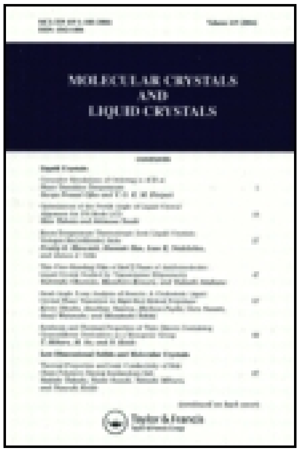

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Mesophasic Properties of Low Molecular Weight Model Compounds Containing Two Rigid Groups Connected by a Flexible Spacer

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Mesophasic Properties of Low Molecular Weight Model Compounds Containing Two Rigid Groups Connected by a Flexible Spacer

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INTRODUCTION

The increasing interest on mesogenic polymers has widened the discussion about basic questions concerning the relationships between stereochemical nature and mesophasic properties of the molecules.

One point concerns the evaluation of the degree of order of the nematic phase exhibited by many rigid or semiflexible linear polymers. A second question, concerning the latter class of polymers, is about the way the flexible spacers, on one side, contribute to the ordering of the nematic phase and, on the other side, are subjected to conformational limitations.

Very few cases are known of experimental evaluation of the order parameter at the isotropization transition on nematic polymers in bulk. One reason for this paucity is that orienting a polymeric nematic phase with a magnetic field has proved to be sometimes a difficult task that requires high fields and long exposure times.[1]

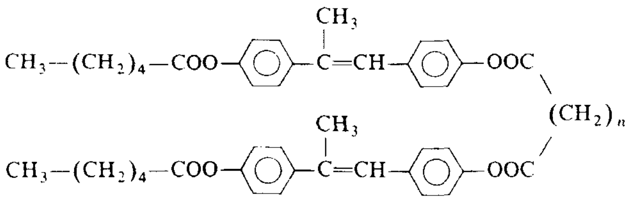
Only very recently order parameters for nematic polyesters of formula $(C_{10}H_{20}\text{—O-}\phi\text{-COO-}\phi\text{-O—}C_{10}H_{20}\text{—O-}\phi\text{-OCO-}\phi\text{-O})_x$ have been evaluated from magnetic susceptibility measurements.[2] They are reported to be in agreement with the theory that calculates, for this class of semiflexible polymers, higher values of the order parameter than for low molecular weight (monomer) molecules, although not as high as expected for rigid rod-like macromolecules.[3]

As an indirect indication of the degree of order of a nematic phase at the isotropization temperature the ratio $\Delta S_i/\Delta S_t$ has been utilized, ΔS_i being the molar isotropization entropy and ΔS_t the total molar entropic change associated to the multistage transformation "most stable solid phase at low temperature" → "isotropic liquid". For a large number of low molecular weight nematics the $\Delta S_i/\Delta S_t$ ratio, which can be evaluated in a straightforward way from scanning calorimetry measurements, ranges between ~ 0.02 and ~ 0.05.

The evaluation of $\Delta S_i/\Delta S_t$ for nematic polymers causes some difficulty. The molar isotropization entropy, ΔS_i, has been measured without problems for several nematic semiflexible polymers[4-7] and the corresponding values are usually significantly higher than those measured for low molecular weight molecules whose stereochemical nature is coincident or very similar to that of the monomeric unit of the polymer. This is particularly true for polymers whose monomeric unit contains an even number of atoms in the backbone chain of the flexible part.

The value of ΔS_t for polymeric samples cannot be obtained from a single calorimetric measurement unless the crystallinity of the sample is known. We have recently evaluated the molar melting enthalpy of some semiflexible nematic polyesters by the diluent method. The ratios $\Delta S_i/\Delta S_t$ could be calculated.[8] They range between ~ 0.07 and ~ 0.17, the higher values being obtained with polymers having an even number of atoms in the backbone chain of the flexible part of the monomeric unit. Similar results have been reported by Griffin and Havens[5] for other semiflexible polymers.

These results favour the assumption that even in the presence of flexible spacers of considerable length and conformational mobility the coupling between successive monomeric units is effective in producing some stiffening of the polymer chain that pushes the degree of order of the nematic phase to values higher than those usually observed for an assembly of independent low molecular weight monomeric units. To find a simple check for this idea we have examined the liquid crystal behavior of low molecular weight compounds of formula:



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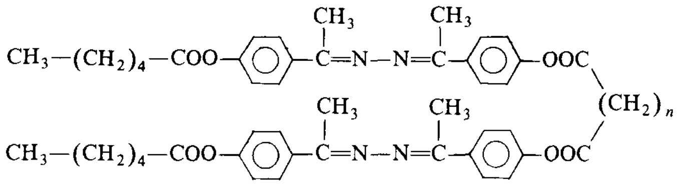


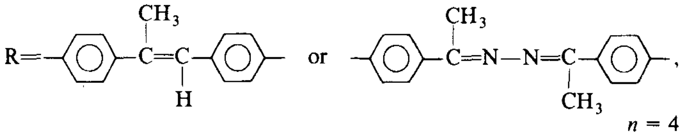
These are the simplest molecules that contain the structural element peculiar to the related polymers namely a flexible spacer bound at both ends to a mesogenic rod-like molecular group. For the sake of brevity these molecules will sometimes be called "dimers".

