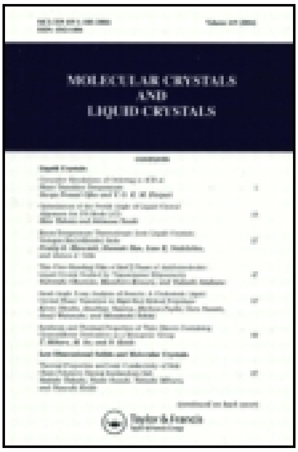


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Thermotropic Liquid Crystals from Hydrogen-Bonded Amphiphiles: N-Alkyl-Substituted Iminodiacetic Acids

J. Michas [a], C. M. Paleos [a], A. Skoulios [b] & P. Weber [b]

[a] NRC “Demokritos”, Aghia Paraskevi, Attiki, Greece

[b] Groupe des Matériaux Organiques, Institut de Physique et Chimie des Matériaux, 6, rue Boussingault, Strasbourg, France

To cite this article: J. Michas , C. M. Paleos , A. Skoulios & P. Weber (1993): Thermotropic Liquid Crystals from Hydrogen-Bonded Amphiphiles: N-Alkyl-Substituted Iminodiacetic Acids, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 237:1, 175-184

To link to this article: http://dx.doi.org/10.1080/10587259308030133

Mol. Cryst. Liq. Cryst., 1993, Vol. 237, pp. 175–184
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Thermotropic Liquid Crystals from Hydrogen-Bonded Amphiphiles: *N*-Alkyl-Substituted Iminodiacetic Acids

J. MICHAS and C. M. PALEOS†
NRC "Demokritos", Aghia Paraskevi, Attiki, Greece

and

A. SKOULIOS and P. WEBER
Groupe des Matériaux Organiques, Institut de Physique et Chimie des Matériaux, 6, rue Boussingault, Strasbourg, France

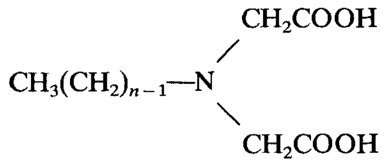
(Received November 10, 1992)

Alkyl derivatives of iminodiacetic acid, i.e. $CH_3(CH_2)_{n-1}N(CH_2COOH)_2$, with n = 12, 14, 16, 18, were studied by polarizing optical microscopy, differential scanning calorimetry, and x-ray diffraction. They were found to exhibit liquid crystalline behavior and specifically to produce disordered smectic phases above about 130°C. Observed for the first time with saturated aliphatic acids, the smectic ordering may be attributed to the intramolecular segregation of the alkyl chains from the polar zwitterionic iminodiacetic endgroups which interact through hydrogen boding and coulombic forces.

Keywords: N-alkyl-iminodiacetic acid derivatives, hydrogen-bonded amphiphiles, lipophilic and hydrophilic moieties, thermotropic liquid crystals

INTRODUCTION

In a recent paper,[1] the thermotropic polymorphism of some long-chain *N*-alkyl derivatives of iminodiacetic acid, $NH(CH_2COOH)_2$, was investigated by optical microscopy and differential scanning calorimetry. These compounds were found to be liquid crystalline in nature above temperatures of the order of 130°C. By analogy with ionic surfactants,[2-6] their mesomorphous character was attributed to the formation in the melt of distinct and alternating layers of polar heads and lipophilic moieties. This type of lamellar ordering remained, however, to be substantiated by systematic x-ray studies revealing the exact crystallographic structure of the mesophases. Such a study is the very object of the present paper. It has been carried out with the four following compounds (abbreviated to C$_n$IDA):



$$CH_3(CH_2)_{n-1}\text{—}N\begin{matrix} \diagup CH_2COOH \\ \diagdown CH_2COOH \end{matrix}$$

$n = 12, 14, 16, 18$

Before proceeding with the description of the results obtained in this work, it is useful to note that lamellar liquid crystals may be obtained, not only from ionic amphiphiles, but also from n-alkyl substituted carbohydrates[7–8] and amphiphilic diols or polyols.[9] The amphiphilic character responsible for the formation of such mesophases[10] is of course related as usual to the presence in the molecules of distinct polar and lipophilic moieties, but here it is significantly enhanced by the strong hydrogen bonding of the hydroxylated endgroups.

