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Liquid-Crystalline Polymorphism in a Class of Low Molar Mass Analogues of Mesogenic Polyesters

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Liquid-crystalline polymorphism in a class of low molar mass analogues of mesogenic polyesters

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Low molar mass analogues of liquid-crystalline polyesters were prepared in which two α-methylstilbene groups are joined through an alkyl spacer. Their mesogenic behaviour was investigated using differential scanning calorimetry, X-ray diffraction and optical microscopy. The experimental results show that the formation of smectic phases is favoured by increasing the length of the terminal chains and by decreasing the length of the flexible spacer. For a given flexible spacer, the melting point and the nematic–isotropic transition temperature are enhanced by decreasing the length of the terminal chains. The terminal chains seem to have no substantial effect on the large odd–even effect exhibited by the thermodynamic properties associated with the nematic–isotropic transition.

1. Introduction

There have been several reports of low molar mass analogues of liquid-crystalline polymers that consist of two semi-rigid mesogenic groups joined by a flexible spacer [1–7]. Model compounds of this class are usually called dimers and normally exhibit mesogenic behaviour that is more closely related to that of the corresponding polymer having the same flexible spacer than the analogous monomeric compound containing a single mesogenic group attached to which are two alkyl chains.

We have shown [3] that a homologous series of dimers incorporating the α-methylstilbene group

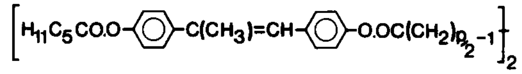
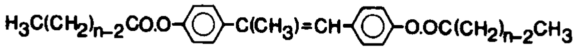


exhibit a very pronounced odd–even effect in their thermodynamic properties at the nematic–isotropic transition; this alternation is, however, smaller than for the corresponding polymers. This odd–even effect was detected also in the orientational ordering of the nematic phases by the measurement of order parameters using X-ray diffraction [8]. These large alternations may be attributed largely to the role played by the flexible spacer in governing the correlations between the rigid groups and hence, in determining the shape of the molecules in the nematic phase [3, 9, 10].

The influence that the terminal alkyl chains have on the liquid-crystalline properties of dimeric compounds, however, has received little attention [7]. These terminal chains do not connect the two rigid units as does the flexible spacer and hence, they should have a much smaller influence on the orientational correlation between the two semi-rigid groups of the molecule but have a greater conformational mobility than the spacer. Therefore, the parity of the terminal chains would not be expected to have a significant effect on the pronounced alternations already discussed.

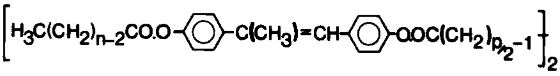
Increasing the length of the flexible terminal chains may, however, be expected to favour the formation of a layered structure in which there is a separation of the rigid and flexible molecular segments. The formation of a smectic structure on melting the solid may, therefore, be driven by a conformational disordering of the flexible segments in the molecules. Indeed, there are examples of mesogenic compounds for which the solid–smectic transition may be considered to be simply the 'melting' of the terminal alkyl chains [11], although this observation is not a general one and instead is probably valid only for compounds possessing relatively long alkyl chains that melt to give highly ordered smectic phases. This behaviour has been observed for monomeric compounds [12–15]. For example, increasing the length of the terminal alkyl chains in mesogens containing the α-methylstilbene moiety [12]



results in the appearance of smectic phases and, for long chains, the compounds exhibit only smectic behaviour.

There are, however exceptions to this behaviour. For example, increasing the terminal chains in the α,ω-bis-(*p*-(4-alkoxyphenoxycarbonyl)phenoxy)-alkanes [7] results in a decrease in smectic stability. Also, for these dimers, a significant odd–even effect in the molar isotropization enthalpy as a function of the length of the terminal chains is observed.