EXPERIMENTAL

Two sets of compounds have been synthesized corresponding to the following general formula:

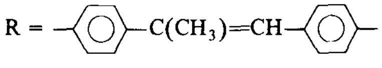
$$CH_3(CH_2)_4COOR—OOC(CH_2)_{n-2}—COO—R—OOC(CH_2)_4—CH_3$$

where

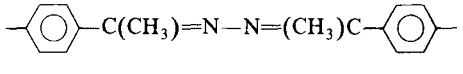


$n = 4 \rightarrow 16.$

For the sake of conciseness compounds with



will be indicated by the symbol An while those containing the group



will be indicated by the symbol Bn.

Compounds An may exist in three isomeric forms corresponding to three different ways in which two methylstilbene groups may follow each other. Nothing has been purposively done to resolve this structural ambiguity which, by the way, is present also in the polyesters containing the same rigid group. Compounds An should therefore be considered as mixtures of three isomers.

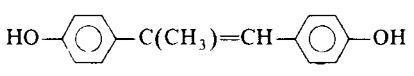
Synthesis of compounds An

The procedure followed for the synthesis of this class of compounds will be illustrated by the detailed description of the preparation of A10. Compounds with formula

$$CH_3(CH_2)_4\text{—}COCl, \qquad (I)$$

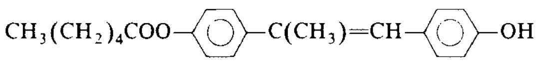
$$ClOC(CH_2)_8COCl \qquad (II)$$

and



(III)

were preliminarily synthetized following standard procedures.[9] Compound



(IV)

was prepared as follows. 30.0 g of (III) were dissolved in a mixture of 140 cc anhydrous dioxane and 25 cc anhydrous pyridine. 17.8 g of (I), dissolved in 50 cc dioxane were slowly (1 hour) added at room temperature. The reaction was allowed to proceed for further 20 minutes. The reacted mixture was then poured in 2500 cc ice water containing 4.64 cc sulfuric acid. The solid precipitate was filtered and treated with boiling $CHCl_3$. The suspension was filtered with Na_2SO_4 and finally refiltered and cooled at ~ −15°C. Unreacted (III) separates and is eliminated by filtration. *n*-heptane is added to the chloroform solution which is cooled again at ~ −15°C and (IV) is obtained by crystallization. The compound was purified from diester by successive (at least two) crystallizations from *n*-heptane/chloroform (25%) solutions and its melting behavior monitored by differential scanning calorimetry. The proton NMR spectrum (Figure 1) is in accordance with the formula.

(IV) is a mesogenic compound that melts at 362.3 K and becomes isotropic at 368.0 K. The nature of the mesophase was not investigated

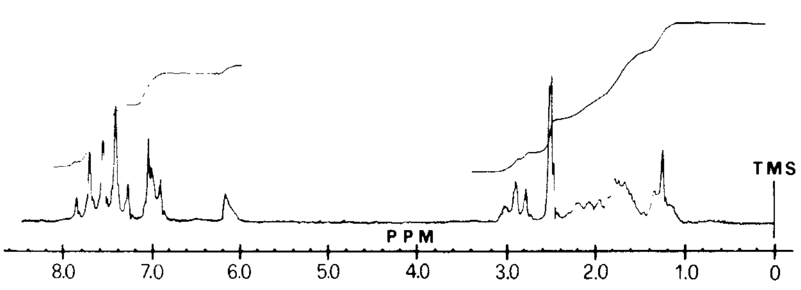


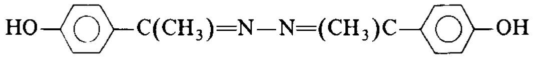
FIGURE 1 Proton NMR spectrum of $CH_3(CH_2)_4COO\text{-}\phi\text{-}C(CH_3){=}CH\text{-}\phi\text{-}OH$.

but the value of the molar isotropization enthalpy (1.0 kJmol^{-1}) is probably indicative of a nematic phase.

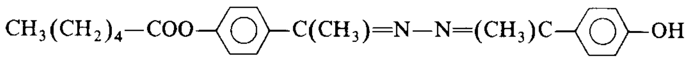
For the preparation of A10, 0.5076 g of (IV) were dissolved in a mixture of 6 cc chloroform and 0.3 cc pyridine. To this solution, 0.1870 g of (II) (10% less that the stoichiometric amount) were added at room temperature in ~ 30 minutes. The reacted mixture was then poured to 300 cc ice water containing 0.18 cc sulfuric acid. The chloroform phase was separated, dried with sodium sulphate and filtered. A10 was crystallized from a chloroform (15%)–ethanol solution. Further purification was obtained by column chromatography (silica gel + chloroform as eluent). The proton NMR spectrum is consistent with the formula.