EXPERIMENTAL

All *N,n*-alkyl-iminodiacetic acids (C$_n$IDA) studied in the present work were synthesized following the method reported by Stein *et al.*[11] Dodecyl derivative, $C_{16}H_{31}NO_4$: Anal. calcd: C63.76, H10.37, N4.34. Found: C63.65, H10.69, N4.45. Tetradecyl derivative, $C_{18}H_{35}NO_4$: Anal. calcd: C65.62, H10.71, N4.25. Found: C65.88, H10.56, N3.93. Hexadecyl derivative, $C_{20}H_{39}NO_4$: Anal. calcd: C67.19, H11.00, N3.92. Found: C67.19, H11.33, N3.71. Octadecyl derivative, $C_{22}H_{43}NO_4$: Anal. calcd: C68.53, H11.43, N3.63. Found: C68.53, H11.24, N3.63.

The thermal stability of the compounds was investigated using a Mettler TC10A instrument coupled with a TA processor and a Mettler M3 balance. It was found appropriate for the subsequent thermal studies planned in this work, especially for the rather lengthy (typically a few hours long) x-ray experiments at high temperature. A typical weight loss thermogram is shown in Figure 1. Although readily degrading at very high temperatures (due to decarboxylation), the samples proved to withstand two-hour heating at 145°C, without excessive weight loss.

Optical microscopy observations were performed employing a Leitz-Wetzlar polarizing microscope equipped with a Mettler FP 82 hot stage. Differential scanning calorimetry measurements were carried out with a Perkin-Elmer DSC-7 coupled with a TAC 7/DX controller (heating and cooling rates of 10°C/min). Small and wide-angle x-ray diffraction patterns of powder samples, contained in 1 mm Lindemann capillaries, were recorded photographically, using monochromatic CuK$_{\alpha 1}$ radiation (bent quartz monochromator) and a Guinier focusing camera equipped with a purpose-built heating sample-holder controlling the temperature within less than 1°C.

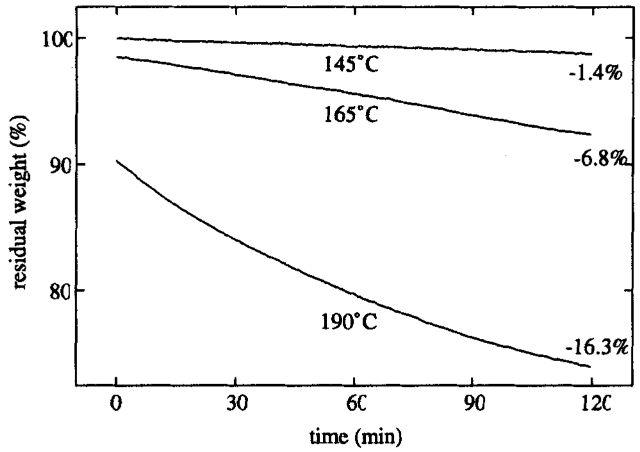


FIGURE 1 Thermogravimetric graph of C_{18}IDA recorded in nitrogen upon isothermal heating at 145, 165, and 190°C. Temperatures were reached by stepwise heating. Inserted percentages represent the weight losses measured during the two-hour heating at each temperature.

RESULTS AND DISCUSSION

The polymorphic behavior of the C_nIDA compounds was first studied by polarizing optical microscopy. A phase transition was detected at about 130°C for all the samples. The solid crystalline material present at room temperature transformed into a viscous, birefringent fluid at 130°C. The focal conic textures and oily streaks observed (Figure 2) are typical of smectic mesophases. Heating to still higher temperatures showed the textures to gradually lose their characteristic features and completely vanish between 170 to 200°C. Obviously, the phase transition into the isotropic liquid is smeared out by the thermal degradation of the compounds.

The thermal behavior of the C_nIDA compounds was then analyzed by differential scanning calorimetry. Typical DSC thermograms are shown in Figure 3. On heating, the phase transition from the crystal into the mesophase is revealed by a strong endothermic peak at a temperature of about 130°C (Figure 3a), in agreement with the optical observations. Immediate cooling of the molten samples, without undue heating to higher temperatures, brings about the reverse transition as expected (Figure 3b); crystallization proceeds with a significant hysteresis (of about 30°C), associated as customary with nucleation and crystal growth kinetics. Upon heating to high temperatures, the samples start to thermally decompose as mentioned previously; the baseline in the thermograms then deviates strongly from the horizontal and the transition into the isotropic liquid cannot be detected.

