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Odd liquid crystalline dimers can be linear

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Odd liquid crystalline dimers can be linear

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The crystal and molecular structures of two liquid crystalline symmetric dimers containing the mesogenic group α,α'-dimethylbenzalazine and flexible polymethylenic spacers of different parity (even and odd) are reported. They show nematic phases with strong odd–even effects. The unusual result we have found is that the odd dimer crystallizes adopting a molecular conformation in which the two mesogenic groups are aligned with respect to each other, as for the even dimer. The crystal packing of the two dimers is also analogous.

1. Introduction

Mesogenic dimers (liquid crystalline twins) have received scientific interest since the discovery of thermotropic semiflexible liquid crystalline polymers [1]. In fact, they contain the basic structural unit of polymers (a flexible spacer linking two mesogenic groups) and so they can reproduce features of the mesogenic behaviour of polymers [2, 3]; among those, odd–even effects are particularly noteworthy [4]. According to these effects, some properties related to the degree of order of the nematic phase (the molar entropy of isotropization, as an example) have a discontinuous and oscillatory behaviour depending on the flexible spacer (a polymethylenic chain in the most simple case) having an even or odd number of carbon atoms.

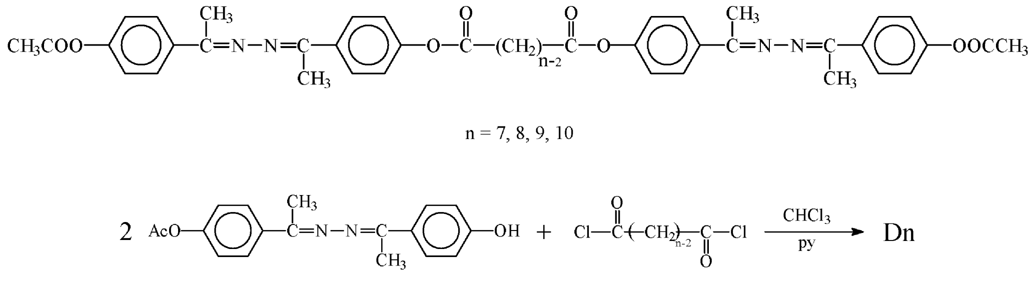
The study of the crystal structures of dimers is intriguing [5]. In fact, dimers have high conformational flexibility in the central part of the molecule and contain terminal groups with high spatial anisometry (the mesogens); furthermore, the chemical nature of the molecular fragments is in general different (aliphatic for the spacer, aromatic for the mesogens). In the packing of these compounds, the lateral interactions between mesogenic cores of different molecules can be relevant in many cases; these interactions, from the crystallographic point of view, depend on the relative orientation of the two mesogens in the single (crystallographically independent) molecule; and that orientation, in turn, is directly influenced by the conformation of the spacer.

In the present paper we report the synthesis and characterization of some dimers D*n* whose formulae are reported in scheme 1, and the X-ray structures of the dimers with $n=8$ and 9. These are the first reports of X-ray structures of full ester-type mesogenic dimers.

2. Experimental

2.1. *Synthesis*

Dimers were prepared according to scheme 1, as described in [2*b*, *c*]. They were precipitated from the



Scheme 1

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reaction mixture by addition of ethanol and recovered by filtration. Purification was obtained by column chromatography (silica gel, chloroform as eluant). Final recrystallization from chloroform/ethanol gave yellow crystalline products. The identity and purity of compounds was confirmed by ^{1}H NMR analysis. Dichlorides of dicarboxylic acids were obtained by standard procedures (i. e. by reaction of the diacid with excess thionyl chloride and final distillation of the dichloride under vacuum). The acetylated monoester (T_{CrN}=160°C, T_{NI}=168°C) was obtained by reaction of the corresponding diphenol with acetic anhydride following a procedure already described [2*c*, *d*]. Analytical data of the acetylated monoester (AM) and of D8 and D9 are reported as examples.

AM: ^{1}H NMR (CDCl$_3$) δ: 2.27(s, 3H), 2.30 (s, 3H), 2.32 (s,3H), 5.81 (s, 1H), 6.80 (d, 2H), 7.14 (d, 2H), 7.77 (d, 2H), 7.92 (d, 2H).

