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Preliminary communication

Amphotropic liquid crystallinity of *N*,*N*′-diundecenoylbenzene-1,4-diamine (DUBDA)

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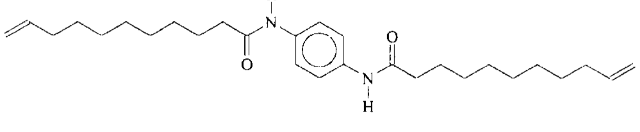
N,*N*′-diundecenoylbenzene-1,4-diamine (DUBDA), an amide with long symmetric aliphatic chains, is shown to exhibit monotropic thermotropic liquid crystallinity as well as lyotropic liquid crystallinity in highly polar solvents on the basis of differential scanning calorimetry, polarized optical microscopy, temperature-variable FTIR, and X-ray diffraction analysis. There are obvious differences between the two mesophases in terms of molecular stacking and driving force, although the two mesophases originate from the same molecule. In addition, a possible lamellar model for the lyotropic mesophase is proposed.

Liquid crystals are generally classified as being either thermotropic or lyotropic depending on whether their self-organization occurs only on heating for the pure compounds (thermotropic liquid crystals) or is induced by isotropic solvents (lyotropic liquid crystals) [1]. There exist obvious differences between the two liquid crystalline phase types in terms of molecular structure and manner of their self-organization. In the last few years, however, many amphotropic compounds such as carboxylates [2, 3], quaternary ammonium amphiphiles [4–7], carbohydrates [8–10], and derivatives of cellulose [11–13], which can form thermotropic as well as lyotropic liquid crystalline phases, have been reported. The integration of thermotropic and lyotropic liquid crystallinity in one molecule is of significance in the further probe into the essence of liquid crystals [14]. Amide molecules especially polyamides such as poly(*p*-benzamide) [15], poly(*p*-phenyleneterephthalamide) [15], and poly(*p*-benzanilide-terephthalamide) [16] have long been known for their lyotropic liquid crystallinity. In recent years, some other amide molecules giving thermotropic mesophases, such as alternating aliphatic-aromatic poly(ester amides) [17] and diamides of alkyl substituted 1,3- or 1,4-diaminobenzene [18–20], have also been reported. The formation of either thermotropic or lyotropic phases in amide molecules is related to the hydrogen bonding interactions which are now regarded as an important driving force for liquid crystal formation [21–23]. Hydrogen bonding interactions, as in carbohydrates, would favour the formation of amphotropic mesophases for amide molecules provided that a suitable molecular structure was found. However, to our knowledge, there are very few reports [24] on the amphotropic liquid crystallinity of amide molecules. In this study, we have found serendipitously that *N*,*N*′-diundecenoylbenzene-1,4-diamine (DUBDA) an amide molecule prepared as a semi-rigid intermediate, shows monotropic thermotropic liquid crystallinity and gives a lyotropic mesophase, i.e. exhibits amphotropic liquid crystallinity. M.p. 186–187°C. ^{1}H NMR (DMSO-d_6, ppm) 1.3 (w. 20H), 1.6 (t, 4H), 2.0 (m, 4H), 2.2 (t, 4H), 5.0 (t, 4H), 5.8 (m, 2H), 7.5 (s, 4H), 9.8 (s, 2H). Elemental analysis (calc.%/found%) C (76.36/76.23), H (10.00/9.79), N (6.36/6.44), O (7.27/7.46).

The structure of DUBDA is:



This structure is similar to that of unsubstituted *N*,*N*′-dialkanoylbenzene-1,4-diamines studied recently by Matsunaga *et al.* [20]. In Matsunaga's paper, there is no mesomorphism reported for these compounds, only two or three solid–solid transitions occurring above 100°C. If we concentrate solely on the DSC curve (measured using a Perkin-Elmer DSC-7 differential scanning calorimeter with a heating and cooling rate of