The crystal to mesophase transition temperatures measured, together with the corresponding enthalpies are reported in Table I. Within the experimental error, the transition enthalpies seem to increase linearly with the number of methylene groups in the alkyl chains (Figure 4). The straight line going through the results has been determined by a least square fit method and obeys the equation: ΔH(kJ/mol) = $2.85n + 18$ (the standard errors on the slope and Y-intercept of the line being 0.78 and 12 kJ/mol, respectively). The slope of the line corresponds to an

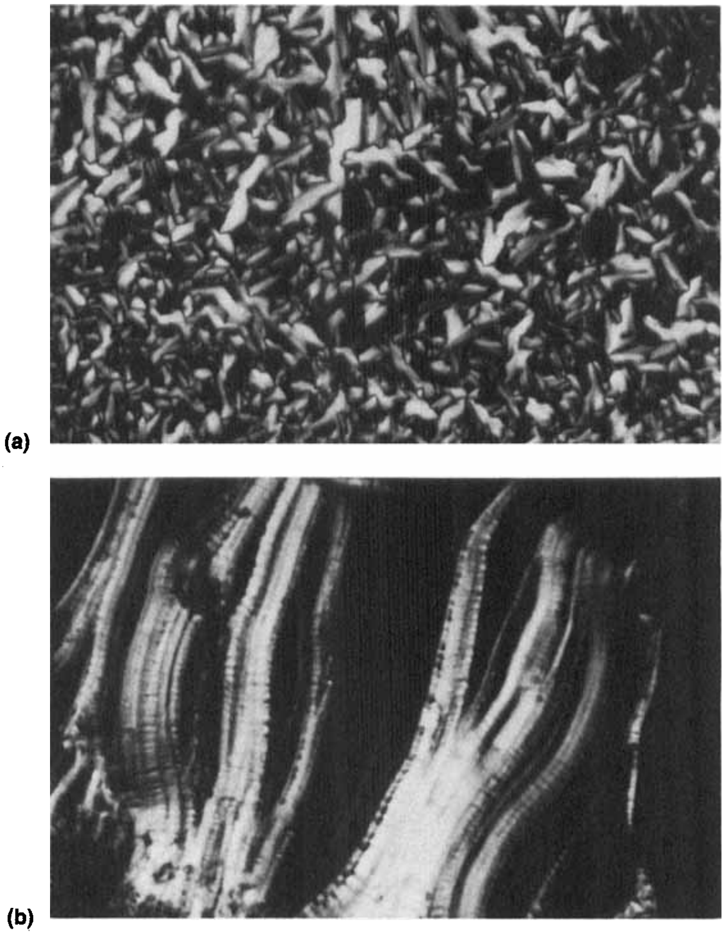


FIGURE 2 Optical textures of C_{14}IDA at 140°C (X200): (a) focal conic texture and (b) oily streaks. See Color Plate XI.

enthalpy of 204 J/g for the fusion of the methylene groups. Lower than that (289 J/g) found for the fusion of linear paraffins,[12] this value is comparable to that (183 J/g) found for the crystal to mesophase transition of copper (II) soaps.[13] In the case of the copper soaps, the weak value of the melting enthalpy was interpreted as mainly due to the unusual arrangement of the paraffin chains in the crystalline state (the zig-zag planes of the all-trans chains are parallel to one another instead of being packed in a chevron-type arrangement as in normal paraffins), imposed by their anchoring conditions onto the copper carboxylate polar heads. In the case of the C_nIDA compounds, the strong hydrogen bonding of the carboxylic endgroups might affect in a similar way the arrangement of the alkyl chains in the crystal.