Here we present the transitional properties of model compounds (dimers) incorporating the α-methylstilbene group:



and we vary both the length of the terminal chains and that of the flexible spacer. The mnemonic used to describe these dimers is $R_{n,p,n}$ where n is the total number of carbon atoms in the terminal chains and p is the total number of carbon atoms in the spacer.

2. Experimental

The $R_{n,p,n}$ series was synthesized using procedures described elsewhere [3]. The final products were purified by recrystallization from ethanol/chloroform and were passed through silica gel using chloroform as eluent. The ^{1}H-N.M.R. spectra of the compounds are consistent with their formula. The differential scanning calorimetric analysis was performed under a dry nitrogen atmosphere using a Mettler TA3000 differential scanning calorimeter. An Indium sample of high purity (Fluka 99·999 per cent) was used as the reference standard for the determination of the transition temperatures and enthalpies. A heating rate of 10 K/min was used. The optical textures of the mesophases were observed using a Leitz polarizing microscope equipped with a Mettler FP5 microfurnace.

X-ray diffraction patterns of the mesophases were recorded using a Rigaku flat film camera, equipped with a microfurnace, using CuK_α and CrK_α radiation. The uncertainties in the smectic layer spacings are ± 1 Å.

3. Results and discussion

All the compounds examined exhibited mesogenic behaviour. Table 1 summarizes the liquid-crystalline behaviour of the $R_{n,p,n}$ compounds; it is apparent that these model compounds can exhibit either a smectic or nematic phase, or both, and that

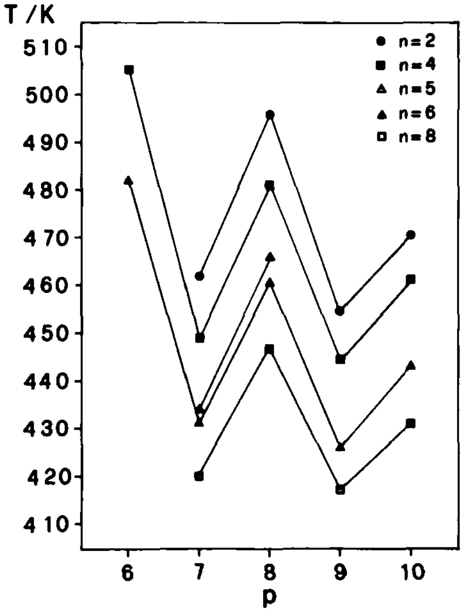


Figure 1. The dependence of the nematic–isotropic transition temperature on length of the spacer (p) for various lengths, n, of the terminal chains.

Table 1. Enantiotropic liquid-crystalline phases of compounds $R_{n,p,n}$.

	p										
n	4	5	6	7	8	9	10	11	12	14	16
2				N	N	N	N				
4	N		N	N	N	N	N				
5				N	N						
6	S, N	S, N	S, N	N	N	N	N				
8	S		S	S*, N	S*, N	N	S, N		N*		
10				S*	S*	S*, N	S*	N*	S*, N	N	N

N denotes nematic phase; S indicates smectic phase; compounds marked with an asterisk exhibit a second smectic phase, see table 2.

this depends on the relative lengths of the terminal chains and the spacer. The transitional properties of the $R_{n,p,n}$ compounds are listed in table 2.

Figure 1 shows the dependence of the nematic–isotropic transition temperatures on the length of the flexible spacer for various values of n; the nematic–isotropic transition temperature increases with decreasing length of the terminal chains for a given spacer. Also, it is apparent that the magnitude of the large odd–even effect exhibited by the T_{NI}s shows very little dependence on the length of the terminal chains; this alternation does, however, decrease with increasing spacer length. In addition, the alternation exhibited by ΔH_{NI} and the values of the ratio $\Delta H_{NI}/\Delta H_t$ in which ΔH_t is the sum over all phase changes, are essentially independent of the length of the terminal chains; this is also the case for the entropy change associated with the liquid crystal–isotropic transition. It was shown [3] that for odd members of the series with $n = 6$ there is a regular increase in the molar isotropization enthalpy and

Table 2. Thermodynamic data of compounds $R_{n,p,n}$.