Synthesis of compounds Bn

For the preparation of compounds Bn a synthetic route analogous to that described above was followed. The compound with formula



was prepared according to a well established procedure.[10] The intermediate compound



was purified by crystallization from chloroform (25%)–*n*-heptane solutions. Its proton NMR spectrum is consistent (Figure 2) with the formula. It melts to an isotropic liquid at 394.5 K. The purification of compounds Bn was obtained via crystallization from chloroform (15%)–ethanol solutions and successive column chromatography on silica gel-chloroform. The proton NMR spectra are consistent with the formula. The mesophasic properties of compounds An and Bn were examined by differential scanning calorimetry (Perkin–Elmer DSC-2), X-ray diffraction (flat-film camera, CuKα and CrKα radiations) and polarizing microscopy (Leitz polarizing microscope + Mettler FP5 microfurnace).

The DSC examination of both classes of compounds confirmed their uniform purity. At 10 K min^{-1} heating rate the melting transition of compounds An takes place within 4 K and the isotropization transition is accomplished within 2 K. The corresponding values for compounds Bn are respectively 3 K and 1.5 K. At the same heating rate the melting of a comparable amount of an indium standard (Fluka 99.999% purity) takes place within 2 K. The systematically

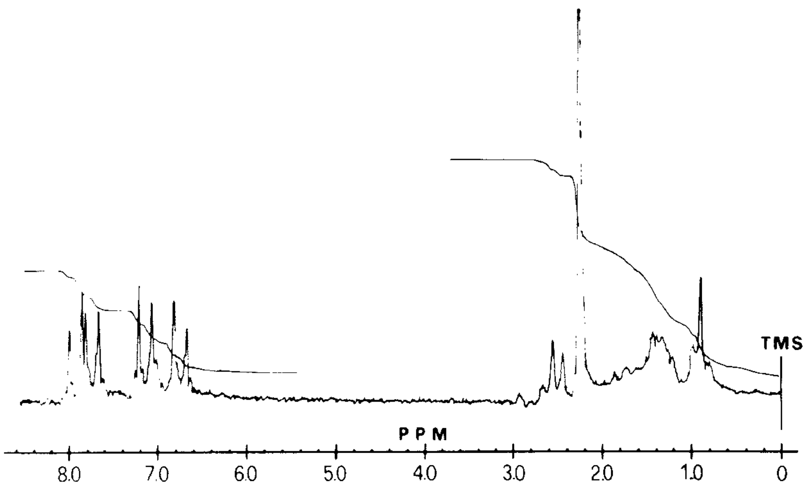


FIGURE 2 Proton NMR spectrum of $CH_3(CH_2)_4COO\text{-}\phi\text{-}C(CH_3){=}N{-}N{=}(CH_3)C\text{-}\phi\text{-}OH$.

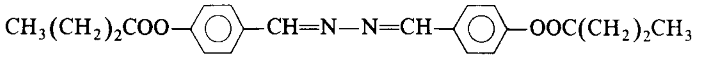
larger melting interval observed for compounds An might be connected to the occurrence of constitutional isomerism, as previously indicated. A further control was performed by extrapolating at zero scanning rate isotropization and anisotropization temperatures. Differences not larger than 0.6 K were obtained.

RESULTS AND DISCUSSION

The first point that deserves discussion is the elucidation of the nature of the liquid crystal phases shown by compounds An and Bn.

They were prepared under the assumption that they might be nematogenic. In this case the comparison with their polymeric homologues would have had a more direct significance. The observation at the polarizing microscope led to the conclusion that, with the exception of A4, A5, A6 and A8 which exhibit two mesophases all the examined compounds show one liquid crystal phase. Schlieren textures were easily observed in all cases (for A4, A5, A6 and A8 schlieren textures were observed with the mesophase stable at higher temperatures). This, however, is not sufficient to qualify the nature of the mesophase. The X-ray diffraction pattern of the mesophase, registered at an appropriate temperature for each compound (the high temperature form was examined for A4, A6 and A8) is compatible with a nematic structure. However, because of instrumental limits, this feature by itself does not rule out the possibility for the mesophase to be smectic with a periodicity larger than ~ 75 Å. A Bragg diffraction line corresponding to a lattice distance of 44.7 ± 1 Å for A4, 47.0 ± 1 Å for A6, and 50.5 ± 1 Å for A8 characterizes the X-ray diffraction pattern of the mesophase stable at lower temperatures. These values have been measured at 458 K (0.97), 423 K (0.93) and 413 K (0.98) respectively for A4, A6 and A8. To make data more easily comparable the measuring temperatures were chosen for nearly equal values of the ratio T/T_t, (given in parentheses) T_t being the liquid–liquid transition temperature.