1,8-Octanedioic acid, bis{4-[1-[[1-[4-(acetyloxy)phenyl]ethylidine]hydrazono]ethyl]phenyl}ester (D8): ^{1}H NMR (CDCl$_3$) δ: 1.40 (q, 4H), 1.70 (q, 4H), 2.19 (s, 6H), 2.20 (s, 6H), 2.21 (s, 6H), 7.03 (d, 8H), 7.82 (m, 8H). MS (*m*/*z*) 758.71 (100%) (*M* calc. for C_{44} H_{46} N_4 O_8 758.85).

1,9-Nonanedioic acid, bis{4-[1-[[1-[4-(acetyloxy)-phenyl]ethylidine]hydrazono]ethyl]phenyl}ester (D9): MS (*m*/*z*) 772.63 (100%) (*M* calc. for C_{45} H_{48} N_4 O_8 772.87).

The phase behaviour of the dimers was investigated by thermal analysis (Mettler DSC20, scanning rate 10 K min^{-1}, N_2 atmosphere) and optical microscopy (Leitz polarizing microscope equipped with Mettler FP5 hot stage).

2.2. *X-ray analysis*

Crystals were obtained by slow evaporation at room temperature of chloroform/ethanol (D8) or chloroform/*n*-hexane (D9) solutions. Data collections were performed in flowing N_2 at −100°C on a Bruker–Nonius kappaCCD diffractometer (MoK_α radiation, CCD rotation images, thick slices, φ-scans + ω-scans to fill the asymmetric unit); see table 1. Structures were solved by direct method (SIR97 package [6]) and refined by the full matrix least-squares method (SHELXL program of SHELX97 package [7]) on F^2 against all independent measured reflections. H atoms were located in difference Fourier maps and refined by the riding model, with the exception for H atoms of the aliphatic chain of D9 and methyl groups, whose positions were geometrically determinated. Within the polymethylenic spacer of D9 some C–C bond lengths are shorter, and C–C–C bond angles are wider, than standard values, as a consequence of thermal motion effects; in fact, for these atoms, thermal vibrations occur mainly in the direction perpendicular to the bond [8]. All crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC). Deposition numbers are CCDC 278365 for D8 and CCDC 278366 for D9.

Table 1. Crystal and refinement data for D8 and D9.

	D8	D9
Chemical formula	$C_{44}H_{46}N_4O_8$	$C_{45}H_{48}N_4O_8$
Formula weight	758.85	772.87
T(K)	173	173
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	40.83(5)	41.03(4)
b (Å)	8.908(8)	9.03(1)
c (Å)	10.75(1)	10.83(2)
β (°)	91.09(9)	93.5(1)
V (Å^3)	3909(7)	4005(9)
Z, D_x (g/cm^3)	4,1.289	4,1.282
μ (mm^{-1})	0.089	0.088
2θ range	3.01–25.91	3.00–22.92
N-total/R_{int}-total	24400/0.0676	18432/0.0448
data/parameters	7413/589	4894/568
$R1$ on F ($I>3\sigma(I)$)	0.0504	0.0596
w$R2$ (F^2, all data)	0.1837	0.1969

3. Results and discussion

D*n* dimers show thermotropic mesomorphism with odd–even fluctuations in the associated thermodynamic data (table 2, figure 1). The liquid crystal phase was

Table 2. Thermodynamic data for dimers D*n*.[a]

Dimer	T_{CrN}/K	T_{NI}/K	ΔH_{NI}/kJ mol^{-1}
D7	453	494	4.0
D8	457	516	9.2
D9[b]	442	488	4.0
D10	449	498	8.9

[a]Subscript CrN refers to melting, subscript NI to isotropization. [b]D9 has another crystal phase with lower melting temperature (435 K). The crystal phase described here is the high melting phase.

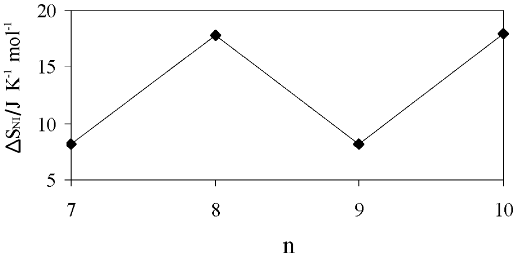

Figure 1. Nematic–isotropic entropies (ΔS_{NI}) of dimers D*n*.

assigned as nematic on the basis of the mobile schlieren texture observed under the polarizing microscope and by the values of ΔH_{NI}. This behaviour is similar to that observed for related classes of compounds [2 *b–d*].

