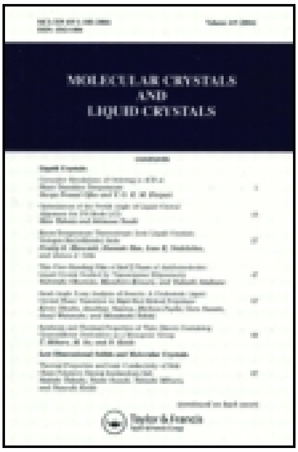

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Mesomorphic Behavior of 2,4-Bis-(4-alkoxybenzylidene)cyclopentanones and Related Compounds

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The mesomorphic properties of homologous series of 2,5-bis(4-alkoxybenzylidene)cyclopentanones, 2,6-bis(4-alkoxybenzylidene)cyclohexanones, and 2,7-bis(4-alkoxybenzylidene)cycloheptanones have been compared with each other. The clearing point is markedly depressed by increasing the size of the cycloalkanone ring. The cyclopentanone derivatives carrying the methoxy to pentyloxy groups are purely nematogenic, the next member exhibits a smectic A phase as well as a nematic phase. Smectic A and C phases are observed for the heptyloxy and octyloxy homologues, and only a smectic C phase for the later members. In both the cyclohexanone and cycloheptanone derivatives, the methoxy to decyloxy homologues exhibit a nematic phase and the higher members exhibit a smectic C phase. In addition, a smectic A phase appears in the nonyloxy and decyloxy homologues of the cyclohexanone series.

Keywords: nematic, smectic C, cycloalkanones, nonlinear molecules

INTRODUCTION

As early as 1907, Vorländer noted that 2,5-bis(4-methoxybenzylidene)cyclopentanone and 2,6-bis(4-methoxybenzylidene)cyclohexanone are mesogenic without mentioning their transition temperatures.[1,2] In 1921, Müller reported that the former compound is not mesogenic but crystals of the latter compound are transformed into a turbit liquid at 160–161°C and then into a clear liquid at 171°C.[3] Then, Vorländer disclosed details of his observations; that is, the appearance of a metastable mesophase at 195°C from a supercooled melt of the cyclopentanone derivative and that of a stable mesophase between 160 and 173°C in the cyclohexanone derivative.[4] Moreover, 2,6-bis(4-ethoxybenzylidene)cyclohexanone was reported to be transformed into a mesophase at 146°C and then into an isotropic liquid at 176°C. Vorländer assumed that the two double bonds between the benzylidene groups and the cycloalkanone ring form one another an obtuse angle.[5] He suggested that the double bonds in the cyclopentane derivative are in one plane but those in

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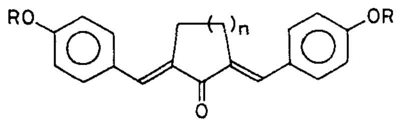
the cyclohexanone derivative are in a different plane and also that the former derivatives may be more strongly mesogenic than the latter. However, recent X-ray diffraction analyses established that the molecular cores of the cyclopentanone and cyclohexanone derivatives are essentially coplanar and linear.[6,7] In connection with our works on the mesomorphic compounds with unconventional molecular structures,[8-10] It seemed interesting to us to examine the properties of the compounds derived from cyclopentanone, cylcohexanone, and cycloheptanone (1, 2, and 3).



(1) n = 1,

(2) n = 2,

(3) n = 3.

EXPERIMENTAL

2,5-Bis(4-alkoxybenzylidene)cyclopentanone was prepared from the reaction of cyclopentanone with 4-alkoxybenzaldehyde in a 1:2 proportion in ethanol at room temperature adding aqueous sodium hydroxide as a catalyst. The other two series of compounds were prepared from cyclohexanone and cycloheptanone employing the same procedure. The products were purified by recrystallization from ethanol until a sharp mesomorphic-isotropic transition was recorded on the calorimetric curve. The transition temperatures and associated enthalpies were determined by a Rigaku Thermoflex differential scanning calorimeter at a heating rate of 5 K min^{-1}.

RESULTS AND DISCUSSION

The transition temperatures and associated enthalpies of the three series are summarized in Tables I–III. Here, the crystalline, smectic C, smectic A, nematic, and isotropic liquid phases are denoted by K, S_C, S_A, N, and I, respectively. The mesophases were classified on the basis of the optical textures, the nematic phase by a schlieren texture, the smectic A phase by a fan-shaped and/or homeotropic texture, and the smectic C phase by a broken-fan and/or schlieren texture.

