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Phase behaviour of some α,ω-dicarboxylic acids containing a mesogenic core

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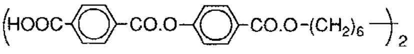
Some α,ω-dicarboxylic acids containing, as a core, well known mesogenic groups have been synthesized and their phase behaviour has been investigated using DSC, optical and X-ray diffraction methods. A feature common to several of the compounds is the occurrence of an enantiotropic polymorphism with an additional phase stable between the low temperature solid phase and the isotropic liquid. The nature of this phase is discussed. Only one compound, among those studied, has shown definite mesomorphic behaviour (although monotropic) with a liquid-crystalline phase of probable smectic A type.

1. Introduction

Within the large array of liquid-crystalline polymers, the linear semiflexible ones, i.e. those constituted with a regular alternation, along the main chain, of rigid and flexible sections, have been widely investigated [1]. Attention to the specific role played by the basic sections of such polymers (i.e. in a simplified and somewhat arbitrary picture, the so-called mesogen and spacer) has resulted, in some cases, in complementary studies on low molar mass, stoichiometrically defined model compounds which, at least qualitatively, behave like the corresponding polymers [2].

The investigation of possible correlations between crystal and mesophase structure has received some attention for low molar mass liquid-crystalline compounds, while little is known for polymeric mesogens. The reason for this includes the intrinsic difficulties related to the usually large dimensions of the monomer units and to the frequent occurrence of solid phase polymorphic forms. In this respect, alkyl-terminated model compounds have the disadvantage of lacking any particular driving force capable of packing the molecules along extended rows, thus simulating long polymeric chains. In order to combine the possibilities for an accurate crystal structure determination offered, in principle, by low molar mass compounds and the presumptive quality of forming long, polymer-like, molecular chains, we have investigated the phase behaviouor of some α,ω-dicarboxylic acids containing a mesogenic core. Taking into account hydrogen bonding between polar carboxylic groups, which is also maintained in the fluid phase, these carboxylic diacids can be considered as constituting a semiflexible polymeric structure, though a peculiar one, having monomeric units joined by hydrogen bonds.

Aliphatic α,ω-dicarboxylic acids have been recognized as model compounds for stereoregular polyolefins [3, 4]; they were found to give rise, in the crystal phase, to well defined linear structures in which the molecules, held together with hydrogen bonds, take conformations and packing modes that are similar to those found in the polymers. Examples of solid phase polymorphism [5, 6] have also been reported for such carboxylic diacids, specifically due to the packing of molecules in different conformations (conformational polymorphism). On the basis of somewhat analogous considerations Hashino *et al.* [7] have synthesized a mesogenic diacid

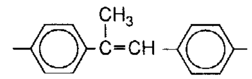


In this case it was assumed that the mesogenic group would form via hydrogen bond coupling, by analogy with the behaviour of 4-*n*-alkyloxy derivatives of benzoic acid [8].

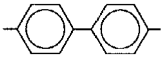
The connection of the conformational and packing features of carboxylic diacids with those of the polymers does not appear to be only a feature of a certain class of polymers, and we assume that it should hold also in the case of our compounds, with the formula

$$HOOC\text{-}(CH_2)_{n-1}\text{-}O\text{-}R\text{-}O\text{-}(CH_2)_{n-1}\text{-}COOH$$

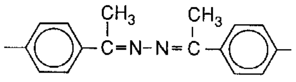
where -*R*- is the α-methylstilbene mesogenic unit



They are indicated, in the following sections, by the symbol An. The phase behaviour of these compounds was studied for various lengths of the flexible terminal chains; moreover, for a fixed chain length, $n = 6$, compounds with two different mesogenic units were considered. They will be referred to as D6 and F6, where the mesogenic unit is now that of biphenyl



and dimethylbenzalazine



respectively. The identification of these -*R*- groups as mesogenic rests on the evidence of a number of experimental data concerning both polymeric and low molar mass compounds [9-11].

2. Experimental part

Compounds An ($n = 2, 6, 8, 12$) and D6 were synthesized according to the route shown in scheme 1.

$$(a)\quad HO\text{-}R\text{-}OH + \underset{(1)}{Br(CH_2)_{n-1}COOCH_3}$$

$$\xrightarrow[K_2CO_3]{HCON(CH_3)_2} \underset{(2)}{CH_3OOC(CH_2)_{n-1}O\text{-}R\text{-}O(CH_2)_{n-1}COOCH_3}$$

$$(b)\quad (2) \xrightarrow[H^+(2)]{OH^-(1)} An\ (3)$$

Scheme 1.