The X-ray molecular structures of D8 and D9 are reported in figure 2, with selected geometric data listed in table 3. It can be noted from table 1 that both dimers crystallize in the same space group with similar values of lattice constants. This is at variance with literature data on crystalline odd–even compounds [9] for which odd dimers generally have a long axis about twice as long as those of even members. The value of the long axis for D8 and D9 is compatible with an extended molecular conformation.

Molecules take an elongated fully extended conformation with *trans*-planar conformation of the polymethylene spacer in D8, while in D9 some deviations from the *trans*-planarity are observed for the bonds adjacent to the carbonyl groups (i.e. C19–C20 and C26–C27, cf. table 3). The most relevant feature is represented by the substantially identical relative arrangement of the mesogenic cores in the two molecular structures and, in particular, by the parallelism of the mesogens.

Actually, by assuming the vectors C3–C16 and C27–C40 as the elongation axes of the mesogenic groups in D8 and C3–C16 and C28–C41, in D9 it is found that the angle τ between the elongation axes of the two mesogens is 0.57° in D8 and 3.4° in D9. This result is surprizing for D9. In fact, for odd nematogenic dimers, both the only X-ray structure reported to date [5 *a*] and the theoretical analyses [10 *a*, *b*] have shown bent molecular shapes. A case of an odd system adopting a linear conformation in the crystal was reported for a smectogenic dimer [5 *b*].

Another relevant feature common to the two molecular structures is the translational pseudo-symmetry between the mesogenic cores. Starting from the first mesogenic group (i. e. atoms from C3 to C18), the second one is obtained by applying the vector $0.5445(7)\mathbf{a} + 0.002(4)\mathbf{b} - 0.984(3)\mathbf{c}$ for D8 and $0.548(2)\mathbf{a} + 0.02(3)\mathbf{b} - 1.07(2)\mathbf{c}$ for D9; the two vectors are, again, almost equal and parallel to the elongation axis of the molecule.

The conformation of the mesogenic group is not planar, because of the torsion angle around the N–N central bond. This torsion is similar in the four

Table 3. Selected bond angles (°) and torsion angles (°) for D8 and D9.

Angle	D8	D9
C16–O4–C19	122.1(2)	122.4(4)
C26–O6–C27	123.3(3)	
C27–O6–C28		123.0(5)
C2–O2–C3–C8	−68.1(4)	67.6(5)
C9–N1–N2–C11	138.0(3)	−138.0(4)
C17–C16–O4–C19	55.6(4)	135.0(4)
O4–C19–C20–C21	−179.8(3)	−166.4(5)
C25–C26–C27–O6		−167.7(7)
C26–O6–C27–C28	53.4(5)	
C27–O6–C28–C29		−95.9(8)
C33–N3–N4–C35	137.5(3)	
C34–N3–N4–C36		−137.7(4)
C41–C40–O8–C43	56.7(4)	
C40–C41–O8–C44		−61.3(5)