Assuming average literature values for bond lengths and bond angles, the length of A4, A6 and A8 in their most extended conformation is 44 Å, 46.5 Å and 49 Å respectively. These values, provided the observed diffraction lines are first order ones, are in favour of a smectic structure with the long molecular axes normal to the smectic planes. In fact, the van der Waals separation between contiguous smectic layers that would bring the calculated smectic periodicity beyond the experimental values may well be compensated by the shortening of the molecular axis connected to the conformational disorder that, even in a smectic phase, possibly affects the polymethylenic portions of the molecule. A fan texture was observed for A4, A5, A6 and A8 in the smectic phase (Figure 3). The mesophasic properties of binary mixtures of A6 with the nematogenic compound with formula[11]



(4,4′-dibutanoyloxybenzalazine) (Figure 4) leads to the conclusion that the high temperature mesophasic form is nematic (only a partial miscibility of the smectic phase of A6 with test compound is observed). On the other hand, the smectic–nematic transition is characterized by a very small, hardly measurable molar enthalpic change. This might qualify the smectic phase as of A type. This is the most disordered of all smectic phases and $S_A \rightarrow N$ phase transitions involving very small thermal effects have been already reported. For example,[12] 4,4′ di-*n*-hexylazoxybenzene exhibits a monotropic $S_A \rightarrow N$ transition with an enthalpic change of 0.02 kJ mol^{-1} while the molar isotropization enthalpy is 0.57 kJ mol^{-1}. On the other hand, the McMillan[13] model for the smectic A phase indicates the possibility for a $S_A \rightarrow N$ phase to be very weakly first order or even second order.

The smectic phase exhibited by A8 transforms into a nematic phase (as we believe it is by analogy with A6) with an even smaller molar

FIGURE 3 Smectic texture shown by A6 at 442 K: crossed polarizers.

enthalpic change. Actually, only with highly purified samples could the phase transition be detected by the DSC method. Among the four compounds exhibiting the suggested smectic phase, A4 shows the highest value of the molar enthalpic change of the smectic–nematic transition.

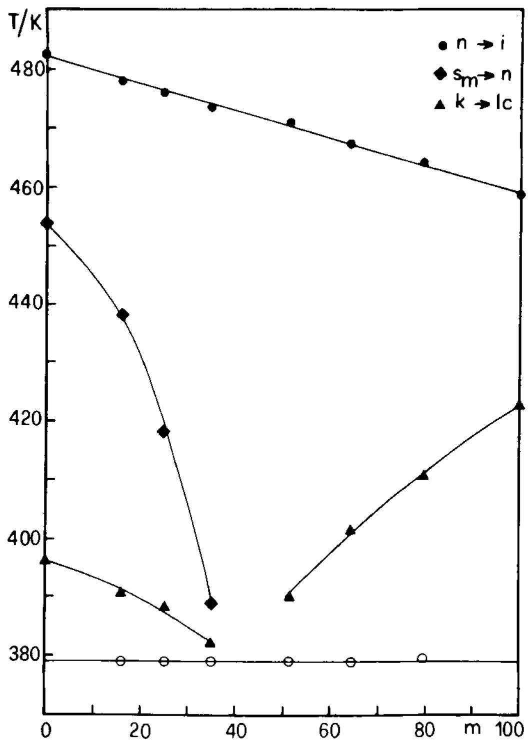
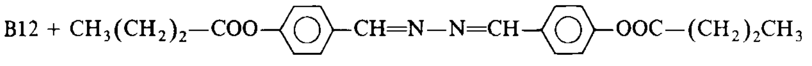


FIGURE 4 Phase diagram of the binary mixture formed by A6 and $CH_3(CH_2)_2COO\text{-}\phi\text{-}CH{=}N{-}N{=}CH\text{-}\phi\text{-}OOC(CH_2)_2CH_3$. $(1 - m/100)$ = mole fraction of A6.

To define the nature of the mesophase exhibited by the series Bn, the phase diagram of the binary system



was examined (Figure 5). The mesophase shown by B12 is nematic.

The regular trend along the series of the thermodynamic quantities of the mesophase, the absence of liquid crystal polymorphism and the lack of any evidence of smectic periodicity in the X-ray diffraction pattern of the shorter member of the series supports the conclusion that the mesophase is nematic for all of them.

To conclude, we think that sufficient evidence has been given supporting the nematogenic character of the examined compounds.

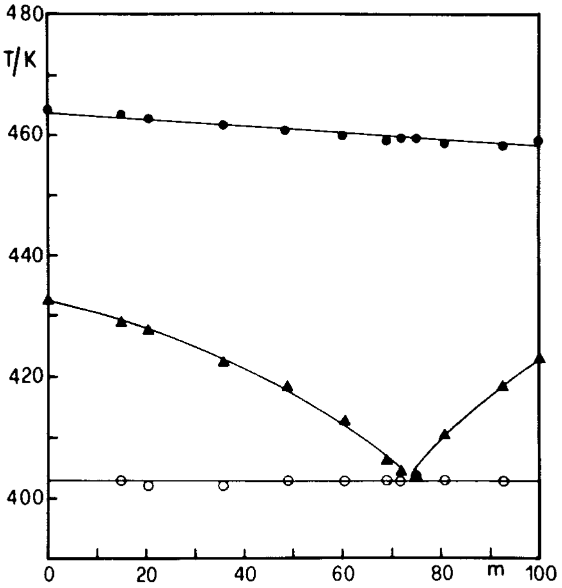
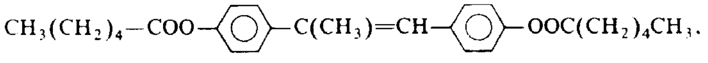


