Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006.

To cite this article: Xujin Bao & L. R. Dix (1996): Smectic Phases Observed in 1, 1,2,2,-tetrahydroperfluoroalkyl-4-nitrobenzoates, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 281:1, 291-294

To link to this article: http://dx.doi.org/10.1080/10587259608042252

Mol. Cryst. Liq. Cryst., 1996, Vol. 281, pp. 291–294
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Smectic Phases Observed in 1,1,2,2,-tetrahydroperfluoroalkyl-4-nitrobenzoates

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(Received May 26, 1995; in final form September 22, 1995)

On studying the thermal behaviour of a series of 1,1,2,2-tetrahydro-perfluoroalkyl 4-nitrobenzoates it was found that the decyl and dodecyl compounds showed smectic mesophases. This illustrates that a polar substituent in the 3-position of the aromatic ring for 1,1,2,2-tetrahydroperfluoroalkylbenzoates is not a requirement for thermotropic behaviour.

INTRODUCTION

It has been demonstrated that a perfluoroalkyl group enhances the thermal stability of the mesomorphic phases exhibited by certain molecules relative to the corresponding molecules containing an equivalent hydrocarbon chain. This was illustrated by the work of Doi *et al.*[1] for a series of (4-alkoxybenzoyloxy)benzoates. Those alkoxybenzoates having a perfluorocarbon chain rather than a hydrocarbon chain in the ester unit gave higher clearing temperatures and in some cases a smectic C phase, where no such phase existed in the corresponding hydrocarbon version. Work by one of these aforementioned authors[2] has shown that some 1,1,2,2-tetrahydroperfluoroalkylbenzoates show smectic phases. The author claims that a polar substituent in the 3-position is indispensable for mesomorphic behaviour. Liquid crystal compounds with a single aromatic ring (of which the former are an example) are rare and are of particular interest. The formation of smectic phases in these 1,1,2,2-tetrahydroperfluoroalkylbenzoates is ascribed to the rigidity of the perfluorocarbon chain which is caused by the steric hindrance between fluorine atoms. In fact, on comparing the difference in energy between the *gauche* and *trans* conformations for fluorocarbon and hydrocarbon chains, it is found that the energy difference is more than twice as great for fluorocarbon chains.[4] The 1,1,2,2-tetrahydroperfluoroalkylbenzoates do not appear to form nematic phases and this is attributed to a bent conformation. In this paper we wish to present an example of a benzoate ester which shows smectic mesophases *without* a lateral substituent in the 3-position.

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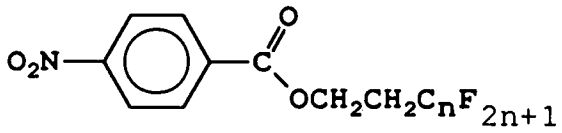
EXPERIMENTAL



(I)

Synthesis of 1,1,2,2-tetrahydroperfluoroalkyl 4-nitrobenzoates (I). A mixture of 4-nitrobenzoyl chloride (1.9 g, 0.01 mol) and 1,1,2,2-tetrahydroperfluoroalkan-1-ol (0.011 mol) was stirred in dry pyridine as solvent at 70°C for five hours. After cooling to room temperature dichloromethane was added and the solution washed three times with dilute hydrochloric acid and three times with water. The organic layer was then dried over anhydrous magnesium sulphate and the solvent evaporated to give the product. This was recrystallised from 3:1 hexane-ethanol mixture (yield 85–95%) to give colourless crystals. δ_H (90 MHz, solvent $CDCl_3$ standard TMS) 2.3–2.9 ppm (m, $CH_2CH_2CF_2$, 2H), 4.7 ppm (t, $CH_2CH_2CF_2$, 2H), 8.1–8.4 ppm (m, 4H). Elemental analysis (C, H, N) for 1,1,2,2-tetrahydroperfluorodecyl 4-nitrobenzoate gave 33.1% C (33.3% expected), 1.15% H (1.3% expected), 2.35% N (2.30% expected).

Characterisation of thermotropic phases

Thermotropic textures were examined using a Nikon Labophot polarising microscope fitted with a Linkam THMS 600 hot stage controlled by a Linkam TMS 91 system. Differential scanning calorimetry was performed using a DuPont thermosystem with a heating/cooling rate of 5°C/min. Melting points were determined on an SMP1 melting point apparatus.

RESULTS AND DISCUSSION

Four 1,1,2,2-tetrahydroperfluoroalkyl 4-nitrobenzoates were prepared having 6, 8, 10 and 12 carbon atoms in the aliphatic chain. The compounds with 10 and 12 carbon atoms in the aliphatic chain showed a monotropic mesophase on cooling, although the latter compound gave a much more stable mesophase than the former (as described below). Transition temperatures and textural assignments are given in Table 1. The transition temperatures were determined by differential scanning calorimetry on a first cooling cycle from the isotropic melt at 5°C/min and corresponding textural assignments made by optical microscopy.

Of the compounds studied here, only the dodecyl compound ($n = 10$) showed a mesophase which was stable over a temperature range of several degrees. A focal conic fan texture was osberved which was assigned as a smectic A phase. On further cooling, a subtle change in the optical texture was observed and we assign this to an unidentified smectic phase. The DSC trace is shown in Figure 1. The decyl compound

TABLE 1

Transition temperatures (in °C) on cooling 1,1,2,2-tetrahydroperfluoroalkyl 4-nitrobenzoates from the isotropic phase. *n* refers to the number of carbon atoms in the fluorocarbon chain. [ ] denotes enthalpies of transition in kJ mol^{-1}. Melting points are indicated as *Tm*.

n (refer to I)	*Tm*	*I*		S_A		S_X		*K*
4	42–43	●					40	●
6	54–55	●					51	●
8[b]	78–80	●					62[a]	●
10[b]	105–106	●	92 [0.023]	●	85 [0.05]	●	68 [0.11]	●

[a] A smectic phase was observed within 1°C of crystallisation.