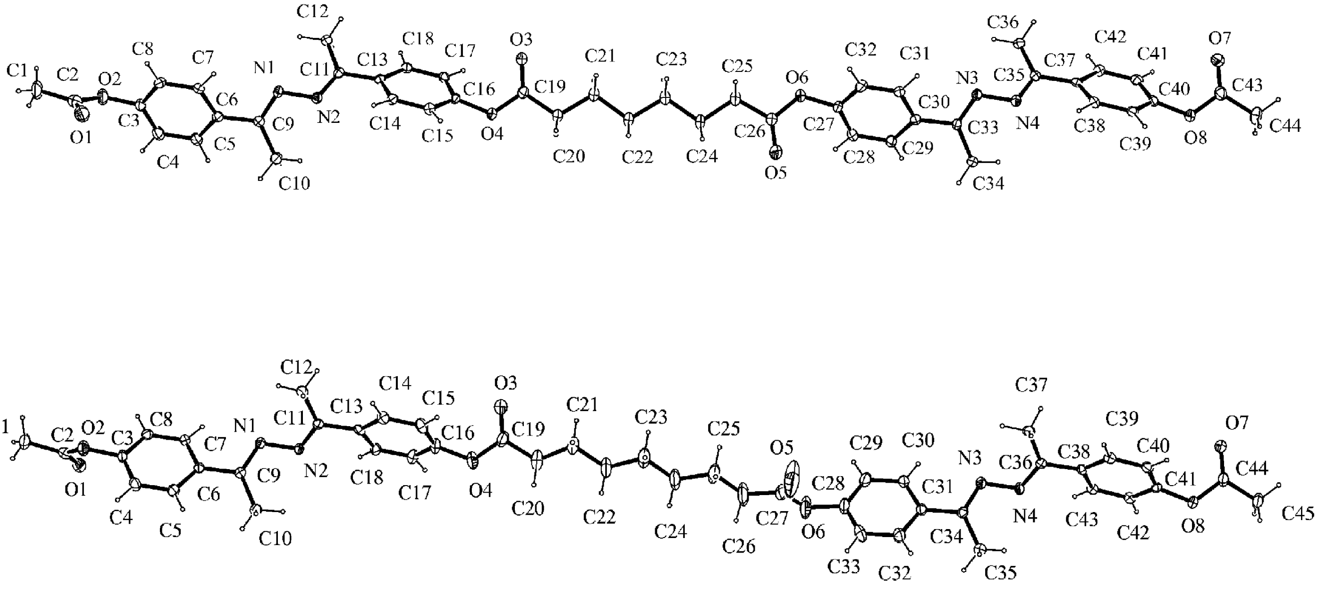

Figure 2. X-ray molecular structures of D8 (upper) and D9 (lower).

mesogenic groups of the two structures (cf. table 2; the dihedral angles between mean plane of the two phenyl rings of the mesogenic groups are 79.6(1)°, 77.5(1)° in D8, and 78.6(2)°, 84.9(2)° for D9). This is consistent with previously reported results in which it was shown that the torsional potential around the N–N bond is low (less than 1 kcal mol^{-1} for torsion angles between 100° and 180°) and that the shallow minimum is actually located at 130°–140° [11, 12]. Moreover, the fact that this conformation is observed with fair regularity in the crystal structures, notwithstanding the low torsional barrier and the shallow minimum, suggests that it is optimum for the packing.

The torsion angles around bonds between alkyloxy O atoms of the spacer and phenyl groups of the mesogenic cores (i.e. O4–C16 and O6–C27 for D8, O4–C16 and O6–C28 for D9) are also relevant conformational parameters of the dimers. The values observed for D8 correspond to the minima of the torsional potential [13]; in D9 the torsion around the bond C28–O6 corresponds, instead, to a secondary maximum [13]. So, for D8 the conformation found in the crystal corresponds to an energy minimum of the isolated molecule, while for D9 this is not the case. Apparently, the conformation of the odd dimer is chosen in order to obtain a more linear shape of the molecule and, hence, a better packing. In fact, with the spacer in the fully *trans*-planar conformation, and with torsion angles around C16–O4 and C28–O6 in the minima of the corresponding torsional potential, τ angles ranging from 9.40° to 74.71° would be observed.

Partial packing diagrams of D8 and D9 are shown in figure 3. A striking feature to be noted is, again, the similarity of the two structures. This is made possible by the analogous arrangement of the mesogenic cores, so that the driving force to the packing of such type of dimeric esters seems to be the optimum interactions between mesogenic cores. In both cases the independent molecule lies in the plane **ac** (along the lattice vector **a**–2**c**, to which the pseudo-translational vector of the molecule, 1/2**a**–**c**, is parallel) and, therefore, the whole packings are made by parallel molecules.

In particular, layers of parallel molecules, in the **b** and **c** directions, are piled up along **a**. The direction of the parallel molecules is tilted with respect to the normal to the layers. The lateral packing of the molecules is dominated by face-to-edge-type contacts among phenyl rings. As is clear from figure 3, these contacts are also present between centrosymmetrically related molecules and this is due to the non-planarity of the mesogen [14]. Molecules are arranged in a head-to-tail fashion forming rows along **a**–2**c**; along the rows, adjacent molecules are related by translations. The lateral packing of the rows, shown in figure 4, is pseudo-hexagonal, with approximate plane reticular constants for D9 X=4.45 Å, Y=5.0 Å, 126°.

