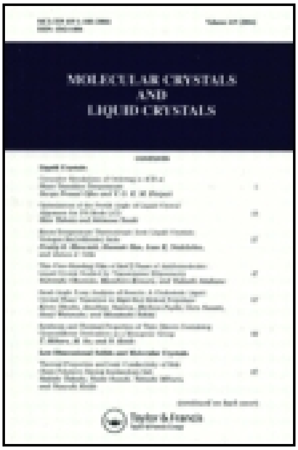

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Mesomorphic Behavior of Symmetric Liquid Crystal Dimers: α,ω-Bis[4-(4-alkoxybenzoyloxy)benzylideneami alkanes

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Mesomorphic Behavior of Symmetric Liquid Crystal Dimers: α,ω-Bis[4-(4-alkoxybenzoyloxy)benzylideneamino] alkanes

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The mesomorphic properties of eight series of α,ω-bis[4-(4-alkoxybenzoyloxy)benzylideneamino]alkanes have been examined. The terminal alkoxy group was varied from ethoxy to octyloxy and the number of methylene units in the spacer was increased from three to ten. While all the dimers with even-membered spacers are nematogenic, the dimers with odd-membered spacers exhibit both a nematic and a smectic phase when the terminal alkyl chain is short and only a smectic phase when the alkyl chain is long. The higher alkoxy derivatives are particularly interesting as the dimers with even-membered spacers possess higher clearing temperatures associated with small entropies of N-I transition and those with odd-membered spacers possess lower clearing temperatures associated with large entropies of S-I transition.

Keywords: Symmetric dimers; nematic; smectic; odd-even effects

INTRODUCTION

Liquid-crystal dimers consisting of two identical mesogenic parts connected by a flexible spacer have been known to show a dramatic alternation of the nematic-isotropic (N-I) transition properties as the parity of the spacer chain is varied [1–4]. This odd-even effect has been explained by the difference in the orientational ordering of the molecules in the mesophase [5].

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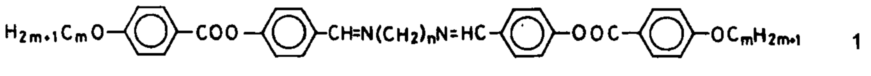
The better ordered nematic phase is achieved with an even number of methylene units in the spacer, leading to a higher N-I transition temperature and a larger associated entropy change. Since then, a number of series in which the dimers with short spacers produce smectic-isotropic (S-I) transition and those with long spacers produce N-I transition have been described [6–9]. When the terminal alkyl groups are long enough, all dimers in a series exhibit only S-I transition [7, 9]. In such cases, the odd-even effects analogous to those found for the N-I transitions are displayed by the S-I transitions [6–9]. The behavior of some series of α,ω-bis(4-alkoxyazobenzene-4′-carbonyloxy)alkanes studied by Niori *et al.*, is entirely different from the above-mentioned; that is, the dimers with even-membered spacers produce a nematic and a smectic A phase, while those with odd-membered spacers produce only a smectic C phase [8]. As the enthalpies of the S-I transitions are larger than those of the N-I transitions, the transition temperature and the associated entropy change in directions opposite to each other.

In this paper, we wish to report eight homologous series of α,ω-bis[4-(4-alkoxybenzoyloxy)benzylidneamino]alkanes (1) which show a mesomorphic behavior similar to the last mentioned. The present dimers will be referred to as *m*N*n*N*m* where *m* denotes the number of carbon atoms in the terminal alkoxy group and *n* denotes the number of methylene units in the flexible spacer. The corresponding monomeric compounds, α-[4-(4-alkoxybenzoyloxy)benzylideneamino]alkanes, were examined by Weissflog *et al.*, employing mostly butoxy to octyloxy as the terminal groups and butane to decane as the spacer [10].