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10°C min^{-1}) of DUBAD during the first heating run in which there appear two solid–solid transitions at 98.3°C ($\Delta H = 14.59$ kJ mol^{-1}) and 142.8°C ($\Delta H = 7.45$ kJ mol^{-1}), and a solid–isotropic transition at 187.1°C ($\Delta H = 74.27$ kJ mol^{-1}) (figure 1), similarly to Matsunaga's results, we should draw the same conclusion as theirs. But we noticed that in the cooling run there appear two peaks at about 174.8°C ($\Delta H = -17.46$ kJ mol^{-1}) and 171.0°C ($\Delta H = -34.91$ kJ mol^{-1}) after significant supercooling relative to 187.1°C, the melting point; this was not referred to in Matsunaga's report. This result is reproducible; it is reasonable to assume that a monotropic mesophase is formed. By polarized optical microscopy (Xintian XP1A model, China, equipped with a Mettler FP-82 hot-stage and a RICOH F-2 camera), we can observe a grainy or sanded texture, figure 2(*a*), in the approximate temperature range 171–175°C, contrasting with the crystal texture at a lower temperature, figure 2(*b*), but fluidity of the sample is hardly observed. Temperature-variable FTIR (TV-FTIR) using a Nicolet 750 FTIR spectrometer equipped with a Mettler FP-84 hot stage at a cooling rate of 10°C min^{-1} after the sample had been heated to above 200°C, showed that there is a small free N–H stretching vibration at 3440 cm^{-1} above 171°C (figure 3), which means that the hydrogen bonds between –CONH– groups are dissociated above 171°C. In other words, the ordered three-dimensional crystal structure of the sample does not exist above 171°C in the cooling sample. When the sample is above 175°C, there is a considerable free N–H stretching vibration. As the temperature decreases to below 175°C, the peak for free N–H stretching decreases remarkably, showing that the sample changes from the isotropic state into a liquid crystalline state. Therefore, TV-FTIR gives clear proof for the formation of a liquid crystalline phase.

Apparently, there is a close relation between the liquid crystallinity and hydrogen bonding, i.e. there exists a dynamic equilibrium of association–dissociation of the hydrogen bonding when the sample is in the melted state, similar to that of carboxylic acid liquid crystals [25]. The intermolecular hydrogen bonding between

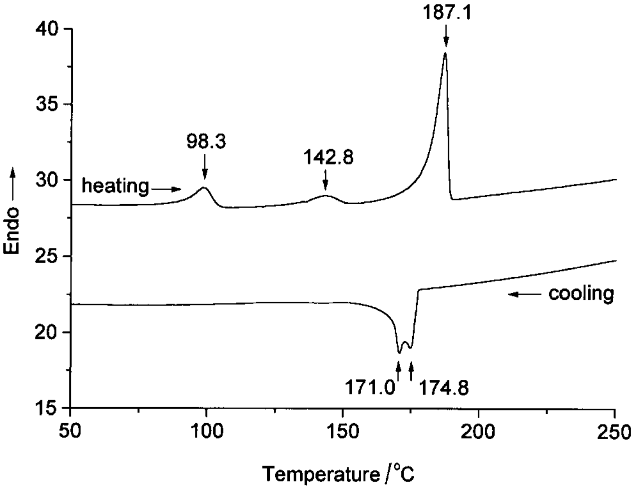

Figure 1. DSC curves for DUBAD.

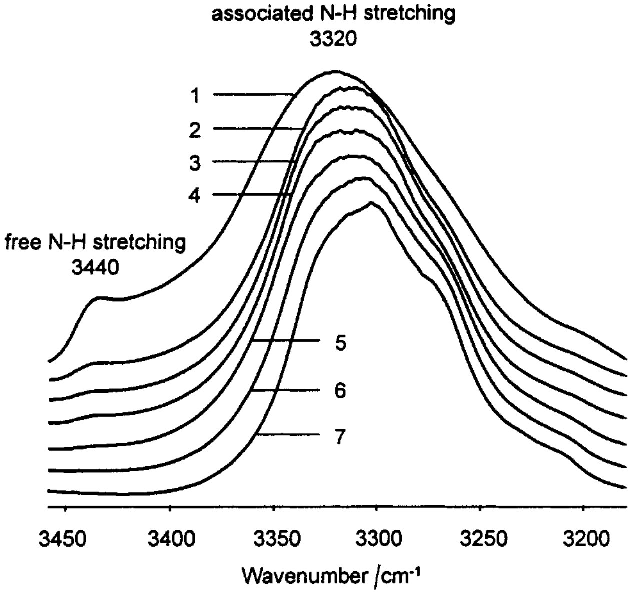

Figure 3. Temperature-variable FTIR spectra of DUBAD. 1: 200°C, 2: 175°C, 3: 173°C, 4: 171°C, 5: 160°C, 6: 100°C, 7: room temperature.