The exact nature of the crystal phases at low temperature and of the smectic mesophases above 130°C was finally examined with x-ray diffraction. The diffraction patterns of the crystal phases contained many Bragg reflections, both at small and wide angles, consistent with the existence of a three-dimensional lamellar ordering of the molecules. Slightly larger than the corresponding lengths of the

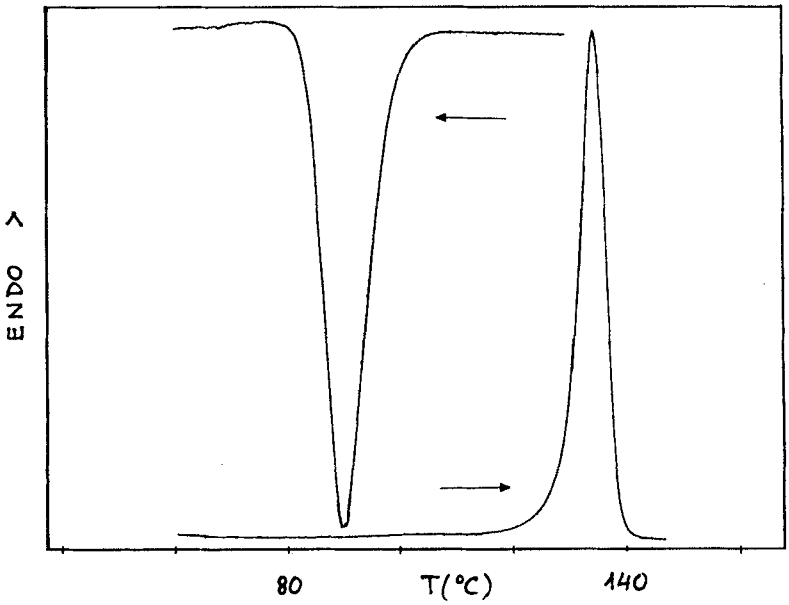


FIGURE 3 Differential scanning calorimetry graphs of C_{16}IDA, recorded at a constant heating or cooling rate of 10°C/min.

TABLE I

Transition temperatures and corresponding enthalpies, recorded for C_nIDA by differential scanning calorimetry

Compound	Temperature (°C)	Enthalpy (kJ/mol)
C_{12}IDA	129	54
C_{14}IDA	130	54
C_{16}IDA	130	66
C_{18}IDA	129	69

alkyl chains, the lamellar periods, *d*, measured from the small-angle reflections, proved to increase linearly with the number of carbon atoms in the alkyl chains (Figure 5). The straight line going through the results was determined by a least square fit method ($R = 99.99\%$): $d(\text{Å}) = 66 + 1.20n$ (the standard errors on the *Y*-intercept and the slope of the line being 0.2 and 0.01 Å, respectively). The *Y*-intercept agrees satisfactorily with what is expected to be the size of the iminodiacetic polar head flanked by one methyl endgroup, and its slope with the length increment per methylene group (2.54/2 = 1.27 Å) of the all-trans paraffin chain.

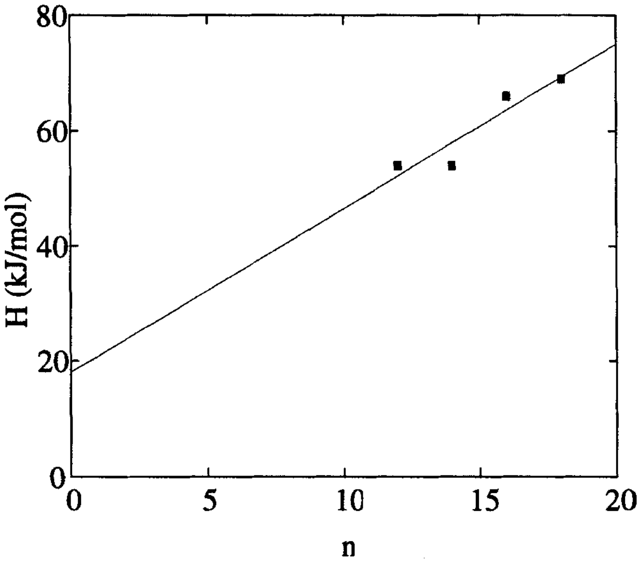


FIGURE 4 The crystal to mesophase transition enthalpies as a function of carbon atoms in the alkyl chains of the C_nIDA compounds.