	C → LC		S → I		S → N		N → I		
n, p, n	T/K	ΔH/kJ mol^{-1}	T/K	ΔH/kJ mol^{-1}	T/K	ΔH/kJ mol^{-1}	T/K	ΔH/kJ mol^{-1}	R
2, 7, 2	422·9	66·17	—	—	—	—	461·0	2·78	0·037
2, 8, 2	418·0	65·80	—	—	—	—	494·5	7·70	0·090
2, 9, 2	409·3	63·23	—	—	—	—	453·6	3·32	0·045
2, 10, 2	408·0	69·09	—	—	—	—	469·0	7·62	0·088
4, 4, 4	423·0	60·80	—	—	—	—	511·0	7·11	0·088
4, 6, 4(*a*)	393·0	51·68	—	—	—	—	504·8	6·45	0·089
4, 7, 4	398·2	61·13	—	—	—	—	448·0	2·65	0·037
4, 8, 4(*b*)	400·5	60·73	—	—	—	—	480·0	7·35	0·096
4, 9, 4	388·5	57·99	—	—	—	—	443·2	3·16	0·046
4, 10, 4(*c*)	388·2	59·53	—	—	—	—	460·8	6·88	0·088
5, 7, 5	389·6	59·52	—	—	—	—	433·6	2·15	0·032
5, 8, 5(*d*)	392·3	55·80	—	—	—	—	465·5	6·18	0·086
6, 4, 6(*e*)	409·0	57·60	—	—	470·5		488·0	6·59	0·087
6, 5, 6	399·0	30·20	—	—	410·0		433·1	1·95	0·031
6, 6, 6	393·0	49·90	—	—	456·0		482·0	6·22	0·092
6, 7, 6	396·3	60·80	—	—	—	—	431·0	2·02	0·030
6, 8, 6	395·8	57·20	—	—	421·5		460·4	6·77	0·092
6, 9, 6	388·5	62·00	—	—	—	—	425·7	2·64	0·037
6, 10, 6	385·0	66·90	—	—	—	—	442·8	6·86	0·082
8, 4, 8	416·6	63·84	477·4	14·19	—	—	—	—	0·182
8, 6, 8	394·7	55·62	469·2	12·66	—	—	—	—	0·185
8, 7, 8(*f*)	402·5	66·73	—	—	410·8	2·12	419·0	2·60	0·036
8, 8, 8	400·1	58·99	—	—	441·1	4·48	447·1	7·76	0·109
8, 9, 8	395·0	64·39	—	—	—	—	416·5	3·20	0·047
8, 10, 8	390·5	61·15	—	—	413·9	1·25	430·0	7·69	0·110
8, 12, 8(*g*)	389·5	71·63	—	—	—	—	420·5	7·67	0·097
10, 7, 10	400·0	76·06	417·5	12·04	—	—	—	—	0·137
10, 8, 10	395·2	78·22	444·5	18·15	—	—	—	—	0·188
10, 9, 10	393·0	78·55	—	—	405·5	5·75	407·5	3·61	0·041
10, 10, 10	387·5	63·91	424·4	15·44	—	—	—	—	0·195

10, 11, 10(*h*)	387·4	74·28	—	—	—	—	402·7	3·23	0·042
10, 12, 10(*i*)	394·3	63·20	—	—	407·8	6·86	411·9	8·83	0·115
10, 14, 10	387·2	79·18	—	—	—	—	409·7	8·58	0·098
10, 16, 10	393·8	83·94	—	—	—	—	401·1	9·19	0·099

C, solid phase; LC, liquid-crystalline phase either smectic or nematic; S, smectic phase; N, nematic phase; I, isotropic liquid phase; T, transition temperature in Kelvin, $\sigma(T)/T \leqslant 0{\cdot}01$; ΔH = molar enthalpic change in kJ mol^{-1} unit, $\sigma(\Delta H)/\Delta H \leqslant 0{\cdot}1$; R, ratio of the enthalpic change at the liquid crystal–isotropic transition to the total enthalpic change from the solid phase stable at low temperature to the isotropic liquid.