FIGURE 5 Phase diagram of the binary mixture formed by B12 and $CH_3(CH_2)_2COO$-ϕ-$CH{=}N{-}N{=}CH$-ϕ-$OOC(CH_2)_2CH_3$. $(1 - m/100)$ = mole fraction of B12.

The thermodynamic data relative to the phase transitions are reported in Table I (Figure 6) and Table II (Figure 7). On Table I data concerning some homologous polymers are listed for comparison.

Several features have to be pointed out. The first, and most important one, concerns the considerably high isotropization molar enthalpies (the same is true for the entropic changes) measured for the even members of the series (*n* even). This produces a very pronounced odd-even alternation the same way it has been observed for the polymers. The following examples illustrate the point. The molar isotropization enthalpy of A12 is 6.7 kJ mol^{-1}. This compound is the dimeric homologue of



which is a nematogenic compound whose molar isotropization enthalpy is 1.09 kJ mol^{-1}. Such a marked difference between the two compounds points out that a dimeric molecule in a nematic phase is not equivalent to two successive uncoupled monomeric units. This is not so evident when the flexible inner part of the dimeric molecule

TABLE I

Thermodynamic data of the series An

	K-K		K-LC		LC-I				
n	T	ΔH	T	ΔH	T	ΔH	ΔH_T	R_d	R_p
4			409.0	57.6	488.0	6.59	64.2	.103	
5	395.4	26.1	399.0	30.2	433.1	1.95	58.2	.033	
6			393.0	49.9	482.0	6.22	56.1	.111	
7			396.3	60.8	431.0	2.02	62.8	.032	
8			395.8	57.2	460.4	6.77	64.0	.106	
9			388.5	62.0	425.7	2.64	64.6	.041	.08
10			385.0	66.9	442.8	6.86	67.0	.103	
11			384.0	67.0	420.0	2.90	74.8	.043	.10
12	342.5	10.8	387.0	57.3	430.4	6.71	78.8	.090	.19
13	376.7	15.5	387.4	59.8	414.9	3.53	79.0	.045	.09
14	344.0	9.6	388.6	54.9	421.4	6.87	82.4	.087	.15
15	377.6	14.8	389.2	63.6	412.3	4.04	90.5	.049	
16	348.5	11.1	390.0	72.7	413.3	6.73		.074	

1. Symbols and units; n = number of carbon atoms in the flexible spacer; K-K = solid phase transition; K-LC = melting transition to an anisotropic liquid; LC-I = isotropization transition. Transition temperatures T are given in Kelvin scale $\sigma(T)/T \simeq 0.001$. Molar transition enthalpies (ΔH) are expressed in kJ mol^{-1} $0.05 \geq \sigma(\Delta H)/\Delta H \geq 0.01$.

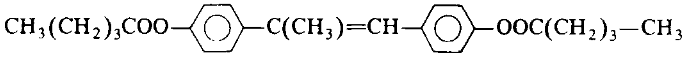
2. A4, A5, A6 and A8 show a smectic-nematic phase transition at 470.5 K; 410.0 K; 456.0 K and 421.5 K respectively with molar transition enthalpy less than 0.5 kJ mol^{-1}.

3. A14 shows an additional solid phase transition at 378.0 K (ΔH = 7.52 kJ mol^{-1}).

4. ΔH_T is the total value of the enthalpic change from the solid phase stable at low temperature to the isotropic liquid.

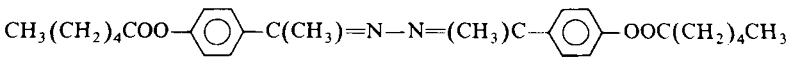
5. R_d and R_p are the ratios ΔH(LC-I)/ΔH_T for dimeric and polymeric homologues respectively.

contains an odd number of carbon atoms (n odd). For example: compound



is nematogenic[14] and the molar isotropization enthalpy is 0.62 kJ mol^{-1}. The dimeric compound that more closely approaches the stoichiometry corresponding to two "monomeric" molecules is A11: its molar isotropization enthalpy is 2.64 kJ mol^{-1}. A similar feature occurs within the series Bn.