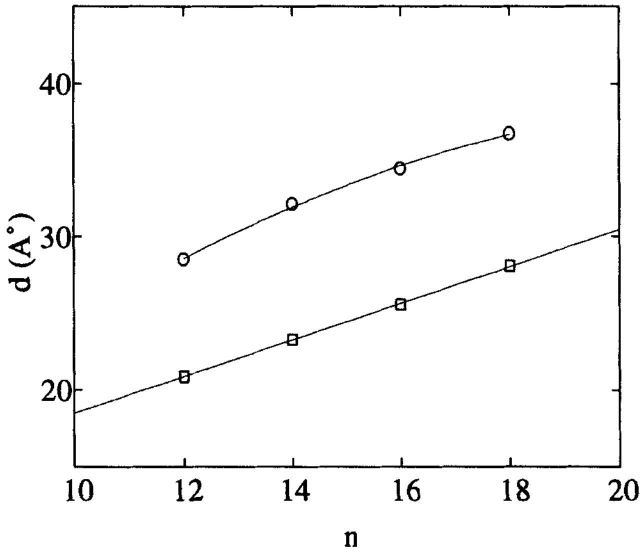


FIGURE 5 Lamellar periods of the C_nIDA compounds as a function of the number of carbon atoms of the alkyl chains: crystalline phases at 25°C (squares) and smectic phases at 145°C (circles).

Evidently, the lamellar structure corresponds to a single-layered arrangement of molecules oriented virtually parallel to the layer normal (tilted in fact by about 20°) and pointing alternately up and down (Figure 6).

The molecular area S, that is, the surface covered by one molecule in the layers may easily be deduced from the slope of the d versus n straight line. Indeed, for

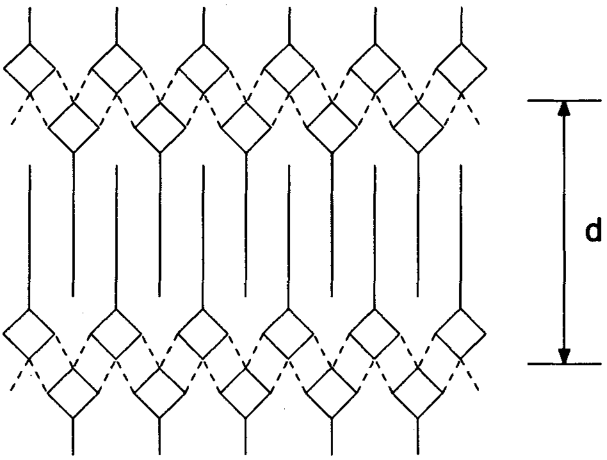


FIGURE 6 Schematic view of the single-layered arrangement of the C_nIDA molecules in the low-temperature crystalline state. Lozenges represent the iminodiacetic endgroups, full lines represent the alkyl chains, and dashed lines simulate hydrogen bonds.

simple geometrical reasons, the volume $V = V_0 + (n - 1)V_{CH2} + V_{CH3}$ of one molecule—V_0, V_{CH3}, V_{CH2} being the respective volumes of the iminodiacetic polar head, the methyl endgroup, and the methylene group—may be taken equal to the product Sd; as a result d may be written as follows:

$$d = \frac{V_0 + V_{CH3} - V_{CH2}}{S} + n\frac{V_{CH2}}{S}$$

From the value of V_{CH2} at room temperature (24.3 Å^3),[14] one immediately obtains for S the value of 20.3 ± 0.3 Å^2, which is consistent with what is expected for the lateral packing area of fully stretched and slightly tilted paraffin chains in the crystalline state.[15]

To discuss the internal structure of the polar sublayers in the lamellar crystals, it is useful to briefly recall some important features of the molecular arrangement of the unsubstituted iminodiacetic acid, $H—N(CH_2COOH)_2$, in the crystalline state. This compound is known to undergo at least three crystalline polymorphic forms.[16-17] Promoted by the conformational freedom of the molecules, this wealth of structures found, which in fact corresponds to a variety of different three-dimensional hydrogen-bonded networks, is fundamentally related to the wealth of distinct combinations of hydrogen bonds among the numerous proton donors and acceptors present in the system. It is further favored by the fact that, in all the crystal structures described until now, the molecules are invariably found to be in a zwitterionic form,[17] $HOOC—CH_2—NH_2^+—CH_2—COO^-$, and thus to interact with one another through strong coulombic forces.