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EXPERIMENTAL

4-Alkoxybenzoic acids, 4-hydroxybenzaldehyde, and α,ω-diaminoalkanes are commercially available. 4-(Alkoxybenzoyloxy)benzaldehydes were prepared by the reaction between 4-alkoxybenzoic acids and 4-hydroxybenzaldehyde following the procedure of Hassner and Alexanian [11]. The desired compound was obtained by the condensation of the aldehyde with the diamine in boiling ethanol employing piperidine as a catalyst [10]. The crude product was repeatedly recrystallized from a mixture of ethanol and toluene. The mesophases were identified by means of optical textures; nematic phases from schlieren texture and smectic phases from focal conic textures. The transition temperatures and enthalpy changes were determined by differential scanning calorimetry. As the compounds are not very stable at high temperatures, the heating rates of 5, 10, and 20°C min^{-1} were employed to check the reproducibility of the transition properties. The temperatures and enthalpies determined at the rate of 20°C min^{-1}, the maximum rate in our apparatus, are taken as the most probable ones when thermal decomposition is noticeable.

RESULTS AND DISCUSSION

Table I summarizes the mesomorphic transition temperatures and associated enthalpy changes. Here, K, S, N, and I stand for the crystalline, smectic, nematic, and isotropic phases, respectively. The smectic phase given by the dimers with even-membered spacers is tentatively denoted by S_1 and the phase given by those with odd-membered spacers by S_2.

TABLE I Transition temperatures (°C) and enthalpy changes (kJ mol^{-1})[a] of α,ω-bis[4-(4-alkoxybenzoyloxy)benzylideneamino]alkanes

m[b]	*K*	S_2	S_1	*N*	*I*
		n[c] = 3			
2	.139 (69)				.
3	.147 (54)				.
4	.112 (44)	[.107 (8.7)][d]			.
5	.121 (55)	[.112 (12)][d]			.
6	.121 (64)	[.117 (15)][d]			.
7	.108 (35)	.113 (17)			.
8	.104 (50)	.110 (18)			.
		n[c] = 4			
2	.164 (54)			.231 (9.2)	.
3	.182 (61)			.205 (7.8)	.
4	.169 (55)			.201 (8.8)	.
5	.163 (60)			.187 (7.8)	.
6	.160 (63)			.183 (9.2)	.
7	.148 (65)			.175 (9.3)	.
8	.122 (60)			.171 (9.6)	.
		n[c] = 5			
2	.119 (52)	[. 94 (0.4)][d]		[.112 (0.1)][d]	.
3	.126 (61)				.
4	.118 (65)	[. 99 (6.2)][d]		[.102 (0.2)][d]	.
5	.103 (45)	.111 (11)			.
6	.123 (70)	[.118 (14)][d]			.
7	.109 (49)	.119 (15)			.
8	. 91 (67)	.118 (16)			.

TABLE I (Continued)

m[b]	*K*	S_2	S_1	*N*	*I*
n[c] = 6					
2	.151 (51)			.202 (8.8)	.
3	.140 (51)			.180 (7.9)	.
4	.163 (56)			.181 (8.7)	.
5	.150 (51)			.163 (7.5)	.
6	.141 (54)			.163 (9.8)	.
7	.138 (61)			.156 (9.8)	.
8	.134 (61)			.154 (9.7)	.
n[c] = 7					
2	. 94 (40)	.106 (0.1)		.130 (0.5)	.
3	.107 (56)	[. 84 (0.4)][d]		[.102 (0.2)][d]	.
4	.109 (50)	[. 96 (0.7)][d]		.113 (0.5)	.
5	. 94 (34)	.102 (8.9)			.
6	. 97 (35)	.114 (13)			.
7	.115 (68)	.117 (15)			.
8	.110 (51)	.118 (16)			.
n[c] = 8					
2	.155 (47)			.184 (8.8)	.
3	.133 (38)			.163 (8.3)	.
4	.124 (41)			.163 (8.8)	.
5	.125 (58)			.151 (8.6)	.
6	.134 (51)			.150 (9.2)	.
7	.124 (51)			.145 (9.9)	.
8	.132 (54)		.137 (1.8)	.143 (10.5)	.
n[c] = 9					
2	. 92 (42)	.108 (– – –)		.134 (0.8)	.
3	. 96 (31)			.111 (0.3)	.
4	. 88 (18)	[. 83 (0.3)][d]		.118 (0.8)	.
5	. 98 (55)	[. 95 (5.3)][d]		.110 (0.7)	.
6	. 83 (37)	.110 (12)			.
7	. 88 (63)	.114 (14)			.
8	.111 (51)	.119 (15)			.
n[c] = 10					
2	.159 (54)			.166 (7.7)	.
3	.148 (63)			[.146 (6.6)][d]	.
4	.120 (60)			.149 (8.5)	.
5	.111 (44)			.140 (8.1)	.
6	.111 (44)			.141 (8.8)	.
7	.116 (49)		.128 (0.6)	.136 (10)	.
8	.124 (50)		.135[e]	.135[e]	

