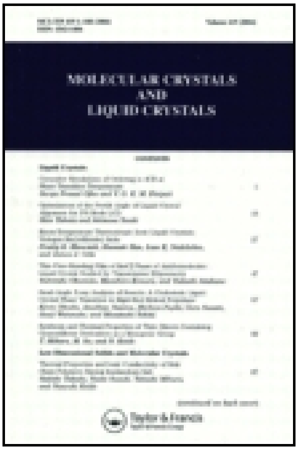

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# Disc-like Mesogens: Synthesis and Characterization of a Series of Rufigallol-hexa-n-alkanoates

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# Disc-like Mesogens: Synthesis and Characterization of a Series of Rufigallol-hexa-*n*-alkanoates†

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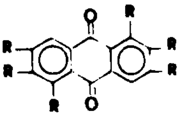
Aliphatic esters of rufigallol with formula



$R = -O\text{-}CO\text{-}C_mH_{2m+1}$

$3 \leq m \leq 13$

have been prepared and their phase transitions studied by differential scanning calorimetry, x-ray diffraction, and optical methods.

Compounds with $6 < m < 13$ give enantiotropic columnar mesophases; those with $7 < m < 9$ give also a monotropic mesophase. Both melting temperature and entropy are sensitive to the parity of the number of atoms contained in the flexible part of the molecules. No similar effect is present at the isotropization transition.

Calorimetric data relative to the phase transitions, x-ray and optical patterns of the liquid crystalline phases are shown.

## INTRODUCTION

Since the discovery of the first disc-like mesogens, several studies have been performed on the characterization of the discotic phase.[1,2]

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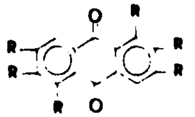
†Presented at the Tenth International Liquid Crystal Conference, York, July 15–21, 1984.

It is well known that for linear mesogenic compounds, both the nature of the mesophase and its range of thermal stability are affected by the stereochemical nature and by the length of the flexible groups present in the molecule. This aspect has not yet been well analyzed for compounds showing discotic mesophases.

The aim of our work is to find correlations between the length of the lateral flexible groups and the existence of discotic mesophases relative to rufigallol as the rigid core.

We wish to report in this paper complete results of the calorimetric and x-ray investigation of esters of general formula:



$R - -O{-}CO{-}C_mH_{2m-1}$

$3 \leq m \leq 13$

## EXPERIMENTAL

Rufigallol has been prepared from gallic acid according to the synthesis previously described.[3]

Esters were prepared according to the following general method. (Compounds will be denoted by the short notation RHC*n*, where *n* is the total number of carbon atoms in a single aliphatic group).

In a typical preparation 3 mmol of rufigallol were dissolved in 100 ml of dry acetone with 20 mmol of dry pyridine. The solution was warmed at $T = 40°C$ and 20 mmol of acyl chloride were added dropwise with stirring. After 60 min the mixture was poured into water. After further washings with water, the residue was dried and recrystallized from an ethanol/chloroform solution. The relative amount of chloroform was increased with increasing molecular weight of the product. Further purification was obtained by column chromatography (silica gel + chloroform as eluent). The purity of all the compounds was checked by IR and NMR spectroscopy. For RHC4 and RHC8, the identity was also checked by molecular weight determination, by means of a Knauer vapour pressure osmometer. The calorimetric behavior of all the esters prepared has been investigated in the range 273/573 K using a Mettler TA 3000 calorimeter, at the scanning rate of 10 K $min^{-1}$ under a $N_2$ atmosphere. The phase transition enthalpies were obtained using as a reference standard a weighed indium sample (Fluka 99.999%, $\Delta H = 28.5$ J $g^{-1}$). The x-ray diffraction patterns of the liquid crystal phases were recorded utilizing a flat-film camera. Cu$K\alpha$ radiation was used. A Leitz polarizing microscope associated with a Mettler FP5 micro-furnace was utilized for the optical analysis of the phase transitions.

## RESULTS AND DISCUSSION

All the aliphatic esters of rufigallol melt in the range 360–490 K. While RHC4, RHC5, and RHC6 do not show liquid crystalline behavior, all the other members of the series exhibit an enantiotropic mesophase. Moreover, RHC7 and RHC9 also exhibit monotropic mesomorphism, at $T = 381$ K and $T = 356$ K respectively, similarly to that described for rufigallol-hexa-*n*-octanoate,[4] with an enthalpy of the order of 20% with respect to isotropization. Figure 1 shows the portion of interest of a typical heating thermogram. The thermal behavior of all the compounds is always reproducible, both in temperature and enthalpy, after various DSC heating scans. Table I reports the thermal data for the compounds investigated. In Figure 2, the melting and isotropization temperatures are reported as a function of $n$. The range of stability is maximum for $9 \leqslant n \leqslant 12$.