(*a*) $R_{4,6,4}$ shows an enantiotropic solid–solid transition at $T = 383{\cdot}2$ K which is not well resolved from the melting transition.

(*b*) $R_{4,8,4}$ shows an enantiotropic solid–solid transition at $T = 396{\cdot}2$ K which is not resolved from the melting transition.

(*c*) $R_{4,10,4}$ shows an enantiotropic solid–solid transition at $T = 386{\cdot}7$ K, again not resolved from the melting transition.

(*d*) $R_{5,8,5}$ shows an enantiotropic solid–solid transition at $T = 386$ K.

(*e*) Data for comounds $R_{6,p,6}$ are taken from [3].

(*f*) Compounds $R_{8,7,8}$, $R_{8,8,8}$, $R_{10,7,10}$, $R_{10,8,10}$, $R_{10,9,10}$, $R_{10,10,10}$, $R_{10,12,10}$ show a smectic–smectic phase transition, detected by optical methods at 391 K (monotropic), 412 K (enantiotropic), 408 K (enantiotropic), 424 K (enantiotropic), 388 K (monotropic), 406 K (enantiotropic), 390 K (monotropic), respectively.

(*g*) $R_{8,12,8}$ shows a monotropic smectic–nematic transition at $T = 391{\cdot}9$ K, too close to the crystallization temperature to be resolved and a monotropic solid–solid transition at $T = 376{\cdot}2$ K.

(*h*) $R_{10,11,10}$ shows a monotropic smectic phase which transforms into a nematic phase at $T = 392{\cdot}7$ K ($\Delta H = 1{\cdot}5$ kJ mol^{-1}) and a monotropic solid–solid transition not resolved from the crystallization.

(*i*) $R_{10,12,10}$ shows an enantiotropic solid–solid transition at $T = 383{\cdot}2$ K ($\Delta H = 4{\cdot}8$ kJ mol^{-1}).

entropy as a function of the length of the spacer. This behaviour, attributed to a progressive attenuation of the unfavourable orientational correlation between the two rigid groups with increasing length of the spacer, has been observed, also, for the orientational order parameters [16]. An incremental factor, per methylenic unit, of about 0·25 kJ mol^{-1} in ΔH_{NI} was noted. This is found also, for example, in the series with $n = 2$ and $n = 4$.

Varying the parity of the terminal chains for a given spacer has a relatively minor effect. For example, $R_{5,7,5}$ and $R_{5,8,5}$ exhibit nematic–isotropic transition temperatures that lie between those found for compounds with the same spacer but with $n = 4$ and 6, (see figure 1) and, in addition, the values of ΔH_{NI} and of the ratios $\Delta H_{NI}/\Delta H_t$ show a similar trend (see table 2).

This experimental data, therefore, suggests that the length and parity of the terminal chains have little effect on the degree of order present in the nematic phase which, in fact, is largely dependent on the parity of the spacer.

However, the length of the terminal chains plays an important role in the formation of smectic phases. In this respect, the behaviour of these dimeric compounds is similar to that of monomeric mesogenic compounds [12–15]. The occurrence of smectic phases is summarized in table 1. The general trend is that the smectic phase is stabilized for long terminal chains and short spacers. The stabilization appears to be greater for the even compounds than for the odd numbers. Therefore, by suitably varying the two structural parameters, namely the lengths of the terminal chains and the spacer, it is possible to change the mesomorphism exhibited by the model compounds; on decreasing n for a given value of p we pass from compounds with only a smectic phase to compounds with a smectic and a nematic phase, to compounds with only a nematic phase. The pattern of the molar enthalpic changes associated with the smectic–isotropic and the smectic–nematic phase transitions (table 2) is in accord with this trend. At a given parity of the spacer, these thermodynamic quantities increase with increasing n and decrease with increasing p. In several cases, the enthalpy change associated with the smectic–nematic transition is almost undetectable within the experimental limits.