[a] The enthalpy changes are in parentheses.

[b] The number of carbon atoms in the terminal alkyl group.

[c] The number of methylene units in the spacer.

[d] Monotropic transition.

[e] The combined enthalpy changes are 15.9 kJ mol^{-1}.

All the dimers with even-membered spacers exhibit a nematic phase. The enthalpies associated with the N-I transition of these dimers are in the range 6.6 to 10 kJ mol^{-1}. As not only the number of carbon atoms in the terminal alkyl group (*m*) but also the number of methylene units in the spacer (*n*) are increased, the transition temperature is lowered (see Fig. 1). This trend is expected for series having high isotropization temperatures as both the increase in the length of the terminal alkyl chain and that of the spacer serve to dilute the core–core interactions. The additional smectic phase with a fan-shaped texture is observed for 8N8N8, 7N10N7, and 8N10N8 in accordance with the tendency noted by Weissflog *et al.*, that the increase in the alkyl chain length of the monomeric mesogen promotes the smectic behavior [10]. For the last dimer, a fan-shaped texture surrounded by a

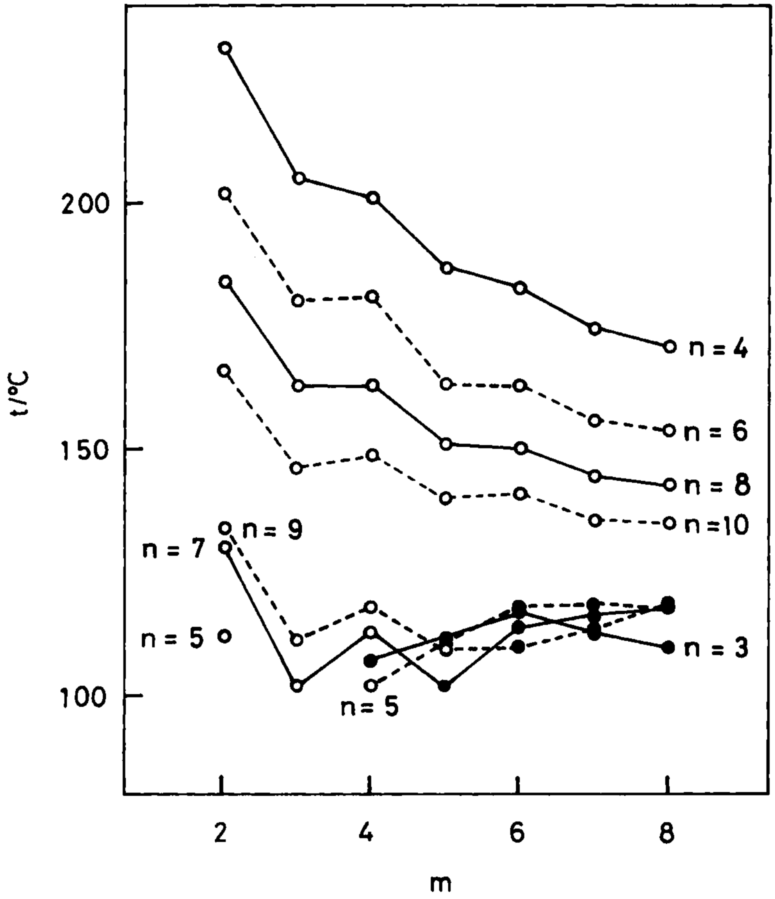

FIGURE 1 Plots of isotropization temperatures of *m*N*n*N*m* against the number of carbon atoms in the terminal alkyl group (*m*). The open circle indicates the N-I transition and the shaded circle indicates the S-I transition.