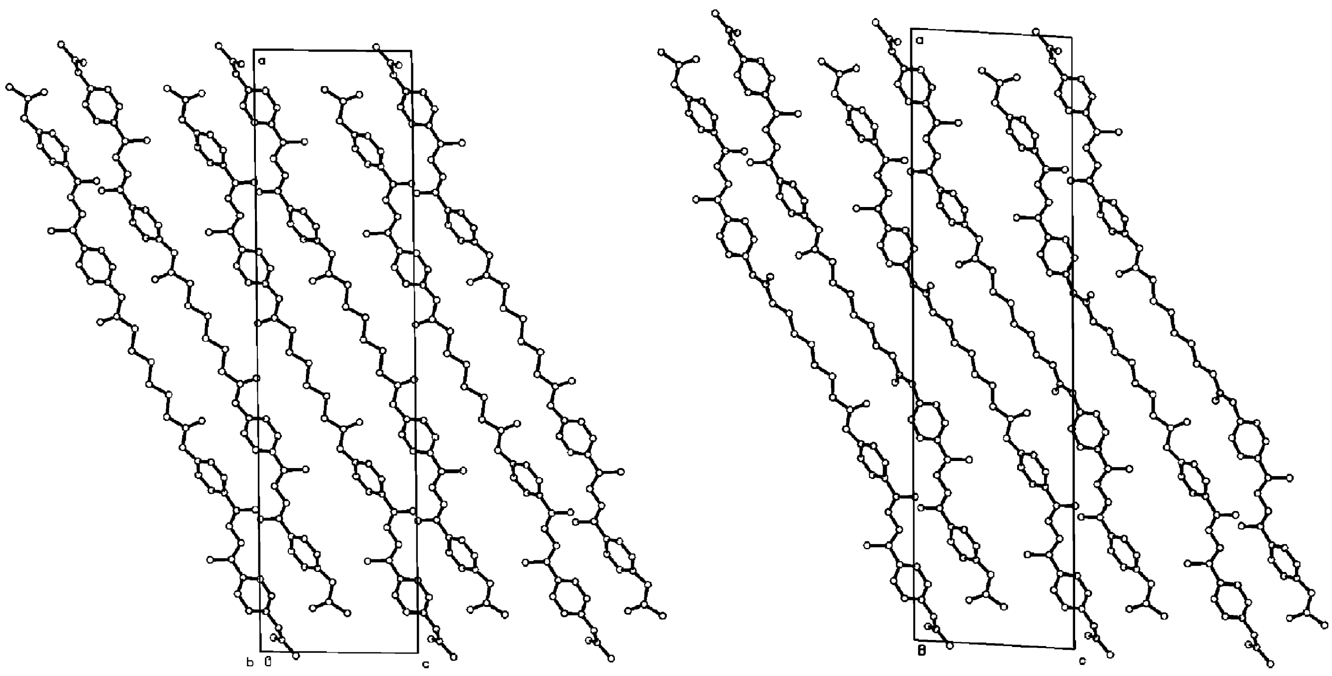

Figure 3. Partial packing diagrams for D8 (left) and D9 (right). The diagrams are built starting only from the independent molecule and its centrosymmetric one. H atoms are not shown.

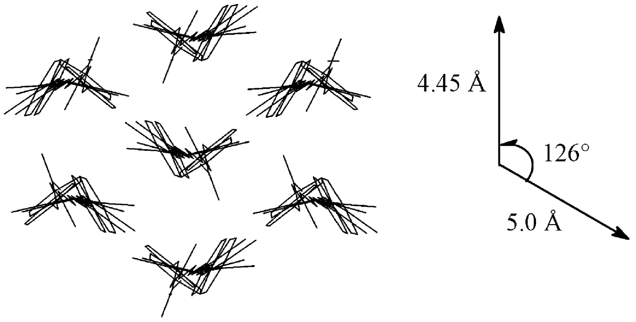

Figure 4. Molecular rows of D9 viewed along **a**–2**c**.

Looking at the packing diagrams shown in figure 3 and considering τ angles of D8 and D9, we find that the order parameter of mesogenic cores in the crystal is 1.0 for both dimers. So we can say that if the chemical potential were the only energy, as it basically is in the crystal, there would be no difference in the orientational order between the two dimers. Upon melting, molecules gain conformational degrees of freedom (and also translational, orientational, etc.) and consequently the phase increases its entropy. Odd–even effects for the nematic–isotropic phase transition have been explained, within mean-field theories, on the basis of the different statistical populations of linear and bent conformers, depending on the parity of the spacers [15].