It is well known that some structural and thermodynamic properties are sensitive to whether an even or an odd number of atoms is contained in the flexible part of the molecular skeleton. In the most simple cases of crystal to isotropic liquid phase transitions, the alternation of the melting temperature appears to be related to an alterna-

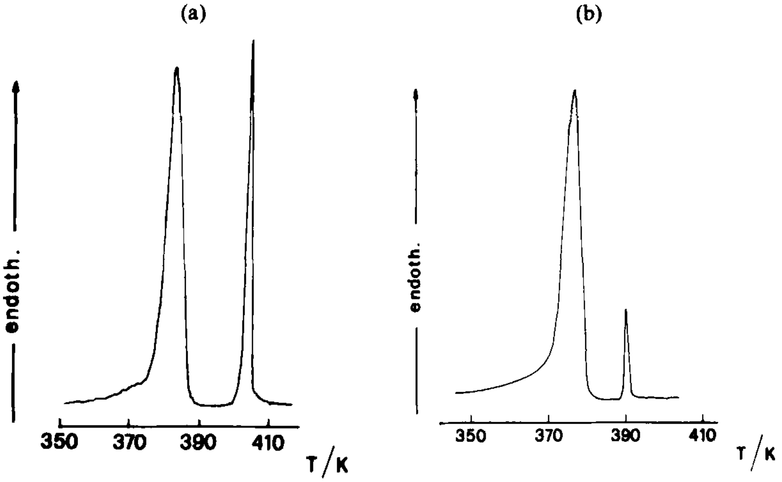


FIGURE 1 (*a*) DSC thermogram of RHC8. (*b*) DSC thermogram of RHC14.

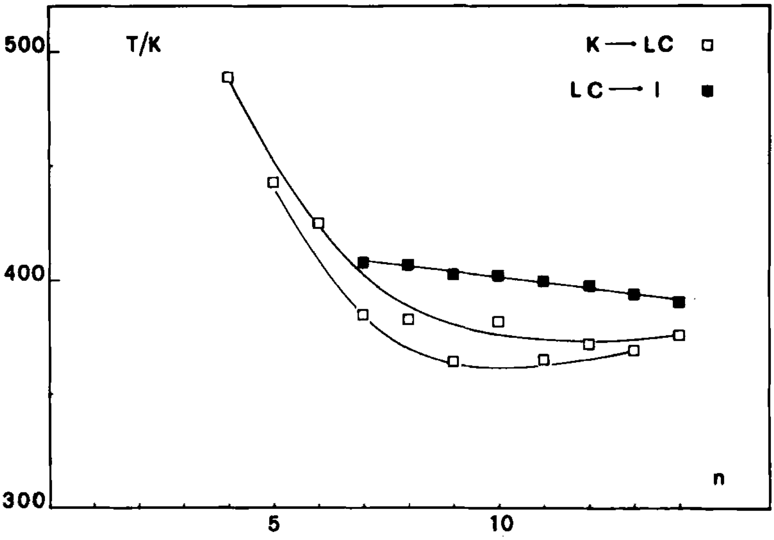


FIGURE 2 Melting and isotropization temperatures.

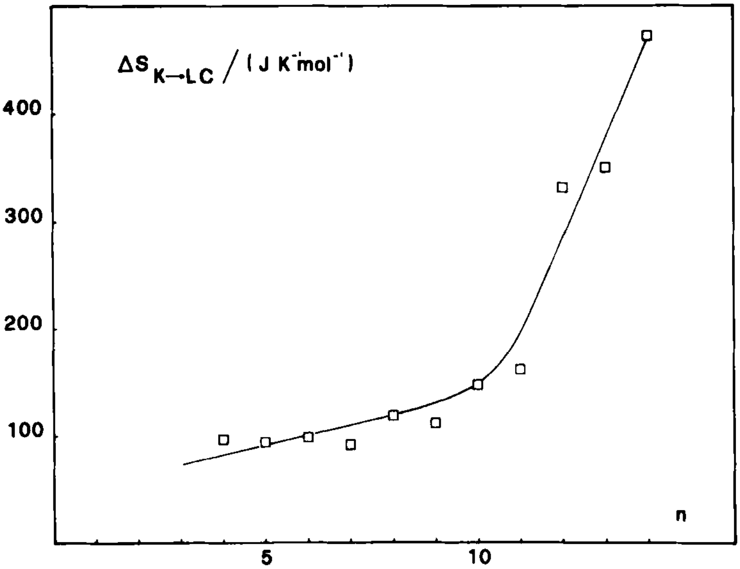


FIGURE 3 Molar melting entropies.