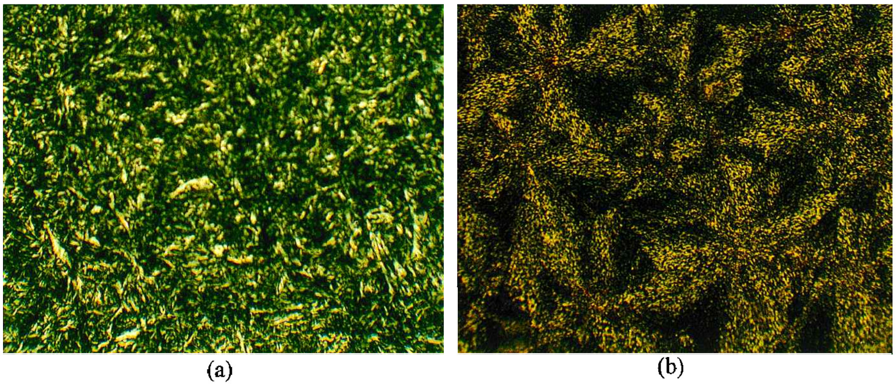

Figure 2. Polarized optical micrographs of DUBAD: (*a*) at 174°C after cooling from isotropic state (100×); (*b*) at 140°C (40×).

amide molecules is represented in figure 4. Considering that the hydrogen bonding is a strong non-covalent interaction, as a consequence a smectic phase would be the most reasonable mesophase to expect and would account for the poor fluidity of the sample in the liquid crystalline state. In addition, it is noted in figure 4 that the molecules adopt a slightly tilted array in order to favour the hydrogen bonding interaction. According to the above analysis, it may be deduced that the sample could form a smectic C mesophase. The grainy or sanded texture is also in accordance with such a mesophase according to the literature [26, 27]. Unfortunately, the XRD pattern for the liquid crystalline state could not be obtained owing to the narrow temperature range of the mesophase. But the XRD pattern (measured using a Rigaku, Japan, D/max-2400 X-ray diffractormeter, Cu K_α) at room temperature reveals a tilted array which gives indirect support for the above supposition ($d = 35$ Å, slightly shorter than the length of amide molecule in its extended conformation, about 36 Å, based on molecular modelling).

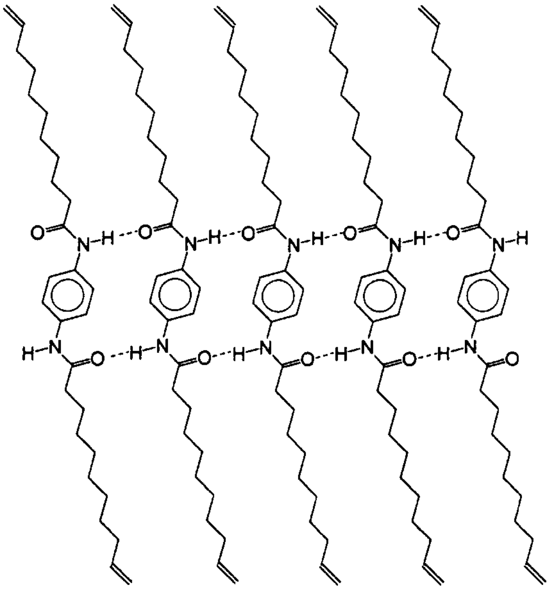

Figure 4. Intermolecular hydrogen bonding interactions between individual molecules of DUBAD.