A detailed description of the synthesis of A8 is given as an example.

2.1. *Synthesis of (1)*

10 g of 8-bromooctanoic acid (44·8 mmol) (Aldrich, 98 per cent) were refluxed with 70 ml of thionyl chloride, until no further evolution of HCl was observed; the excess of thionyl chloride was removed by distillation under reduced pressure and the 8-bromooctanoyl chloride was collected. The chloride was added dropwise, under flowing nitrogen, to an excess of dry methanol (150 ml) which was stirred. The mixture was allowed to react under stirring overnight; the excess of methanol was then removed by distillation under reduced pressure and methyl-8-bromooctanoate was finally isolated. Yield 8·5 g (79·9 per cent).

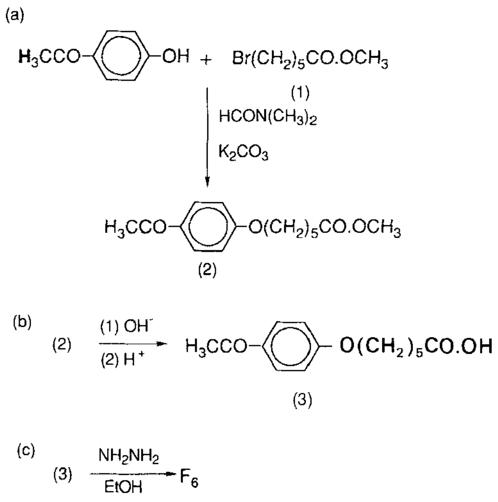
2.2. *Synthesis of (2)*

Into a 250 ml single neck, round bottomed flask, were placed 13·3 mmol (3 g) of 4,4′-dihydroxy-α-methylstilbene, 29·3 mmol (6·95 g) of (1), 55·3 mmol (7·4 g) of potassium carbonate and 100 ml of *N*,*N*-dimethylformamide. The reaction mixture was gently refluxed for 4 h, then allowed to cool to ambient temperature and filtered to remove potassium bromide and the excess potassium carbonate. The solution obtained was poured into an excess of water (≈ 1 l) to induce almost complete precipitation of the final product (2), which was then recovered by filtration. Yield 4·54 g (63·4 per cent). The raw product was purified before use by several crystallizations from hot ethanol and, finally, by column chromatography (silica gel with chloroform as eluent).

2.3. *Synthesis of (3)*

2·19 mmol (1·18 g) of (2) were dissolved in 40 ml of hot ethanol; to this solution were added 4·46 mmol (0·25 g) of potassium hydroxide, previously dissolved in 20 ml of ethanol. An equal amount (*c*. 60 ml) of water was added and the mixture was refluxed for 1 h; then it was allowed to cool to ambient temperature, acidified with dilute hydrochloric acid and filtered to collect the final product (3), A8. Yield 0·91 g (81·3 per cent). Compound *A8* was further purified by crystallization from hot ethanol.

Compound F6, owing to the low stability of the benzalazine moiety in the previous conditions, was prepared according to a slightly different route, shown in Scheme 2.



Scheme 2.

The first two steps are similar to those already described, therefore only the final step is described in detail.

2.4. *Synthesis of F6*

In a 100 ml flask, were placed 2·79 mmol (0·699 g) of (3), 1·33 mmol (0·067 g) of hydrazine hydrate and 50 ml of absolute ethanol. The mixture, after the addition of a few drops of acetic acid, was refluxed to 2 h. The final product separated from the solution as yellow crystals by slow cooling to ambient temperature. Yield 0·350 g (53 per cent). Compound F6 was further purified by several crystallizations from ethanol.

Each compound synthesized gave a proton N.M.R. spectrum, recorded on a Varian XL200 spectrometer, which is consistent with its formula.

The differential scanning calorimetry studies were performed using a Perkin Elmer DSC2 apparatus, under a nitrogen atmosphere. An indium sample of high purity was used as a standard to determine the transition temperatures and enthalpies. Heating and cooling rates of 10 K/min were used. Optical observations were performed using Mettler FP5 microfurnace, combined with a Leitz polarizing microscope. X-ray diffraction data collection was performed, using CuKα radiation, either photographically (Rigaku flat film camera) or with a counter method (Philips powder automatic diffractometer). In both cases the apparatus was equipped with a microfurnace to allow temperature control.

