,N',N''-trialkyl-1,3,5-benzenetricarboxamides. K, S, and I stand for crystalline, smectic, and isotropic phases respectively.

of transition temperatures against alkyl chain length is presented in Figure 1. The even-odd alternation of clearing point is found in the whole series and is particularly remarkable when the alkyl group is octyl or longer. The enthalphy changes at the clearing points, 6 to 22 kJ mol^{-1}, are in the range of values for the non-ordered smectic phase-isotropic phase transitions collected by Demus et al.[3] The supercooling of the isotropic liquid is not detectable with these compounds at a cooling rate of 5 K min^{-1}. It may be worthwhile to note that tris(octadecyl)1,3,5-benzenetricarboxylate melts at 79°C with an enthalpy change of 133 kJ mol^{-1} and exhibits no liquid crystal phase. No identifiable texture is shown by the liquid crystals when the crystals melt, but focal-conic texture appears when the liquid crystal is formed on slow cooling of the isotropic liquid.

The X-ray diffraction patterns observed with the unoriented liquid crystals are similar to those known for smectic A or B phase. The former pattern may also fit a hexagonal disordered columnar structure. Thus, our study yields no precise information regarding the molecular arrangement. However, it may be said that the liquid crystals are probably of the lamellar type as the paraffinic crown is not dense enough to form columnar liquid crystals.[4] The sharp inner peak is accompanied by the second order reflection. The spacing considerably shorter than a full molecular length estimated on the basis of the all-trans configuration of alkyl groups, e.g. 1.82 nm *versus* 2.55 nm in the case of decyl derivative, may be an indication of the conformational melting of alkyl groups. This spacing in the liquid crystal phase is almost independent of temperature and increases nearly linearly from 1.63 nm in the heptyl derivative to 2.26 nm in the octadecyl derivative, but those of the pentyl and hexyl derivatives, 1.40 and 1.48 nm, deviate as much as 0.11 nm from the values expected by the linear relationship (see shaded circles in Figure 2). The corresponding spacings in the crystalline state given by open circles in the same figure are appreciably longer than those in the liquid crystal phases. The values found for the undecyl derivative and the higher homologs are larger than the full molecular lengths suggesting that the alkyl groups on neighboring molecules are differently oriented. On the other hand, the spacings recorded for the decyl derivative and the lower homologs are smaller than the full molecular lengths even in the crystalline state.

The pentyl and hexyl derivatives show a sharp peak near 9.5° Bragg angle (θ). The intermolecular distances (D) calculated using the formula $2D \sin \theta = 1.1547\lambda$ are slightly longer than the values collected for ordinary smectic liquid crystals by de Vries.[5] The molecules seem to 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. The higher homologs give a diffuse peak at the same Bragg angle regardless of the alkyl chain length as shown by open circles in Figure 2, indicating the random arrangement of molecules in the layers possibly due to the entanglement of long alkyl chains.

The conformational melting of alkyl chains in the liquid crystal phases is well demonstrated by an abrupt decrease in the second moment of broad-line proton NMR spectrum at the melting point indicated by an arrow in Figure 3. Values of the order of 0.01 G^2 for the liquid crystal phases of the octyl and hexadecyl derivatives shown by Curves *b* and *c* are indistinguishable from those for isotropic liquids because of the limit of our spectrometer. It must be noted that the non-mesogenic butyl derivative does not give such small second mo-

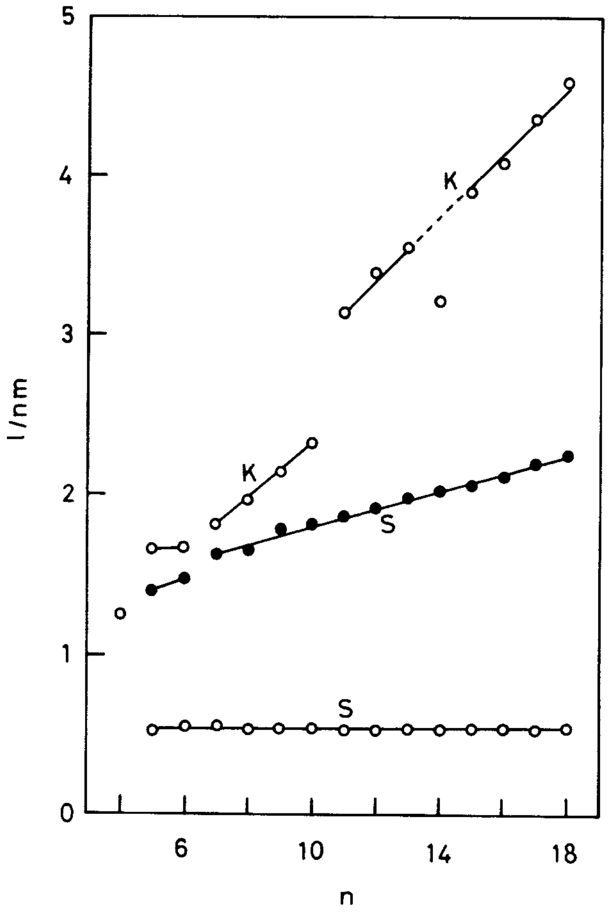


FIGURE 2 Plot of spacings against the number of carbon atoms in the alkyl group for N,N′,N″-trialkyl-1,3,5-benzenetricarboxamides. As to K, S, and I, see the caption of Figure 1.

ments above the transition located at 98°C (see Curve *a*). The difference in the enthalpy of melting between the octyl and hexadecyl derivatives, 19 *versus* 68 kJ mol^{-1}, is reflected by the magnitude of second moment decrease at the transition temperature.

Although the molecules studied in the present work are neither rod-like nor disc-like, the observed behavior fully confirms the formation of liquid crystal phases. The stepwise thermal breakdown in order may be conceivable for these compounds. The interaction between the benzenetricarboxamide units keeps the molecules in layers up to relatively high temperatures, while the long flexible alkyl chains

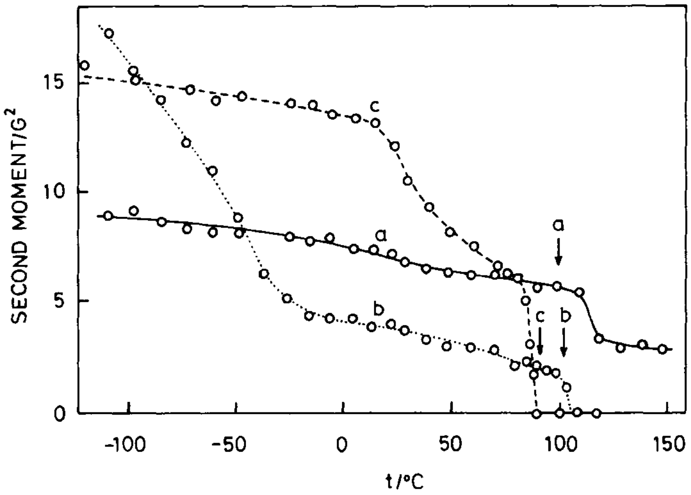


FIGURE 3 Second moments of the broad-line proton NMR spectrum of (a) N,N′,N″-tributyl-, (b) N,N′,N″-tris(octyl)-, and (c) N,N′,N″-tris(hexadecyl)-1,3,5-benzenetricarboxamides. Arrows indicate the transition temperatures determined by differential scanning calorimetry.

are conformationally disordered at lower temperatures. This molecular feature seems to fulfill the primary requirement for the appearance of liquid crystal phases.

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