The identification of the smectic phases was based on morphological observations and X-ray diffraction data. The optical textures of the higher temperature smectic phase consist of regions of both homeotropic and focal-conic fan texture; this is shown in figure 2 for an even compound and in figure 3 for an odd membered compound. This phase is assigned as a smectic A.

For some model compounds, an additional smectic phase is obtained on cooling the smectic A phase and this lower temperature phase was identified as a smectic C, on the basis of the schlieren texture observed when viewed under a polarizing microscope; this texture is shown in figure 4. It should be noted that the smectic–smectic transition was not detected using differential scanning calorimetry.

Table 3 gives the smectic layer spacings measured at approximately the same reduced temperature, $T/T_t = 0{\cdot}97$ where T_t is the smectic–nematic or the smectic–isotropic transition temperature. A feature of these measurements is that for spacers of the same parity the periodicity always increases with the size of the molecules. The values measured for the smectic spacing are comparable with the all-trans molecular lengths. This suggests that the molecules are assembled in an extended conformation with their long axes perpendicular to the smectic layers; this is in accord with the smectic A nature of the phase inferred from the optical analysis of the texture.

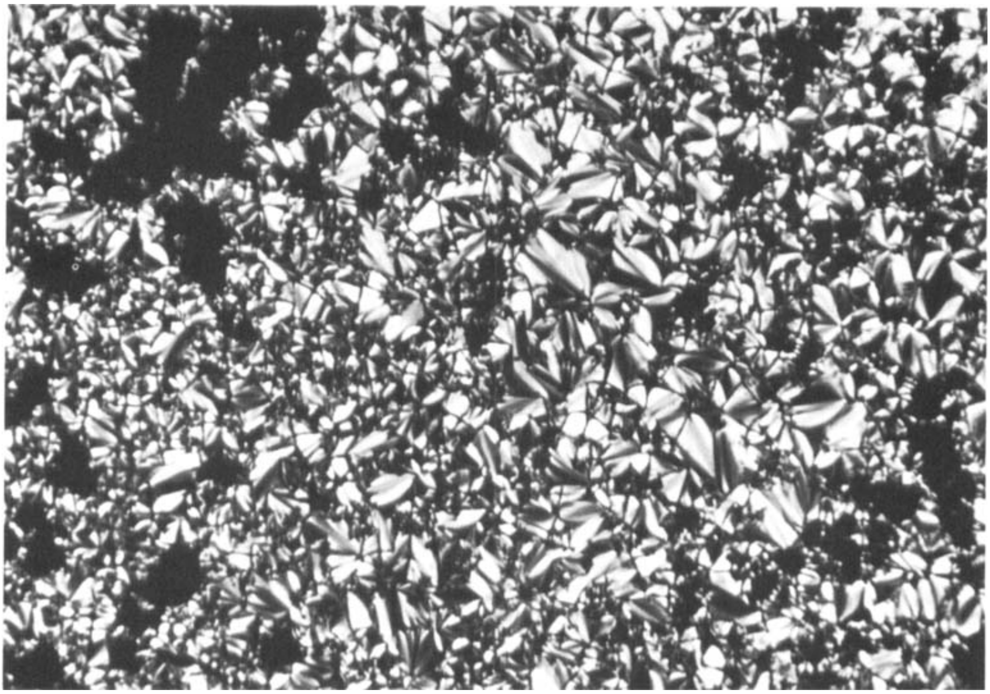


Figure 2. The focal-conic fan and homeotropic textures of the smectic A phase exhibited by $R_{10,8,10}$ $T = 441{\cdot}1$ K, crossed polarizers.