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References

[1] A. Roviello, A. Sirigu. *J. polym. Sci., polym. Lett. Ed.*, **13**, 455 (1975).

[2] (*a*) A.C. Griffin, T.R. Britt. *J. Am. chem. Soc.*, **103**, 4957 (1981); (*b*) J.W. Emsley, G.R. Luckhurst, G.N. Shilstone and I. Sage. *Mol. Cryst. liq. Cryst. Lett.*, **102**, 223 (1984); (*c*) J.A. Buglione, A. Roviello and A. Sirigu. *Mol. Cryst. liq. Cryst.*, **106**, 169 (1984); (*d*) R. Centore, A. Roviello and A. Sirigu. *Liq. Cryst.*, **3**, 1525 (1988).

[3] C.T. Imrie, G.R. Luckhurst. In *Handbook of Liquid Crystals* Vol. 2B, D. Demus, J.W. Goodby, G.W. Gray, H.W. Spiess, V. Vill (Eds), pp. 801–833, Wiley-VCH, New York (1999).

[4] (*a*) A. Roviello, A. Sirigu. *Makromol. Chem.*, **183**, 895 (1982); (*b*) A. Blumstein. *Polym. J.*, **17**, 277 (1985).

[5] (*a*) L. Malpezzi, S. Brückner, E. Galbiati, G. Zerbi, G.R. Luckhurst. *Mol. Cryst. liq. Cryst.*, **195**, 179 (1991); (*b*) J.M. Seddon and D.J. Williams. *Liq. Cryst.*, **18**, 761 (1995); (*c*) J.S. Prasad, M.A. Sridar and V. Surendranath. *Liq. Cryst.*, **26**, 1707 (1999); (*d*) L. Malpezzi, S. Brückner, D.R. Ferro and G.R. Luckhurst. *Liq. Cryst.*, **28**, 357 (2001).

[6] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna. *J. appl. Cryst.*, **32**, 115 (1999).

[7] G.M. Sheldrick. *SHELX-97* University of Göttingen, Germany (1997).

[8] W.R. Busing, H.A. Levy. *Acta Crystallogr.*, **17**, 142 (1964).

[9] V.R. Thallady, M. Nüsse, R. Boese. *J. Am. chem. Soc.*, **122**, 9227 (2000).

[10] (*a*) A. Abe. *Macromolecules*, **17**, 2280 (1984); (*b*) D.Y. Yoon and S. Brückner. *Macromolecules*, **18**, 651 (1985).

[11] (*a*) R. Centore, M.R. Ciajolo, A. Roviello, A. Sirigu, A. Tuzi. *Mol. Cryst. liq. Cryst.*, **185**, 99 (1990); (*b*) R. Centore, M.R. Ciajolo and A. Tuzi. *Mol. Cryst. liq. Cryst.*, **237**, 185 (1993); (*c*) G.S. Chen, M. Anthamatten, C.L. Barnes and R. Glaser. *Angew. Chem., int. Ed. Engl.*, **33**, 1081 (1994); (*d*) R. Centore, B. Panunzi and A. Tuzi. *Z. Kristallog.*, **211**, 31 (1996).

[12] R. Centore, C. Garzillo. *J. chem. Soc., Perkin Trans. 2*, 79 (1997).

[13] (*a*) J.P. Hummel, P.J. Flory. *Macromolecules*, **13**, 479 (1980); (*b*) P. Coulter and A.H. Windle. *Macromolecules*, **22**, 1129 (1989).

[14] (*a*) R. Centore, A. Tuzi. *Macromolecules*, **31**, 8941 (1998); (*b*) R. Centore and A. Tuzi. *Cryst. Eng.*, **6**, 87 (2003).

[15] (*a*) A. Ferrarini, G.R. Luckhurst, P.L. Nordio, S.J. Roskilly. *Chem. Phys. Lett.*, **214**, 409 (1993); (*b*) A. Ferrarini, G.R. Luckhurst, P.L. Nordio and S.J. Roskilly. *Liq. Cryst.*, **21**, 373 (1996).