schlieren texture is observed at the isotropization because the S-N and N-I transitions are hardly separable.

The behavior of the dimers with odd-membered spacers is rather complicated. Only a smectic phase is found for the dimers when $n = 3$ except for 2N3N2 and 3N3N3 which are not mesogenic. The enthalpies associated with the S-I transition are in a range of 8.7 to 18 kJ mol^{-1}. Thus, the smectogenic tendencies of the monomers are greatly enhanced on coupling to form the dimer in the present series. This finding is in contrast to that stated by Date *et al.*, for α,ω-bis(4-alkylanilinebenzylidene-4′-oxy) alkanes [7]. The bâtonnets of the S_2 phase developed on cooling the isotropic liquid have sharp edges and coalesce to form a broken fan-shaped texture. No schlieren texture was obtained by shearing the S_2 phase between glasses. A nematic phase is generated for the dimers with short terminal alkoxy groups and the enthalpies associated with the N-I transition are far less than those given by the dimers with even-membered spacers; namely, 0.1 to 0.8 kJ mol^{-1}, reflecting the difference in the orientational ordering arising from the parity of the spacer chain. Moreover, contrary to the dimers with even-numbered spacers, the N-I transition temperature is raised on increasing the spacer length as is expressed in Figure 1. On the other hand, the dimers with hexyl and longer alkyl groups continue to be purely smectogenic. These observations suggest the presence of strong lateral interactions between the molecules irrespective of the terminal alkyl chain length when the spacer is odd-membered and the nature of the S_2 phase is different from that of the S_1 phase produced by the dimers with even-membered spacers.

Date *et al.*, proposed an empirical rule that if a dimer is to exhibit smectic properties then the terminal chain length must be longer than half the spacer length [7]. The rule appears to hold true for the present dimers with even-membered spacers but undoubtedly not for those with odd-membered spacers because the dimers such as 2N9N2, 2N7N2, and 2N5N2 are smectogenic.

Thus far we have considered the effects of the terminal chain length while holding the number of methylene units in the spacer (n) constant. Now, the transitional properties of the mNnNm compounds and their relationship to the length of the flexible spacer will be inspected. All the dimers in the 2NnN2 and 3NnN3 series exhibit a nematic phase with the exception of 2N3N2, 3N3N3, and 3N5N3 for which no mesophase could be detected. Both the N-I transition temperatures and the associated entropies show a striking odd-even effect in which the dimers with even-membered spacers have the higher values. This is the most common behavior reported for dimeric compounds [6–9]. The alternation of the temperature and also that of the entropy attenuate as the spacer is lengthened.

On increasing the terminal alkyl chain length to four carbon atoms giving the 4N*n*N4 series, an S_2 phase is observed for the first member. Figure 2 shows the dependence of the isotropization temperature and the associated entropy on the number of methylene units in the spacer. The alternation of the entropies is very dramatic and most of the even members have higher values. The ratio of the entropy of the even member to that of the next odd one diminishes from 37 to 10. The dimer 4N3N4 is purely smectogenic and the entropy change associated with the S_2-I transition is larger by a factor of 1.2 than that associated with the N-I transition of 4N4N4; therefore, the first two members deviated from the relationship between the entropies and the spacer length given from the other members.