The molar isotropization enthalpy of B12 is 8.17 kJ mol^{-1} and the corresponding value for a compound with formula



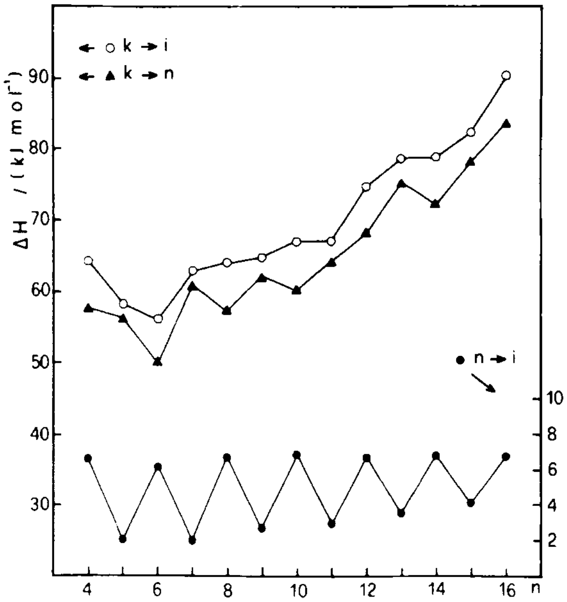


FIGURE 6 Enthalpic changes for the phase transitions shown by the series An.

TABLE II

Thermodynamic data of the series Bn

	K-K		K-LC		LC-I			
n	*T*	Δ*H*	*T*	Δ*H*	*T*	Δ*H*	ΔH_T	R_d
6	449.0	16.0	455.4	45.2	508.9	9.31	70.5	.132
7			437.6	71.8	469.5	3.33	75.1	.044
8			440.7	63.0	491.5	9.04	72.0	.125
9			425.3	69.9	464.6	3.81	73.7	.052
10			432.8	67.9	476.6	8.77	76.7	.114
11			425.4	82.7	458.5	4.59	87.3	.053
12	376.0	3.27	430.0	74.0	464.0	8.17	85.5	.096
13			426.6	90.3	452.0	4.75	95.1	.050
14	390.5	5.55	429.0	78.8	454.9	7.69	92.1	.084
15	393.0	2.04	425.5	88.1	444.9	4.85	95.0	.051
16	397.0	6.31	426.7	82.1	446.5	7.46	95.9	.078

For symbols and units see notes to Table I.

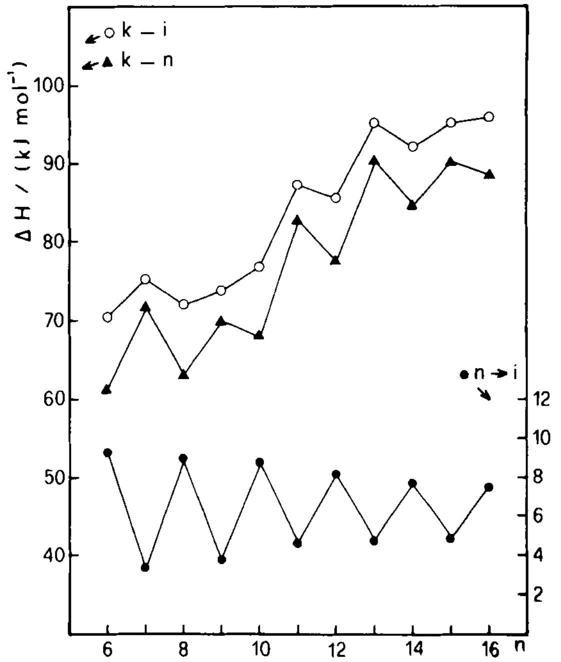
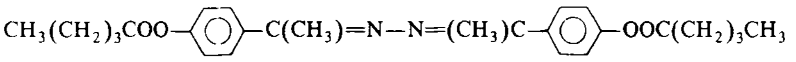


FIGURE 7 Enthalpic changes for the phase transitions shown by the series Bn.

is 1.34 kJ mol^{-1} (Rf. 18). For B11 and for the "monomeric" compound[15] with formula



the measured value are 4.59 kJ mol^{-1} and 0.96 kJ mol^{-1} respectively.

A simple explanation of the large odd-even fluctuations of the thermodynamic quantities involved in the isotropization transition takes into account molecular geometry factors. Figure 8 shows the most extended conformation for one "even" and one "odd" molecule.

It is apparent that the "even" molecule has a more elongated and rectilinear shape than the "odd" one and is capable of packing with identical molecules in a more tightly parallel arrangement with respect to a selected direction. But it is remarkable that in both cases several conformations containing one or more gauche bonds in the inner spacer are possible that do not drastically change, with respect to the extended conformation, the overall molecular shape and elongation (Figure 8). For molecule A4 this conclusion does not hold. The gauche conformations of the inner CH_2—CH_2 bond produce a severe distortion of the molecular shape which is hardly compatible with a nematic packing. It is likely that the trans conformation is highly preferred in