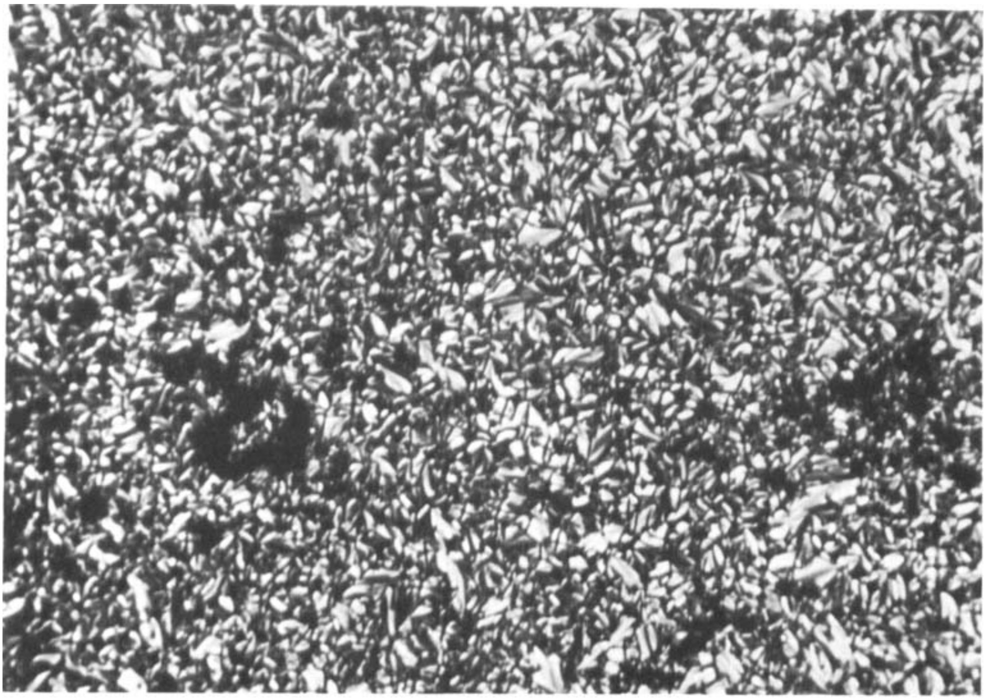


Figure 3. The focal-conic fan and homeotropic textures of the smectic A phase exhibited by $R_{10,7,10}$, $T = 416{\cdot}1$ K, crossed polarizers.