TABLE I

Thermodynamic data for the series of esters of rufigallol. Symbols and units: $n$ = number of carbon atoms in a single aliphatic chain; K–LC = melting transition to an anisotropic liquid; LC–I = isotropization transition. Transition temperatures are given in Kelvin scale $\sigma(T)/T = 0.001$. Molar transition enthalpies ($\Delta H$) are expressed in kJ mol$^{-1}$, $0.05 > \sigma(\Delta H)/\Delta H > 0.01$

| | | | K–LC | | | LC–I | | |
|---|---|---|---|---|---|---|---|---|
| Compound | $n$ | $T$ | $\Delta H$ | $\Delta S$ | $T$ | $\Delta H$ | $\Delta S$ | $\Delta S_{K-LC} + \Delta S_{LC-I}$ |
| RHC4 | 4 | 488.7 | 47.5 | 97.2 | | | | 97.2 |
| RHC5 | 5 | 442.7 | 42.1 | 95.1 | | | | 95.1 |
| RHC6 | 6 | 425.4 | 42.2 | 99.2 | | | | 99.2 |
| RHC7 | 7 | 385.0 | 35.3 | 91.7 | 406.9 | 16.8 | 41.3 | 133.0 |
| RHC8 | 8 | 383.3 | 45.8 | 119.5 | 405.8 | 15.1 | 37.2 | 156.7 |
| RHC9 | 9 | 363.7 | 40.4 | 111.1 | 401.3 | 11.9 | 29.3 | 140.4 |
| RHC10 | 10 | 382.0 | 56.4 | 147.6 | 401.2 | 12.2 | 30.4 | 178.0 |
| RHC11 | 11 | 364.8 | 59.1 | 162.0 | 398.8 | 11.3 | 28.3 | 190.3 |
| RHC12 | 12 | 371.7 | 123.5 | 332.0 | 396.7 | 10.8 | 27.2 | 359.2 |
| RHC13 | 13 | 368.6 | 129.2 | 350.0 | 393.3 | 10.1 | 25.7 | 375.7 |
| RHC14 | 14 | 375.7 | 175.3 | 467.0 | 390.3 | 8.6 | 22.0 | 489.0 |

tion of the crystal structure. In our case a significant odd-even fluctuation affects both melting temperatures and molar melting entropies, while no such effect is detectable for isotropization temperatures and isotropization entropies. The molar melting entropy (Fig. 3) shows a quasi-linear increase with $n$ with an incremental factor of 1.7 J K$^{-1}$mol$^{-1}n^{-1}$ from $4 \leqslant n \leqslant 11$. A sharp increase is observed for $n = 12, 13, 14$.

The x-ray diffraction data for the crystal phases afford some hint of an explanation of this feature. Compounds RHC4, RHC6, RHC8 and RHC10 show homologous diffraction patterns which are however different from those exhibited by RHC12 and RHC14 which, in turn, are homologous to one another. The same is true of compounds RHC5, RHC7, RHC9 and RHC11 on the one hand and RHC13 on the other. The x-ray analyses performed on the mesophase do not indicate any discontinuity for the liquid structure as a function of $n$. X-ray diffraction photographs of the enantiotropic mesophase of two representative compounds (RHC8 and RHC9) are shown in Figure 4. The outermost ring, which corresponds to $2\theta \cong 19.7°$, is quite faint and diffuse and is characteristic of liquid-like disorder. On the other hand, a sharp inner ring is clearly evident and corresponds to a Bragg spacing of 16.6 and 17.2A for RHC8 and RHC9 respectively. If the hypothesis is held that in the mesophase the molecules are arranged one on the top of the other in columns ordered in a nearly hexagonal array, this spacing can be assumed to be a function of the disc