[b] These compounds showed monotropic transitions (*i.e.* the K → Sa transition was not observed on heating.)

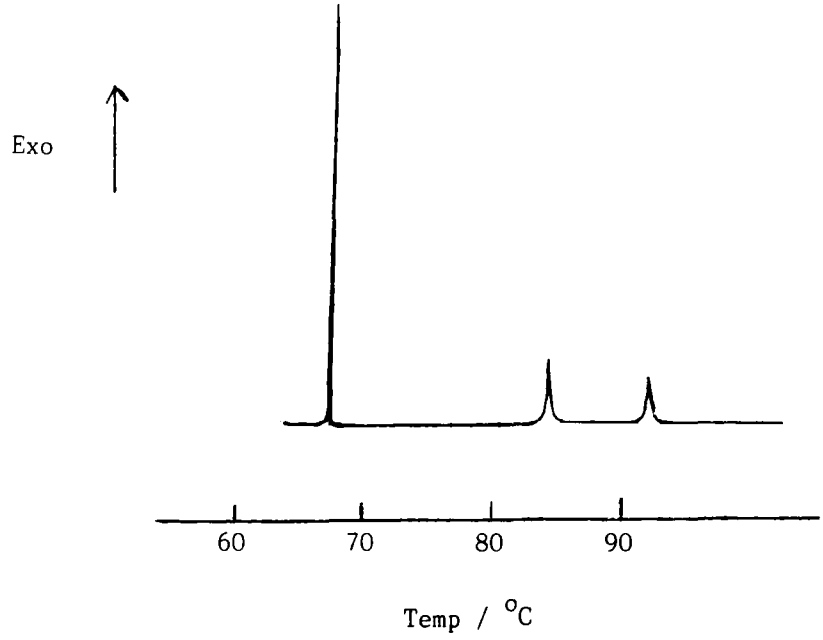


FIGURE 1 DSC trace on first cooling cycle (5 °C min^{-1}) for 4-nitro-1,1,2,2-tetrahydroperfluorododecyl benzoate. Transition temperatures indicated are in °C.

($n = 8$) did show a transient smectic A texture very close to the crystallisation temperature and this was only registered as a slight shoulder on the crystallisation exotherm by DSC.

Takenaka[2] prepared a series of 4-substituted 1,1,2,2-tetrahydroperfluoroalkylbenzoates, none of which showed mesomorphic behaviour. The substituents were methoxy, decyloxy, fluoro, nitrile, trifluoromethyl and n-butyl. Both the decyl and dodecyl esters were studied. As mentioned above, he proposes that a polar substituent in the 3-position is required to form mesophases in these compounds. Our observations

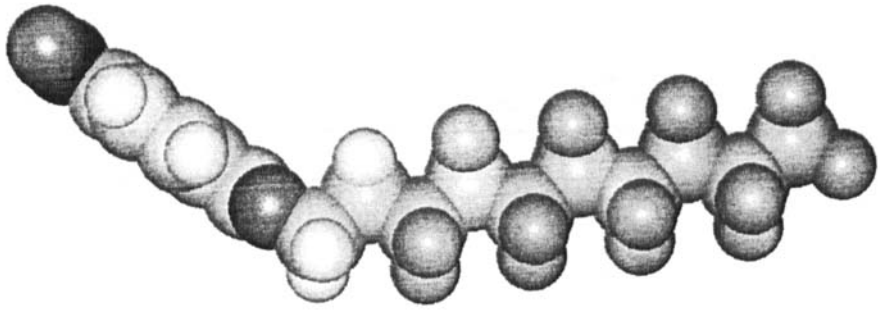


FIGURE 2 Molecular model for 4-nitro-1,1,2,2-tetrahydroperfluorodecyl benzoate showing bent configuration. The fluorinated aliphatic chain is horizontal, with the aromatic unit at approximately 45°C.

show an example where this is not the case. We propose that, on the basis of the results presented here and elsewhere, it is possible to obtain thermotropic 1,1,2,2-tetrahydroperfluoroalkyl benzoates without a lateral substituent provided that there is a highly polar 4-substituent and a perfluoroalkyl chain of sufficient length. A feature of our observations on 1,1,2,2-tetrahydro-4-nitroperfluorododecylbenzoate is that two smectic phases are formed; a smectic A phase at higher temperatures and an unidentified smectic phase at lower temperatures, as was the case for several of the compounds reported by Takenaka. The most interesting feature of these compounds is that the fluoroalkyl chain appears to enhance mesogenicity. For our series of compounds, increasing the fluoroalkyl chain length increases the crystallisation temperature and this is the same trend as found in the observations of Takenaka.[2] A molecular model[5] as represented by Figure 2 shows that 4-nitro-1,1,2,2-tetrahydroperfluorodecyl benzoate has a profoundly obtuse shape. This kind of structure is unfavourable for the formation of nematic phases and indeed these are not observed for any of the above mentioned compounds.

References

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5. Obtained using Molecular Mechanics MM^+ program optimised to 0.01 kcal gradient.