3. Results and discussion

The relevant thermodynamic data concerning the phase transitions are reported in the table. The compounds examined do not exhibit identical behaviour. The simplest concerns A2 and F6 whose DSC curves show a single endothermic signal corresponding to the melting of the crystal phase to an isotropic liquid. Compounds A6, A12 and D6 undergo an intermediate phase change, as detected both by DSC analysis (figure 1 reports the DSC curves for D6 as an example) and by polarizing

Thermodynamic data.

	I → IL		I → II		II → IL		IL → II
	T_m/K	ΔH_m/kJ mol^{-1}	T_1/K	ΔH_1/kJ mol^{-1}	T_2/K	ΔH_2/kJ mol^{-1}	T/K
A2	528·9	89·8	—	—	—	—	
A6		—	434·3	37·5	454·2	45·0	450·7
A8†		—	411·3	29·1	430·8	41·8	428·0
A12‡		—	399·5	58·2	409·1	50·0	405·6
D6		—	471·9	33·4	484·9	47·0	481·2
F6	482	69·5	—	—	—	—	

I is the low temperature solid phase; II is the additional solid (?) phase (see text); IL is the isotropic liquid phase; T is the transition temperature, [$\sigma(T)/T \leqslant 1$ per cent]; temperatures were measured at the onset of the thermal phenomenon, by linear extrapolation of the DSC curves; ΔH = enthalpy change at the transition, [$\sigma(\Delta H)/\Delta H \leqslant 10$ per cent].

† Compound A8 exhibits a monotropic smectic phase (on cooling the isotropic liquid) at 428 K, which transforms into the phase II at 425·8 K. The two transitions are too close to be resolved, however approximate integration gives $\Delta H = 18$ kJ mol^{-1} for the smectic to phase II transition.

‡ Thermodynamic data of A12 refer to the second heating DSC cycle where the two transitions are better resolved.

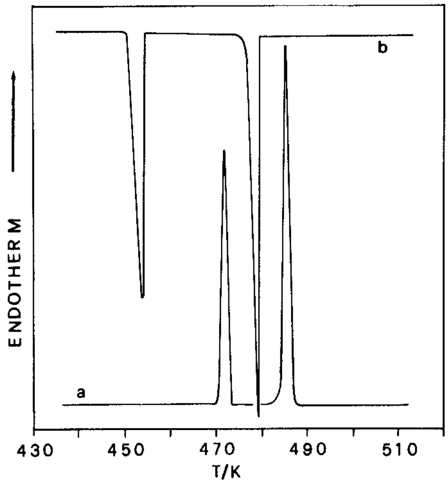


Figure 1. D6: DSC thermograms on heating (*a*) and cooling (*b*). Scanning rate 10 K/min.

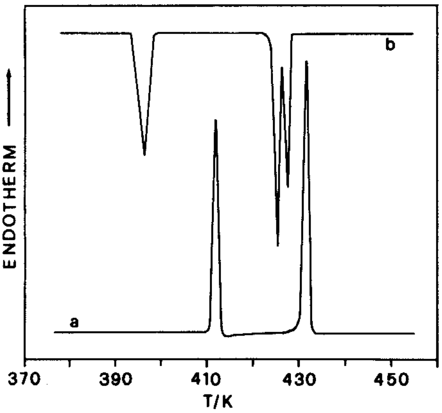


Figure 2. A8: DSC thermograms on heating (*a*) and cooling (*b*). Scanning rate 10 K/min.

microscopy, prior to melting to an isotropic liquid. The reverse sequence is observed on cooling the latter. Similar behaviour is exhibited by A8 (see figure 2) on heating, while a liquid–liquid crystal transition occurs on cooling the isotropic liquid. The smectic nature of the mesophase is suggested by the optical pattern most frequently observed: batonnets dispersed in an homeotropic texture, in some cases combined in clusters (see figure 3) to give a fan texture. Smectic A and B phases are two possible explanations for these features. However, because of the narrow temperature (and time) interval available to study the mesophase, we were unable to record an X-ray diffraction pattern which would help to discriminate between these two possibilities. The enthalpic change involved at the smectic–isotropic transition is rather large, although this could only be determined approximately ($\approx$ 18 kJ/mol) because of the incomplete resolution of the DSC exothermic signals.