In addition to the above-mentioned monotropic thermotropic liquid crystallinity, DUBAD also exhibits a lyotropic liquid crystalline phase in strongly polar solvents such as dimethyl sulfoxide (DMSO) or *N*,*N*-dimethylformamide (DMF). DUBAD is insoluble in water and alcohol due to the strong intermolecular hydrogen bonding and the hydrophobicity of the long aliphatic chains, but it is fairly soluble in DMSO, DMF, chloroform, and 1,1,2,2-tetrachloroethane (TCE); the solubility can be markedly improved by increasing the temperature to above 90°C. A small amount of sample is placed on a slide, then a drop of solvent is added and a coverglass is used to sandwich the sample. As the temperature is elevated to above 90°C, the sample completely dissolves and an isotropic solution is

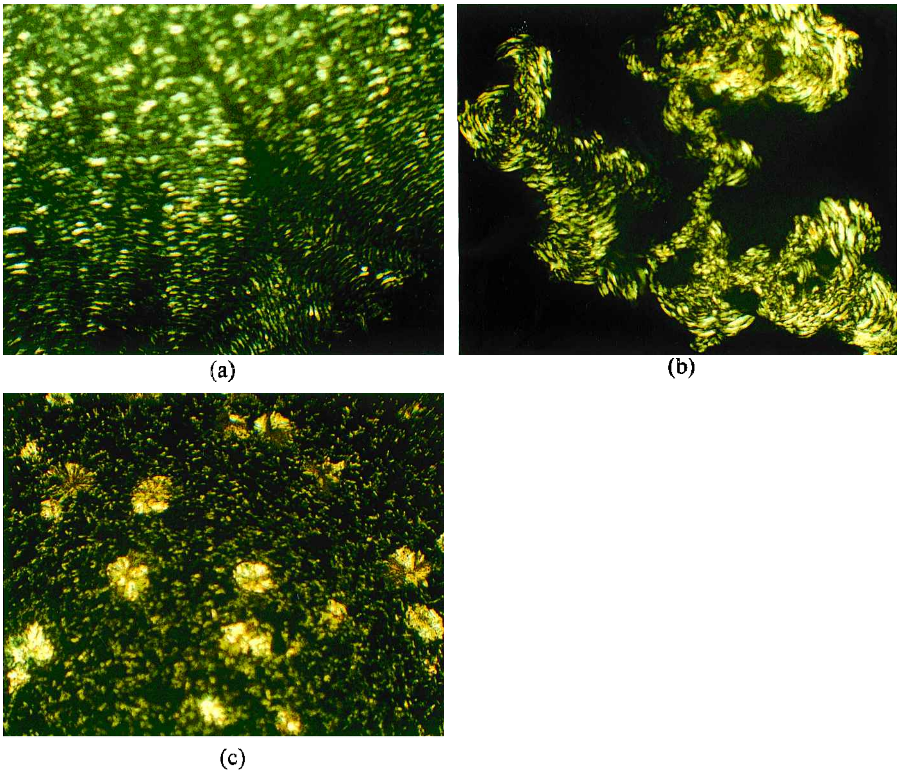

Figure 5. Polarized optical micrographs of DUBAD in (*a*) DMSO, (*b*) DMF, and (*c*) TCE at room temperature after cooling from the isotropic state at 100°C (40×).

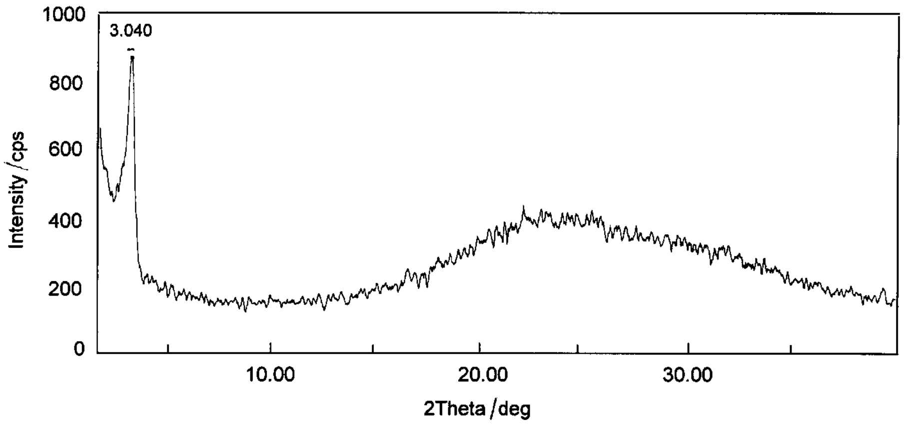

Figure 6. XRD pattern of DUBAD in DMSO at room temperature after cooling from the isotropic state.