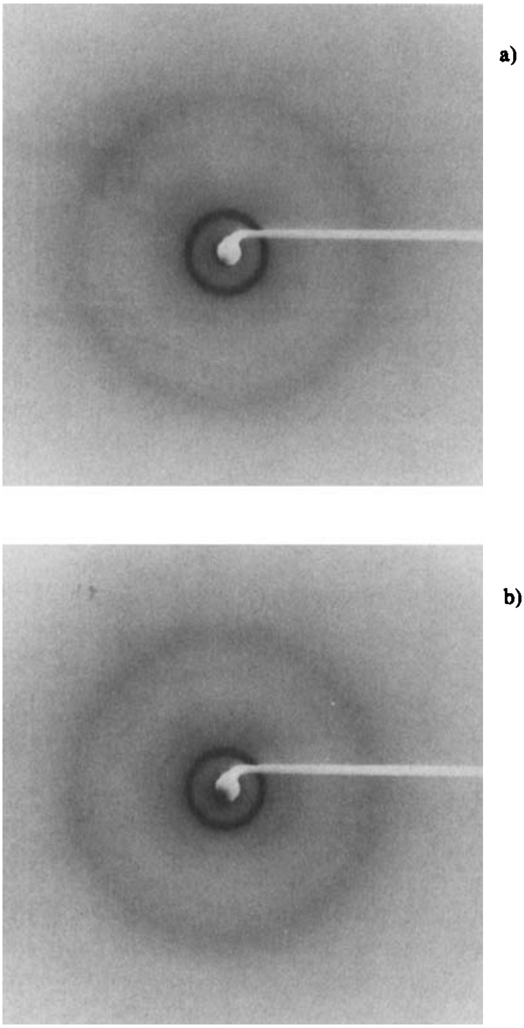


FIGURE 4 (*a*) X-ray diffraction pattern of the discotic phase of RHC8: $T = 393$ K. (*b*) X-ray diffraction pattern of the discotic phase of RHC9: $T = 393$ K.

diameter: $r = d_{100}/\cos 30°$. Figure 5 gives the $r^2$ values *vs* the length of the lateral chains. A fairly linear dependence of the disc area upon $n$ can be observed. The substantial constancy of the position of the maximum relative to the diffuse outer ring indicates that the packing of the molecules along a column is practically independent of the alkyl chain length. However no sharp ring is visible in the zone of the

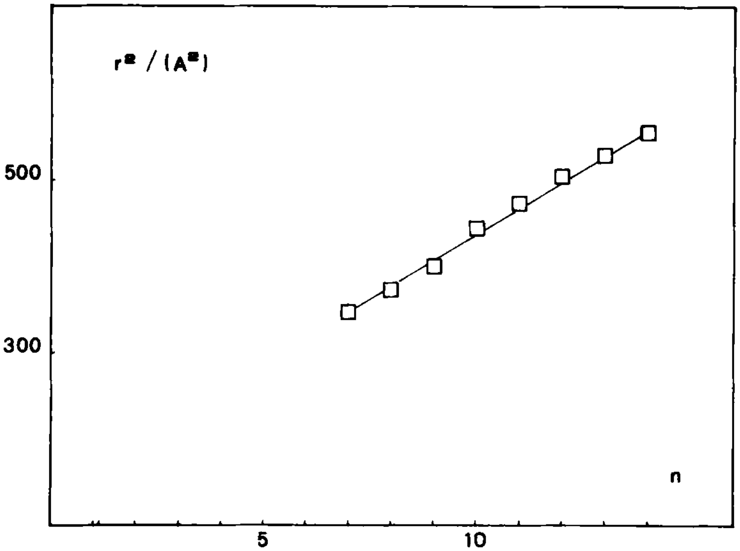


FIGURE 5 Disc area ($r^2$) *vs.* the number of carbon atoms (*n*) in a single aliphatic group.

diffuse halo, indicating that the discs are irregularly spaced. The x-ray analysis extended also to the monotropic mesophases and revealed no significant difference from the enantiotropic mesophases.

The transition temperatures have been clearly observed by means of the polarizing microscope when the sample was cooled from the optically isotropic phase. Typical textures are illustrated in Figure 6. The mesophase appeared as flower-like particles (Fig. 6*a*) which on further cooling grew and filled the entire field of view (Fig. 6*b*).