In conclusion, out of the six dicarboxylic acids, only one exhibits a definite mesomorphic behaviour, although in a monotropic sequence.

Figure 3. A8: Optical texture of the liquid crystal phase at 430 K on cooling. Crossed polarizers.

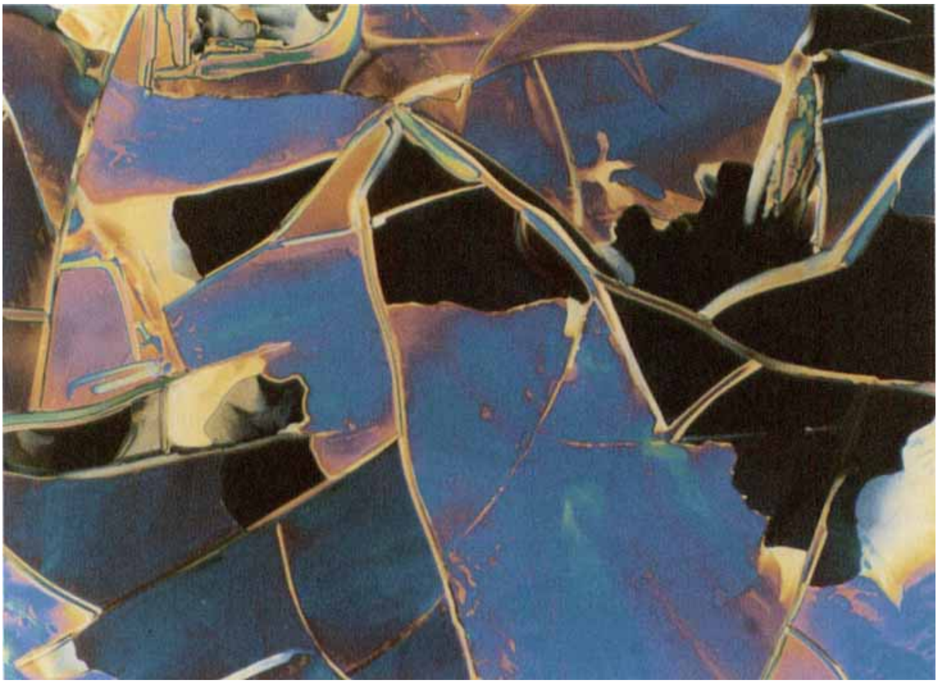


Figure 4. A12: Optical texture of phase II at 406 K. Crossed polarizers.

The available thermodynamic data do not afford any unambiguous evidence with which to interpret this feature. In fact, on one side and not unexpectedly, the melting temperature (T_2) decreases with increasing length of the aliphatic terminal chains and, if the strictly homologous An compounds are taken into account, nothing peculiar distinguishes the melting temperature of A8. On the other hand, A8 is characterized by having the minimum value of $\Delta H_1 + \Delta H_2$ per unit mass (≈ 27 per cent below the average value) which might indicate significant peculiarities in the molecular packing.

The question regarding the nature of the phase (phase II) stable between the low temperature solid phase (phase I) and the isotropic liquid (IL) does not have a straightforward answer. (The general definition of phase I or phase II is used here only for conciseness and should not be taken as an assumption of isomorphism among the corresponding phases of different compounds.) It will be discussed later.

As can be seen from the table and figures 1 and 2, substantial supercooling is observed for the low temperature transition (II → I), while phase II forms from the isotropic liquid with only a few degrees of supercooling. This difference could be taken as a further indication that a large molecular reorganization is needed for the low temperature transition to occur (we recall incidentally, that a small degree of supercooling is typical for transitions from isotropic liquids to mesophases). As far as A8 is concerned, the supercooling of the isotropic liquid is smaller by about 1 K than that observed for the other compounds, while the onset of phase II takes place with a total supercooling (i.e. T_2–T(smectic $\rightarrow$ II)) which is larger by approximately 1·5 K. These differences are so small, and probably of marginal significance, that it should still be possible to observe a conventional liquid crystal phase for the other compounds also even if a larger supercooling of the isotropic liquid were to occur.