The dependence of the isotropization temperature and the associated entropy on the length of the spacer for the *m*N5N*m* series is presented in

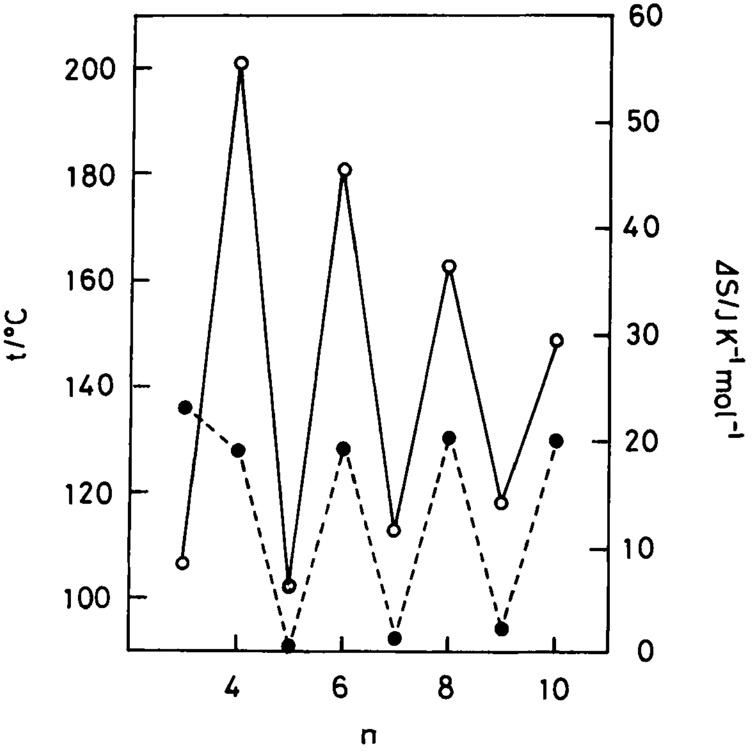

FIGURE 2 Plots of the isotropization temperatures (shown by open circles) and associated entropy changes (shown by shaded circles) of the 4N*n*N4 series against the number of methylene units in the spacer (*n*).

Figure 3. All the dimers with odd-membered spacers exhibit an S_2-I transition with the exception of 5N9N5. The transition temperatures of this series show also a marked alternation in which the even members have the higher values. The entropy changes show an odd-even effect with the odd members having the higher values up to $n = 8$. This alternation is less significant than that exhibited by the 4N*n*N4 series which is composed mostly of nematogens. The ratio of the entropy of the odd member to that of the next even one is small and becomes progressively less, from 1.8 to 1.2, on increasing the spacer length. Because 5N9N5 is nematogenic, the corresponding entropy ratio is as large as 11.

In the 6N*n*N6 series, all the dimers with odd-membered spacers are purely smectogenic; therefore, the isotropization temperature and the associated