No significant odd-even effect was detected for the isotropization entropies. This leads us to two extreme hypotheses:

a. the flexible chains are largely disordered in the discotic phase and therefore no further entropic contribution is to be expected at the isotropization transition. This implies that the degree of freedom of the flexible part of the molecules in the mesophase is practically the same as that in an isotropic liquid, and that the residual anisotropy peculiar to the liquid crystalline phase does not involve the flexible molecular segments.

b. the isotropization transition cancels out any long range correlation in the molecular packing, but local anisotropy is largely preserved even in the isotropic liquid.

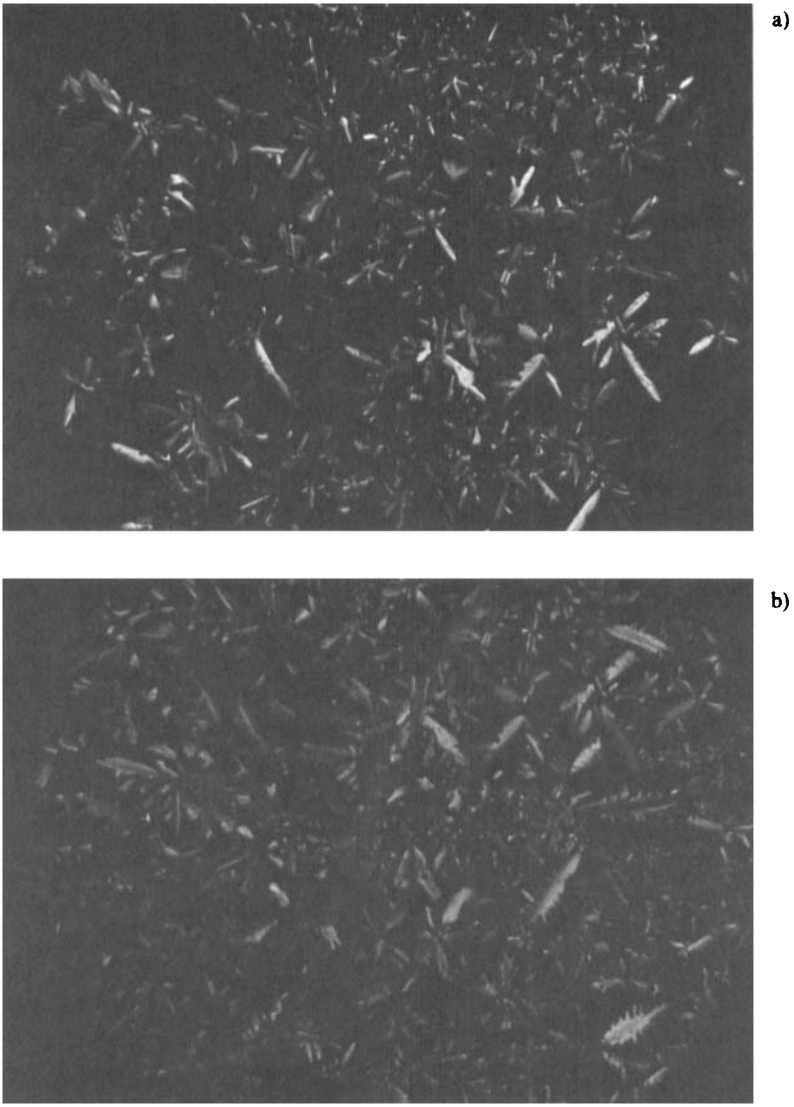


FIGURE 6 Discotic phase of RHC8. $T = 393$ K (*a*); $T = 383$ K (*b*); on cooling. Crossed polarizers.

Hypothesis b might be supported by the observation that the sharp diffraction ring which characterizes the molecular packing in the discotic phase is preserved in the isotropic state, although considerably broadened, even at temperatures well above the isotropization

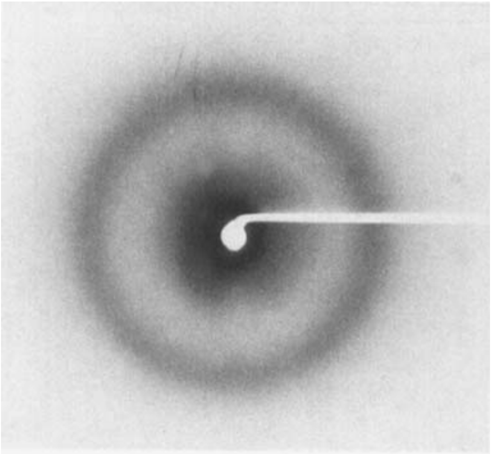


FIGURE 7 X-ray diffraction pattern of the optically isotropic phase of RHC14; $T = 420$ K.