Phase II is characterized by a remarkable plasticity. During the optical observations with the polarizing microscope the glass slide and cover slip can be made to glide over one another with a little pressure. A8 was easily extruded in phase II in an attempt to obtain macroscopically oriented samples for X-ray diffraction studies. These features are quite typical of conventional plastic crystals [12] which, however, have melting entropies considerably lower than the values taken by ΔS_2. As a further difference, phase II is birefringent, while plastic crystals, as a consequence of their usually cubic structure, are optically isotropic. Multiple optical textures of phase II have been observed, also for the same compound, by cooling the isotropic liquid. One of them is shown in figure 4. A segmented mosaic texture was observed for A8 quite analogous to that reported for the smectic H phase of methyl 4[4-ethoxy-benzylideneamino]cinnamate [13].

The I → II phase transition produces a strong change in the X-ray diffraction pattern. The number of diffraction lines, recorded for powdered samples, is drastically reduced to a roughly common pattern with by far the strongest diffracted intensity around 2θ of 20° (figure 5 shows the X-ray diffraction pattern for phases I and II of A8 as an example), superimposed on a diffuse halo included between 2θ of 15° and 25°. As far as this wide angle section of the diffraction pattern is concerned this is quite analogous to that observed for highly ordered smectic phases such as smectic H or G [14]. However only A12 shows the low angle lines (specifically three diffraction orders corresponding to a lattice distance of 30·1 ± 0·5 Å) which characterize the structural periodicity normal to the molecular layers of a smectic phase. No similar evidence was detected for compounds A6, A8 and D6 in phase II. The experimental evidence collected so far does not allow, at present, an unambiguous definition of the nature of phase II.

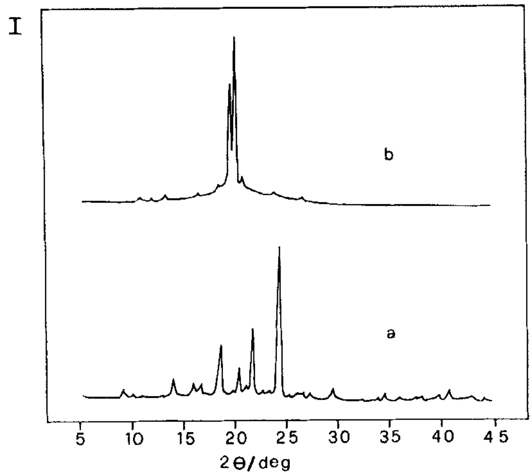


Figure 5. Powder X-ray diffraction patterns of compound A8: at (*a*) 298 K (phase I)· (*b*) 420 K (phase II). CuKα radiation.

The picture is complicated by the seemingly only partial homology in the behaviour of those compounds having strict chemical homology. However, two hypotheses might be useful to direct further investigation.

(*a*) Phase II is a crystal phase. The considerable enthalpy and entropy changes at the I → II phase transition suggest the onset of conformational disorder and possibly of diffusive molecular mobility. This last point is suggested by the remarkable tendency of originally microcrystalline samples to recrystallize in coarse grain after the transition to phase II had taken place. A reference model for this phase may be offered by the high temperature solid phase of higher paraffins. For this purpose a comparison between A12 and tritriacontane ($C_{33}H_{68}$) [15] may be useful. The high temperature solid phase (D phase in [15]) melts to the isotropic liquid with ΔH = 79·53 kJ/mol (171·4 J/g) and ΔS = 230·7 J/Kmol. The melting entropy is 68·5 per cent of the sums over all four phase transitions leading from the solid phase stable at room temperature to the liquid. A12 melts with ΔH_2 = 80·4 J/g and ΔS_2 = 122·2 J/Kmol. The latter value is 45·6 per cent of the total transition entropy. This considerable difference of the melting entropies must be significant because, as far as the conformational mobility is concerned, the number of relevant chemical bonds is not largely different between the two molecules (30 CH_2–CH_2 bonds for tri-triacontane; 26 CH_2–CH_2 + C–O bonds for A12).

(*b*) Phase II is some highly ordered liquid-crystalline phase. Neither the presence of a few wide angle X-ray diffraction lines, nor the relevant value of the molar isotropization enthalpy are incompatible with this hypothesis. Concerning the latter point, the existence of smectic phases (or of sequences of progressively less ordered liquid crystal phases) whose isotropization involves a relevant fraction of the total crystal to isotropic liquid transition enthalpy is documented and not uncommon (see [16] for a review). The intriguing feature, which, however, would not concern A12, is the absence of X-ray diffraction signals apparently connected to a smectic periodicity which is to any reasonable extent comparable to the molecular length.

A structural study by X-ray diffraction analysis of single crystals is under way, with a preliminar attention to the basic features of phase I.

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