In the case of the *N*-alkyl substituted iminodiacetic acids, the hydrogen-bonded network must be different. This is due to the substitution of one alkyl group for one hydrogen atom, which leads to the suppression of one proton donor, but more importantly to the introduction of long alkyl chains tending to organize themselves in layers and thus break the three-dimensional hydrogen-bonded networks into stacks of two-dimensional ones. To our best knowledge, no detailed information on the structure of these two-dimensional hydrogen-bonded polar layers is available as yet. In the expectation of specific inquiries in the field (x-ray and/or neutron scattering experiments on single crystals, for instance), it suffices to note the thickness measured in the present work for the sublayers (6.6 Å) and the molecular area of the polar heads (20.3 Å^2).

The structure of the smectic mesophases above 130°C was ascertained and described by x-ray diffraction. To reduce the risk of thermal degradation to a minimum, special care was taken not to heat the samples at too high temperatures for unduly long times. X-ray patterns recorded at 145°C, that is a few degrees above the transition temperature from the crystal, with exposure times not exceeding two or three hours, proved clear enough to establish the disordered (*A* or *C*) smectic nature of the mesophases. They contained two or three sharp and equidistant Bragg reflections in the small-angle region, indicative of the smectic layering, and one diffuse ring in the wide-angle region at 4.5 Å, suggesting the liquid-like conformation of the alkyl chains and the absence of in-layer long-range ordering of the molecules. The smectic periods measured are reported in Figure 5.

Inspection of Figure 5 shows the lamellar spacings to considerably increase at the transition from the crystal to the smectic mesophase, passing from one to about 1.35 fully extended molecular lengths. The spacing jump largely exceeds that expected from the usual volume expansion associated with the heating from 25 to 145°C (about 5%) and with the melting of the molecules (about 10%). This means that, upon the occurrence of the smectic phase, the packing mode of the hydrogen-bonded iminodiacetic groups is drastically modified, their two-dimensional packing density suddenly increasing by at least 20%. Evidently, the molecular area suddenly decreases at the transition by more than 20%, that is, by as much as 4 Å^2, passing from 20.3 to about 16.3 Å^2. In the same time, the alkyl chains adopt a shrinked and dynamically random conformation and, as a result, their interdigitation, shown in Figure 6 for the crystal, vanishes. As in the case of the thermotropic smectic liquid crystals of sodium soaps,[18] the disordered molecules are arranged in double layers, with a molecular area ($S = 2V/d = 2 \times 16.3$ Å^2) of about 32.6 Å^2, which is reasonable as compared to that typically (40 Å^2) obtained with smectic amphiphiles.[10]

Unlike the lamellar period of the crystalline phases, the smectic period of the C_nIDA compounds does not increase linearly with the number of carbon atoms in the alkyl groups (Figure 5); in fact, it grows less rapidly for the long than for the short chains. This is easy to understand as the smectic phase is disordered in nature; it simply means that, for entropic reasons, the molecular area, which is directly related to the lateral spreading of the layers, increases measurably with the length of the molten chains, instead of remaining strictly constant as in the crystal. The variation of the molecular area suggests that the hydrogen-bonded network within the polar sublayers is not unique but actually results from a dynamical equilibrium of many possible hydrogen-bond patterns.

To further analyze this point, a quantitative knowledge of the molecular area, and its dependence on the chain length, is necessary. However, the experimental evaluation of S turns out impossible in the present state of things. Firstly, the molecular area varies with the chain length, so the method described above to calculate S for the crystal is not applicable. And secondly, the molar volume of the C_nIDA compounds cannot be measured experimentally by dilatometry (because the thermal degradation makes the necessary degasing of the samples ineffectual) and the direct calculation of S through the equation $V = Sd$ is not feasible.