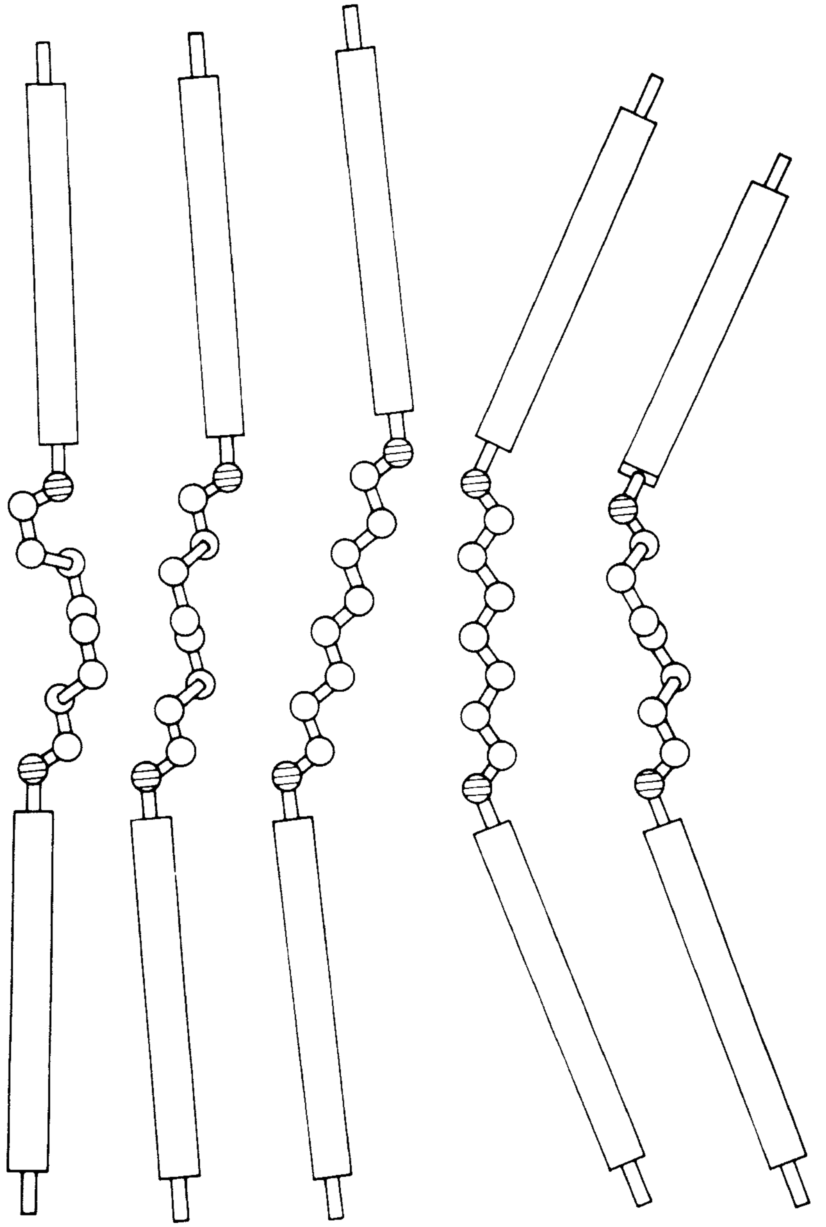


FIGURE 8 Simplified stereochemical models for one "even" (A8, B8) and one "odd" (A7, B7) dimeric molecule. Only the main chain bonds of the spacer are shown. The non-trans conformations (a, b, e) contain two gauche bonds.

the nematic phase. The molar isotropization enthalpy of A4 (6.6 kJ mol^{-1}) should therefore include a substantial conformational contribution relative to the onset of gauche conformations in the inner spacer. This contribution, however, should not be greater than ~ 1.1 kJ mol^{-1}. (This quantity is calculated taking into account the statistical weight of the two gauche conformations at 490 K provided the energy difference between gauche and trans conformation is 2.1 kJ mol^{-1} (i.e. has only intramolecular origin) and no gauche conformations occur in the nematic phase). The conclusion is that the major contribution to the isotropization enthalpy is related to the loss of orientational order and to volume change.

A detailed explanation of the trend followed by the molar isotropization enthalpies as a function of the length of the inner spacer is not a straightforward matter. In fact we must expect that nematic ordering and conformational mobility play interactive roles. The following discussion offers only a tentative scheme.

For both series of compounds, An and Bn, the molar isotropization enthalpy of the odd members increases with increasing *n*. The average incremental factor is 0.25 Δn kJ mol^{-1} for An and 0.20 Δn kJ mol^{-1} for Bn. Let us suppose, as an extreme hypothesis, that this increment is totally to be ascribed to conformational transformations of the inner flexible spacer to take place at the isotropization transition. Taking into account that the energy difference between trans and gauche conformations in an isolated polymethylene chain is 2.1 kJ mol^{-1}, the conclusion would be that the isotropization produces a rather small increase of gauche conformations (one more gauche bond every ~ seven bonds for the An series, one more every ~ nine for the Bn series) with respect to the nematic phase. This means that, unless an ad hoc hypothesis is made for the structure of the isotropic phase (namely the persistence of a high fraction of trans bonds), the average conformation of the flexible parts is largely disordered also in the nematic phase. This is also the most likely conclusion to be drawn for the even members of the series.