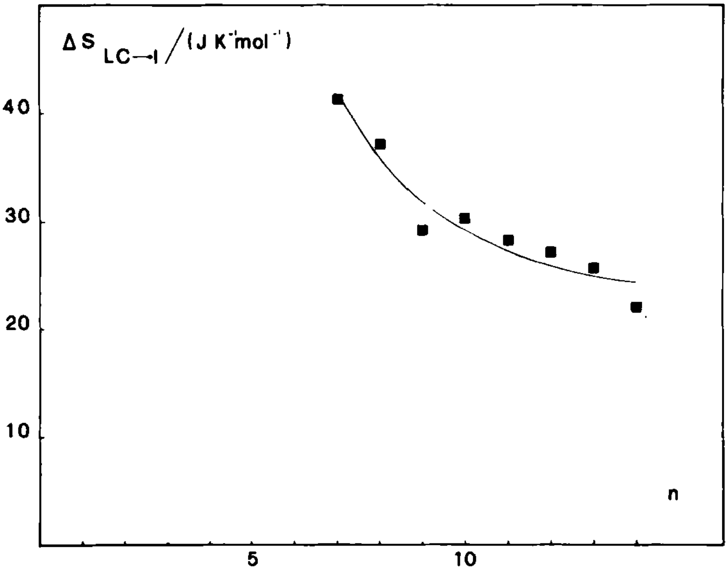


FIGURE 8 Molar isotropization enthalpies.

temperature. Figure 7 shows the diffraction photograph for RHC14 taken 30°C above the isotropization temperature.

In Figures 8 and 9, the isotropization enthalpies and entropies are reported respectively. These values decrease with increasing molecular

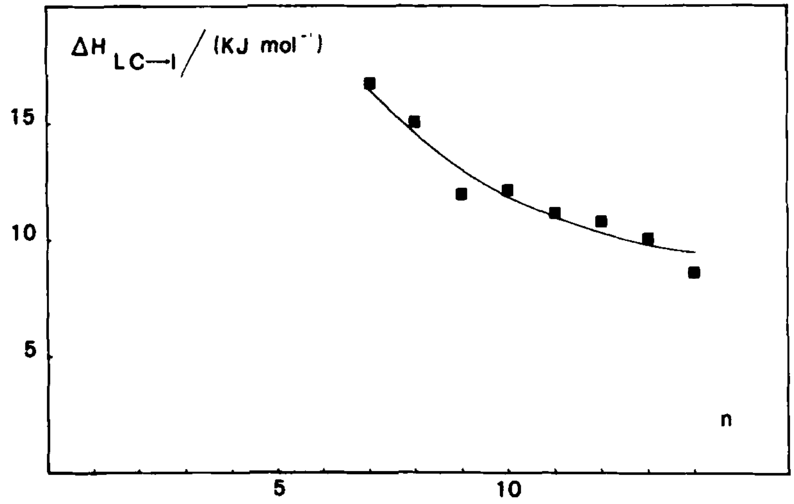


FIGURE 9 Molar isotropization entropies.

weight of the title compounds. A similar effect has been observed in other studies for the series of benzene-hexa-*n*-alkaonates.[5]

This is not surprising, following the hypothesis that the major part of the conformational freedom of the chains is gained upon melting (hypothesis a), if one considers that with increasing molecular weight, the volume fraction of the *disordered* flexible part increases. The isotropization transition would, therefore, imply a loosening of the correlation in the packing of the rigid cores only. This is still compatible with the permanence of a "discotic halo" in the diffraction pattern of the optically isotropic phase.

## References

1. A. M. Levelut, *J. Phys.* (*Paris*) *Lett.*, **40**, L-81 (1979).
2. S. Chandrasekhar, B. K. Sadashiva, K. A. Suresh, N. V. Madhusudana, S. Kumar, R. Shashidar, and G. Venkatesh, *J. Phys.* (*Paris*), **40**, 120 (1979).
3. J. Grimshaw and R. D. Haworth, *J. Chem. Soc.*, **56**, 4225 (1956).
4. J. Billard, J. C. Dubois, C. Vaucher, and A. M. Levelut, *Mol. Cryst. Liq. Cryst.*, **66**, 115 (1981).
5. S. Chandrasekhar, B. K. Sadashiva, and K. A. Suresh, *Pramana*, **9**, 471 (1977).