CONCLUSION

The main result of the present work is that the *N*-alkyl substituted iminodiacetic acids are indeed liquid crystalline above 130°C, as already suggested[1] from optical observations, their detailed structure being disordered smectic in nature. To our best knowledge, they are the first well-established examples of saturated aliphatic acids showing smectic behavior. All the organic acids reported up to now to produce liquid crystals are in fact conjugated systems, either aromatic as *p*-substituted benzoic and cinnamic acids, or unsaturated fatty acids as 2,4-nonadienoic acid.[19] In the case of the latter acids, the smectic behavior is due to the high polarizability of the conjugated moieties, which induces strong effective van der Waals repulsions between the alkyl and conjugated moieties; in contrast, in the case of the iminodiacetic derivatives, the smectic ordering may readily be attributed to the intramolecular segregation of the alkyl chains from the polar zwitterionic endgroups which interact through hydrogen bonding and coulombic forces.

References

1. C. M. Paleos, J. Michas and A. Malliaris, *Mol. Cryst. Liq. Cryst.*, **186**, 251 (1990).
2. K. Iwamoto, Y. Ohnuki, K. Sawada and M. Seno, *Mol. Cryst. Liq. Cryst.*, **73**, 95 (1981).
3. G. H. Needham, R. D. Willet and H. F. Franzen, *J. Phys. Chem.*, **88**, 1984 (1984).
4. V. Busico, A. Ferraro and M. Vacatello, *Mol. Cryst. Liq. Cryst.*, **128**, 243 (1985).
5. J. D. Gault, H. A. Gallardo and H. J. Muller, *Mol. Cryst. Liq. Cryst.*, **130**, 163 (1985).
6. A. Malliaris, C. M. Paleos and P. Dais, *J. Phys. Chem.*, **91**, 1149 (1987).
7. G. A. Jeffrey, *Acc. Chem. Res.*, **19**, 168 (1986).
8. J. W. Goodby, *Mol. Cryst. Liq. Cryst.*, **110**, 205 (1984); B. Pfannenmuller, W. Welte, E. Chin and J. W. Goodby, *Liq. Cryst.*, **1**, 357 (1986); J. W. Goodby, M. A. Markus, E. Chin, P. L. Fin and B. Pfannenmuller, *Liq. Cryst.*, **3**, 1569 (1988); K. Praefcke, A. M. Levelut, B. Kohne and A. Eckert, *Liq. Cryst.*, **6**, 263 (1989); H. A. van Doren, R. van der Geest, C. F. de Ruijter, R. M. Kellogg and H. Wynberg, *Liq. Cryst.*, **8**, 109 (1990).
9. C. Tschierske, G. Brezesinsky, F. Kuschel and H. Zaschke, *Mol. Cryst. Liq. Cryst. Lett.*, **6**, 139 (1989); C. Tschierske and H. Zaschke, *J. Chem. Soc. Chem. Comm.*, 1013 (1990); F. Heinrich, C. Tschierske and H. Zaschke, *Angew. Chem. Int. Ed. Engl.*, **30**, 440 (1991); K. Praefcke, B. Kohne, S. Diele, G. Pelzl and A. Kjaer, *Liq. Cryst.*, **11**, 1 (1992).
10. A. Skoulios and D. Guillon, *Mol. Cryst. Liq. Cryst.*, **165**, 317 (1988).
11. A. Stein, H. P. Gregor and P. E. Spoerri, *J. Am. Chem. Soc.*, **77**, 153 (1955).
12. R. Weast (editor), *Handbook of Chemistry and Physics*, 56th edition, CRC Press, C-717–719.
13. M. Ibn-Elhaj, D. Guillon, A. Skoulios, A. M. Giroud-Godquin and P. Maldivi, *Liq. Cryst.*, **11**, 731 (1992).
14. P. Weber, D. Guillon, A. Skoulios and R. D. Miller, *Liq. Cryst.*, **8**, 825 (1990).

15. A. I. Kitaigorodskii, *Organic Chemical Crystallography*, Consultants Bureau Enterprises, N.Y. 1961.
16. M. C. Etter, *Acc. Chem. Res.*, **23**, 120 (1990).
17. J. Bernstein, M. C. Etter and J. C. MacDonald, *J. Chem. Soc. Perkin Trans.*, **2**, 695 (1990).
18. A. Skoulios and V. Luzzati, *Acta Cryst.*, **14**, 278 (1961).
19. H. Kelker and R. Hatz, in *Handbook of Liquid Crystals*, Verlag Chemie, Weinheim and Basel (1980), p. 66.