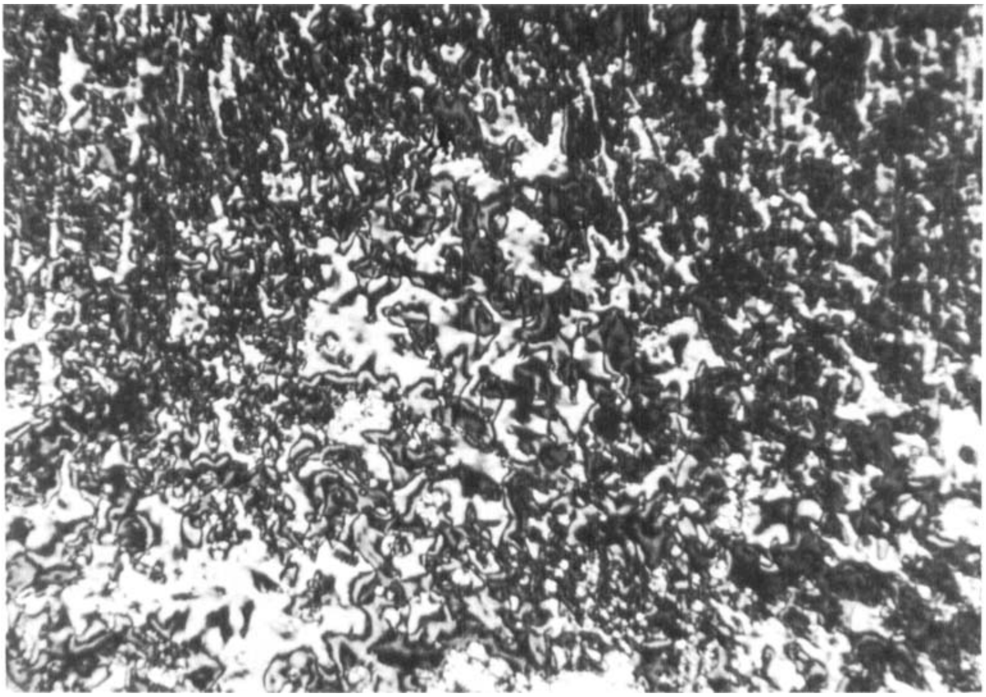


Figure 4. The schlieren texture of the smectic C phase shown by $R_{10,7,10}$, $T = 401{\cdot}2\,K$, crossed polarizers.

Table 3. The smectic layer spacings of the $R_{n,p,n}$ compounds; the values for the $R_{6,p,6}$ compounds are taken from [3].

n, p, n	T/K	T_r	d/Å
6, 4, 6	458	0·97	44·7
6, 6, 6	423	0·93	47·0
6, 8, 6	413	0·98	50·5
8, 4, 8	463	0·97	47·0
8, 6, 8	453	0·97	50·3
8, 8, 8	433	0·98	53·2
8, 10, 8	404	0·98	55·4
10, 7, 10	405	0·97	53·3
10, 8, 10	431	0·97	57·7
10, 9, 10	404	0·99	55·4
10, 10, 10	413	0·97	60·2

The molecules with an odd length spacer, however, show smectic periodicities that are somewhat smaller. This is because both the all-trans conformation and also several conformations containing gauche bonds are not as elongated and rectilinear in shape as the even membered molecules. Similar differences have been pointed out recently [17] to distinguish analogous semi-flexible mesogenic polymers having even and odd spacers along the polymer backbone; the odd membered polymers exhibit a 'wavier' molecular shape than the even ones.

The different molecular shape of even and odd membered molecules does not appear intrinsically to prevent the compatibility of the respective smectic phases. The

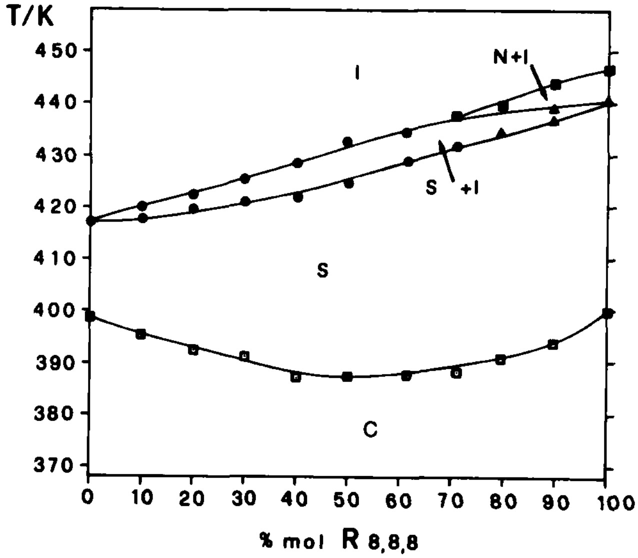


Figure 5. The phase diagram of the binary system formed by $R_{8,8,8}$ and $R_{10,7,10}$. An investigation into the possible formation of a smectic C phase in the binary system has been deliberately neglected.

phase diagram of the binary system $R_{8,8,8}$ and $R_{10,7,10}$ has been investigated and is shown in figure 5; it should be noted that the smectic phases of these two compounds have the same periodicity at equal T/T_t. There is a complete miscibility over all compositions between the smectic phases of the two compounds. This shows that even and odd membered molecules exhibit the same type of smectic phase.