obtained. Then the temperature is allowed to fall slowly. When the temperature is below 65°C, it is interesting to note that an arc-lined or fingerprint texture gradually develops in the solution with DMSO or DMF as solvent, while in the solution in TCE, only micro-crystalline grains are formed (figure 5). Due to the complexity of the mesomophism of lyotropic liquid crystals, it is difficult to assign a structure to the lyotropic mesophase from the optical texture alone. The texture of the sample in DMSO or DMF solution remains unchanged till room temperature. A cell sandwiched with a saturated solution of DUBAD in DMSO prepared as above was subjected to XRD measurement at room temperature. The XRD pattern (figure 6) shows only one sharp peak in the small angle region ($2\theta = 3.04°$ corresponding to a d value of 29.6 Å), which suggests a typical lamellar structure (possibly an L_α phase) for the lyotropic mesophase [28]. The formation of a lyotropic phase in DMSO and DMF, but not in TCE may be because the strongly polar DMSO and DMF solvents are capable of forming strong hydrogen bonds with the amide molecules such that the hydrogen bonding association between the amide molecules themselves is destroyed. Meanwhile, segregation effects can induce the aggregation of aliphatic chains that leads to the lyotropic mesophase. With the solvent TCE, its polarity is too low to break the intermolecular hydrogen bonding between the amide molecules, and therefore crystallization occurs normally at lower temperatures. According to the molecular structure of DUBAD and the solvent effect mentioned above, we propose a possible lamellar model for the lyotropic phase as represented in figure 7.

In conclusion, DUBAD exhibits both thermotropic and lyotropic liquid crystallinity. The driving force for the monotropic thermotropic liquid crystal formation is the intermolecular hydrogen bonding between the amide

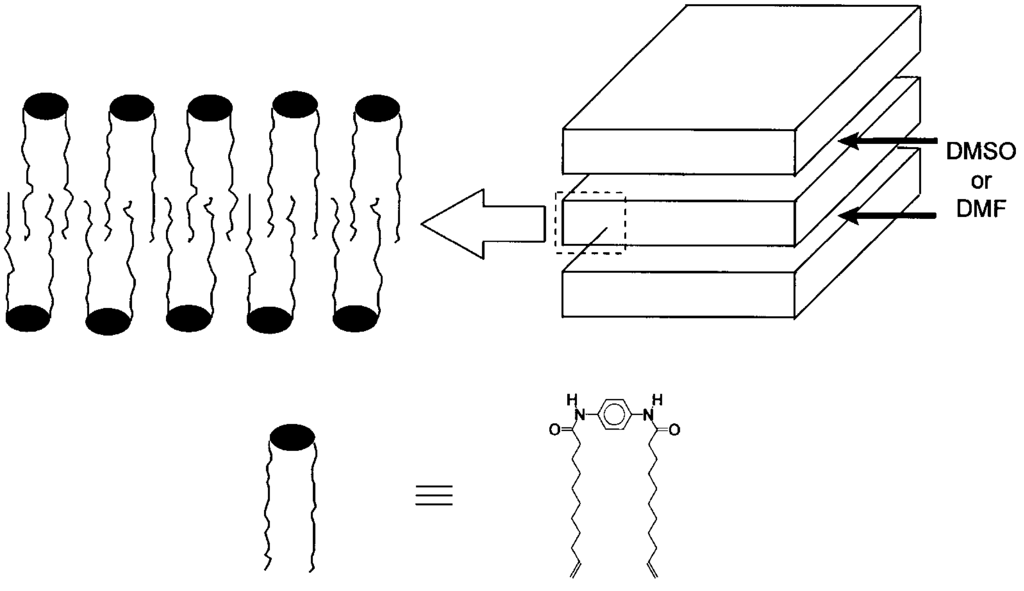

Figure 7. Schematic representation of the possible lamellar structure of the lyotropic phase of DUBAD.

groups of individual molecules in a dynamic equilibrium of association–dissociation, while for the lyotropic mesophase the formation of a lamellar structure is attributed to the aggregation of the long aliphatic tails due to segregation effects as well as to the strong hydrogen bonding interactions between DUBAD and the solvents. It is worth pointing out here that the formation of a lyotropic phase for this amide molecule carrying reactive double bonds is particularly promising because pre-arranged monomers in solution are favourable in the formation of materials with ordered structures via further reaction or polymerization. Exploration of this aspect is currently being undertaken.

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