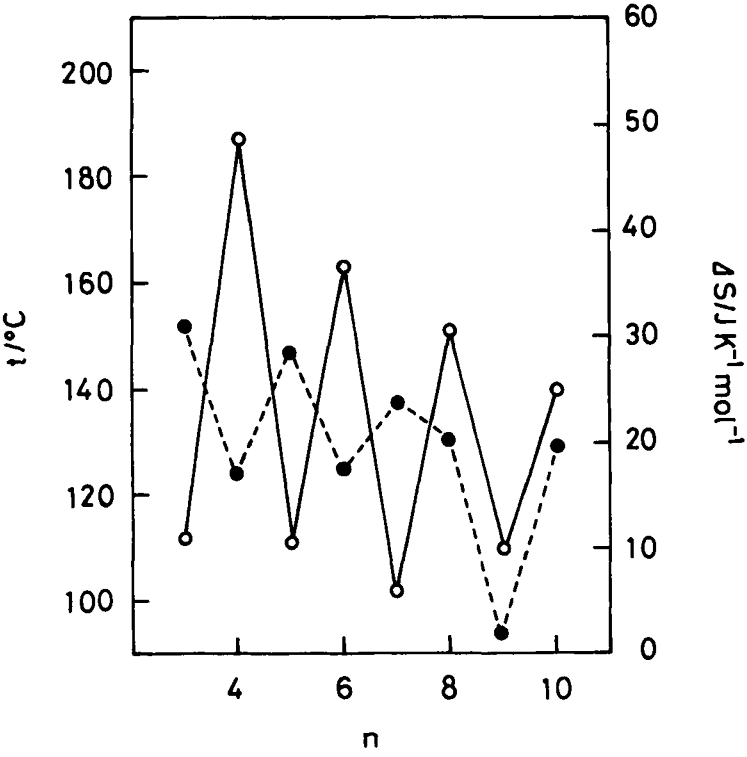

FIGURE 3 Plots of the isotropization temperatures (shown by open circles) and associated entropy changes (shown by shaded circles) of the 5N*n*N5 series against the number of methylene units in the spacer (*n*).

entropy alternate perfectly in directions opposite to each other; namely, the even members have higher transition temperatures and the odd members have larger entropy changes without any anomaly as is illustrated in Figure 4. The ratio of the entropy of the odd member to that of the next even one decreases from 1.9 to 1.5 as *n* is increased.

Niori *et al.*, discovered the odd-even effects similar to those given by 6N*n*N6 and characterized the smectic phase of their dimers with odd-membered spacers as the C type, whereas that of the dimers with even-membered spacers as the A type. They proposed that the bent arrangement of two mesogenic parts stabilizes strongly the smectic layer structure [8]. The generation of a smectic C phase was also disclosed by Attard *et al.*, for some non-symmetric dimers with odd-membered flexible spacers [12]. Moreover, a smectic C phase is generally formed by molecules with an obtuse-angled

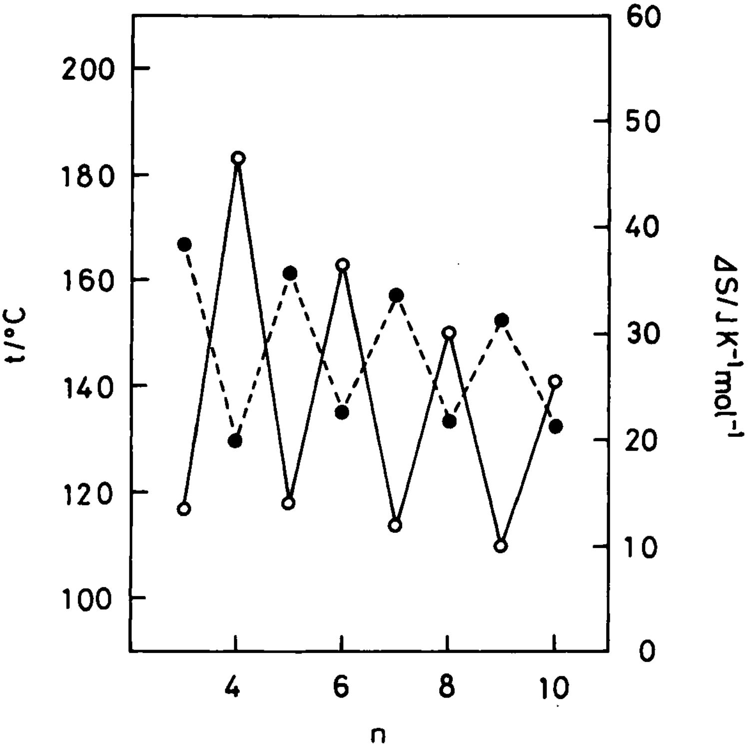

FIGURE 4 Plots of the isotropization temperatures (shown by open circles) and associated entropy changes (shown by shaded circles) of the 6N*n*N6 series against the number of methylene units in the spacer (*n*).

configuration in which two identical moieties are rigidly connected by a non-polar group [13–15]. Indeed, the texture of the present S_2 phase is identical with that of the smectic C phase given by some diphenylmethane derivatives. We tested the miscibility between the S_1 phase of 7N10N7 and the S_2 phase of 8N9N8 by the contact method. The mesomorphic transition temperatures are depressed by mixing and the N-I transition can be lowered below the S_2-I transition. In such a temperature range, the S_1 and S_2 phases are partitioned by a nematic zone on the 7N10N7-rich side and also by an isotropic zone on the 8N9N8-rich side. Although the assignment of the S_2 phase needs further examination, the afore-mentioned observations can be readily explained if the S_1 and S_2 phases are of the A and C types respectively.