The picture outlined appears to be fairly regular and may be summarized as follows:

(1) the parity of the spacer has a strong influence on the thermodynamic quantities associated with the liquid–isotropic transition and has some influence on the relative stability of the smectic and nematic phase;

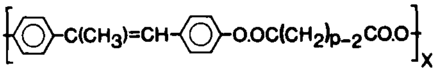
(2) the parity of the terminal chains has no substantial effect on the thermodynamic properties at the liquid crystal–isotropic transition;

(3) the length of the spacer has a strong 'nematogenic' effect and it tends to increase the stability of the nematic phase with respect to smectic behaviour;

(4) the length of the terminal chains has a strong 'smectogenic' effect, and smectic mesomorphism is favoured by longer terminal chains.

In conclusion, it is interesting to note that:

(*a*) the corresponding polymers



with values of p up to 14 are solely nematogens [18];

(*b*) the dimers $R_{n,p,n}$ which stoichiometrically correspond to the polymers, either exactly ($p = 2n$) or approximately ($p = 2n \pm 1$), are also nematogenic or are anticipated to be by extrapolating the pattern in table 1.

In this particular example, the agreement between the model compounds and polymers appears to be complete. However, this is not always the case [7] and it is obvious that the definition of dimers as model compounds for the corresponding polymers has to be applied with a great deal of caution.

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References

[1] LUCKHURST, G. R., 1985, *Recent Advances in Liquid Crystalline Polymers*, edited by L. L. Chapoy (Elsevier), Chap. 7.
[2] GRIFFIN, A. C., SIGAUD, G., and DO Y. YOON, 1983, *Macromolecules*, **16**, 875.
[3] BUGLIONE, J. A., ROVIELLO, A., and SIRIGU, A., 1984, *Molec. Crystals liq. Crystals*, **106**, 169.
[4] BLUMSTEIN, A., BLUMSTEIN, R. B., STICKLES, E. M., GAUTHIER, M. M., and VOLINO, F., 1984, *Macromolecules*, **17**, 177.
[5] CARFAGNA, C., IANNELLI, P., ROVIELLO, A., and SIRIGU, A., 1985, *J. therm. Anal.*, **30**, 1317.
[6] BLUMSTEIN, R. B., POLIKS, M. D., STICKLES, E. M., BLUMSTEIN, A., and VOLINO, F., 1985, *Molec. Crystals liq. Crystals.*, **129**, 375.
[7] JIN, J. I., OH, H. T., and PARK, J. H., 1986, *J. chem. Soc. Perkin Trans. II*, p. 343.
[8] CAPASSO, R., IANNELLI, P., ROVIELLO, A., and SIRIGU, A., 1985, *Macromolecules*, **18**, 2773.
[9] ABE, A., 1984, *Macromolecules*, **17**, 2280.
[10] YOON, DO Y., and BRUCKNER, S., 1985, *Macromolecules*, **18**, 651.
[11] DVOLAITSKY, M., POLDY, F., and TAUPIN, C., 1973, *Physics Lett.* A, **45**, 454.
[12] ROVIELLO, A., and SIRIGU, A., 1977, *Gazz. chim. Ital.*, **107**, 333.
[13] ARORA, S. L., and FERGASON, J. L., 1971, *Symp. Faraday Soc.*, **5**, 97.
[14] ROVIELLO, A., and SIRIGU, A., 1976, *Molec. Crystals liq. Crystals*, **33**, 19.
[15] ROVIELLO, A., and SIRIGU, A., 1976, *Molec. Crystals liq. Crystals*, **35**, 155.
[16] CENTORE, R., IANNELLI, P., ROVIELLO, A., and SIRIGU, A. (unpublished results).
[17] AURIEMMA, F., CORRADINI, P., and TUZI, A., 1987, *Macromolecules*, **20**, 293.
[18] ROVIELLO, A., and SIRIGU, A., 1982, *Makromolec. Chem.*, **183**, 895.