For the An series the molar isotropization enthalpy is almost independent of *n* (the incremental factor is 0.04 Δn kJ mol^{-1}) while for the Bn series it decreases with increasing *n*: incremental factor -0.2 Δn kJ mol^{-1}. In both cases the feature is incompatible with the assumption of a large contribution coming from a further conformational disordering of the inner spacer. The more sensible appears the picture that assigns comparable roles to the conformational contribution and to the orientational one, but, if the former is likely to increase with increasing *n* we are left with the conclusion that the latter must be a decreasing function of *n*. This hypothesis is consistent with the decreasing behaviour of the $\Delta H_i/\Delta H_T$ (or $\Delta S_i/\Delta S_T$) ratios as a function of *n* for both series of compounds. Whether all that really means order parameter decreasing with increasing *n* for *n* even and increasing with increasing *n* for *n* odd is now under scrutiny by NMR spectroscopy on deuterated homologues.

We conclude by summarizing the observed similarities between dimers and chemically related polymers.

—The nematogenic character of the dimeric molecules is preserved in the polymers.

—Odd-even fluctuations of the thermodynamic quantities depending on the length of the flexible spacer are observed in a corresponding way for the two classes of compounds.

—Rather large values of the $\Delta H_i/\Delta H_T$ ratios are found both for the dimeric and polymeric molecules particularly for the even members of the series.

It appears that a dimeric molecule may be taken with some confidence as a model compound for the investigation of the mesophasic properties of a polymeric homologue.

SUMMARY

Molecules containing two rigid groups connected by a flexible spacer have been prepared. They have the following general formula:

$$\mathrm{CH_3{-}(CH_2)_4{-}COO{-}R{-}OOC(CH_2)_{n-2}{-}COO{-}R{-}OOC(CH_2)_4{-}CH_3},$$

the rigid group R being either

$$\text{-}\phi\text{-}\mathrm{C(CH_3)CH}\text{-}\phi\text{-} \quad \text{or} \quad \text{-}\phi\text{-}\mathrm{C(CH_3){=}N{-}N{=}(CH_3)C}\text{-}\phi\text{-}\ (4 \leq n \leq 16).$$

The mesophasic, nematogenic, properties of these compounds are compared to those of the monomeric and polymeric homologues.

Dimeric molecules, particularly those containing an even number of carbon atoms in the flexible spacer show considerably high values of the molar enthalpy of isotropization. As a consequence, the odd-even fluctuations of that thermodynamic quantity are remarkably enhanced as compared to the monomeric homologues. In this respect, a similar feature was observed for the homologous polymers.

Both series of compounds exhibit a moderate variation of the molar isotropization enthalpy as a function of the length of the inner spacer.

This feature discourages the hypothesis that the isotropization transition might involve a drastic increase of gauche conformations for the flexible portions of the molecule.

References

1. A. J. Leadbetter and P. G. Wrighton, *J. Phys. Colloq.*, **40**, C3-234 (1979).
2. R. L. Humphries, P. G. James and G. R. Luckhurst, *J. Chem. Soc. Farad. Trans.*, **2**, **68**, 1031 (1972).
3. P. J. Flory and G. Ronca, *Mol. Cryst. Liq. Cryst.*, **54**, 311 (1979).
4. G. Ronca and D. Y. Yoon, *J. Chem. Phys.*, **76**, 3295 (1982).
5. F. Hardouin, M. F. Achard, H. Gasparoux, L. Liebert and L. Strzelecki, *J. Polymer Sci., Polym. Phys. Ed.* **20**, 975 (1982).
6. D. Y. Yoon, G. Sigaud and A. C. Griffin, Dallas Meeting of the American Physical Soc., March 1982.
7. A. Roviello and A. Sirigu, *Makromol. Chem.*, **183**, 895 (1982).
8. A. C. Griffin and S. J. Havens, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 951 (1981).
9. S. Antoun, R. W. Lenz and I. Jin, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 1901 (1981).
10. A. Blumstein and O. Thomas, *Macromolecules*, **15**, 1264 (1982).
11. P. Iannelli, A. Roviello and A. Sirigu, *Eur. Polym. J.*, **18**, 759 (1982).
12. S. H. Zaheer, B. Singh, B. Bhushan, P. M. Bhargawa, I. K. Kackor, K. Ramachandran, V. D. N. Sastri and N. S. Rao, *J. Chem. Soc.*, Part III, 3360 (1954).
13. G. Lock and K. Stach, *Chem. Ber.*, **79**, 295 (1946).
14. A. Roviello and A. Sirigu, *Mol. Cryst. Liq. Cryst.*, **35**, 155 (1976).
15. W. H. de Jeu, *Solid State Commun.*, **13**, 1521 (1973).
16. W. L. McMillan, *Phys. Rev.*, **A4**, 1238 (1971).
17. A. Roviello and A. Sirigu, *Gazz. Chim. Ital.*, **107**, 333 (1977).
18. A. Roviello and A. Sirigu, *Mol. Cryst. Liq. Cryst.*, **33**, 19 (1976).