By a further increase in the terminal alkyl chain length, the alternation of the isotropization temperature is maintained though it is less pronounced compared to that for the 4N*n*N4 series. For example, the temperature difference between the first and second members is 62°C in the 7N*n*N7 series and 94°C in the 4N*n*N4 series. Some anomaly is noted in the alternation of the associated entropy change. As is depicted in Figure 5, the ratio of the entropy of the odd member to that of the next even one in the 7N*n*N7 series reduces gradually from 2.1 to 1.6 as the spacer length is increased and then abruptly to 1.1 at the end of the series.

The entropy of isotropization for 8N10N8 is not clear because the S_1-N and N-I transition temperatures come close together but the ratio of the entropy of 8N9N8 to that of 8N10N8 is certainly not far from 1. If the nematic phase is eliminated from the dimer by a further increase of the terminal alkyl chain length, the inversion in the alternation of the isotropization entropy will start from the last dimer in a series and be completed when all dimers become purely smectogenic. In other words, the even members will have higher values not only in the alternation of the S-I transition temperatures but also in those of the associated entropy. Such cases are known by the works of Data *et al.* and Rozhanskii *et al.* [7,9]. Therefore, the situation in which the isotropization temperature and the associated entropy alternate in directions opposite to each other reported by Niori *et al.* [8] and also in the present paper may be regarded as an intermediate step in the process in which all dimers in a series change from nematogenic to purely smectogenic on the condition that the smectic phases given by the dimers with even-membered spacers and those with odd-membered spacers are not of the same type.

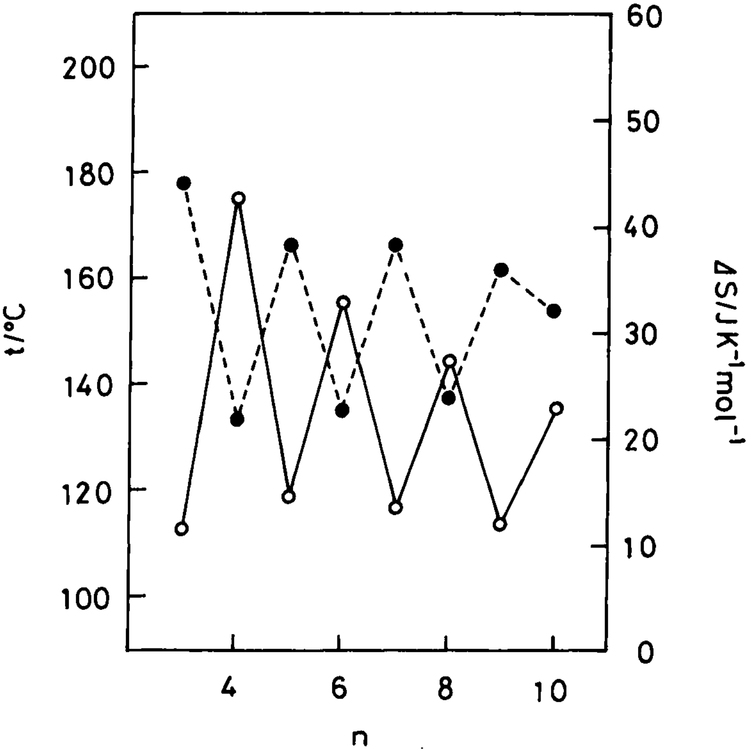

FIGURE 5 Plots of the isotropization temperatures (shown by open circles) and associated entropy changes (shown by shaded circles) of the 7N*n*N7 series against the number of methylene units in the spacer (*n*).

Acknowledgement

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