As is shown in Table I, the nematogenic cyclopentanone series is rather short; that is, the methoxy to hexyloxy homologues except for the propoxy one. The transition temperatures of the first member agree roughly and those of the second one satisfactorily with those reported by Vorländer.[4] The mesophase is thermodynamically stable only for the ethoxy and hexyloxy homologues. Even for these two, the temperature ranges of stable existence are as narrow as 5 and 2°C, respectively. A smectic A phase appears in the hexyloxy to octyloxy homologues and a smectic C phase in the heptyl to hexadecyloxy homologues. Thus, the range of

TABLE I

Transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) of 2,5-bis(4-alkoxybenzylidene)cyclopentanones[a]

n[b]	K	S_C	S_A	N	I
1	. 213 (40)			[. 190 (0.3)] [c]	.
2	. 195 (41)			. 200 (0.4)	.
3	. 194 (42)				.
4	. 189 (51)			[. 181 (1.5)] [c]	.
5	. 172 (52)			[. 172 ( )] [c]	.
6	. 153 (45)		. 174[d]	. 176[d]	.
7	. 155 (54)	. 163 (0.3)	. 172 (3.7)		.
8	. 150 (48)	. 169 (0.6)	. 173 (5.5)		.
9	. 151 (50)	. 166 (6.6)			.
10	. 153 (56)	. 167 (8.0)			.
12	. 153 (59)	. 164 (9.3)			.
14	. 148 (61)	. 159 (9.7)			.
16	. 143 (70)	. 153 (11)			.

a The latter quantities are in parentheses.

b The number of carbon atoms in the alkyl group.

c The transition is monotropic.

d The sum of enthalpy changes is 4.2 kJ mol^{-1}.

homologous members covered by the smectic C phase is the widest among the present three series.

The whole members from the methoxy to decyloxy homologues of the cyclohexanone series are enantiotropically nematogenic, exhibiting an odd-even alternation in the N-I transition temperature (see Table II). Our transition temperatures for the first member agree well with those by Vorländer but those for the second are higher by about 5°C. In contrast to the foregoing series, the nematic phase is thermodynamically stable over the range from 12°C for the methoxy homologue to 38°C for the butoxy one. The nonyloxy and decyloxy homologues exhibit a smectic A phase and the latter and higher members exhibit a smectic C phase.

The N-I transition was measurable for the methoxy to decyloxy homologues of the cycloheptanone series but not for the propoxy one (see Table III). Besides, the transitions in the first and fifth members are monotropic. In this series, the temperature range of stable existence of the nematic phase is again narrow; namely, 2°C for the butoxy homologue and 16°C for the octyloxy one. No smectic A phase

TABLE II

Transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) of 2,6-bis(4-alkoxybenzylidene)cyclohexanones[a]

n[b]	K	S_C	S_A	N	I
1	. 161 (20)			. 173 (0.5)	.
2	. 151 (23)			. 182 (1.1)	.
3	. 123 (25)			. 150 (1.1)	.
4	. 113 (46)			. 151 (1.3)	.
5	. 117 (25)			. 139 (1.3)	.
6	. 117 (28)			. 141 (1.7)	.
7	. 116 (28)			. 136 (1.6)	.
8	. 115 (31)			. 135 (2.1)	.
9	. 115 (61)		. 121 (0.3)	. 130 (2.6)	.
10	. 111 (24)	. 128[c]	. 130[c]	. 132[c]	.
12	. 103 (61)	. 130 (9.0)			.
14	. 107 (65)	. 127 (11)			.
16	. 107 (87)	. 118 (13)			.

[a] The latter quantities are in parentheses.

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

[c] The sum of enthalpy changes is 6.5 kJ mol^{-1}.

is observable for the cycloheptanone derivative and the appearance of a smectic C phase is limited to the dodecyloxy to hexadecyloxy homologues.

The N-I and S_C-N/I transition temperatures in the present three series are depicted in Figure 1. On replacing of the cyclopentanone ring with the cyclohexanone ring, the N-I transition temperature is depressed, by 17°C in the case of the methoxy homologue and by 35°C in the case of the hexyloxy one. The temperature is further and more significantly lowered by the replacement of the central ring with a cycloheptanone. The reduction is as large as 58°C in the first homologous member and 33°C in the last one. The variation in the structure of cycloalkanone moiety should account for the following characteristic features: (1) the decrease in the N-I and/or S_C-N/I transition temperatures and (2) the decrease in the incidence of a smectic C phase.

These cycloalkanone rings are appreciably broader than a 1,4-phenylene group. While the breadth of a 1,4-phenylene group is about 0.66 nm, those of cyclopentanone, cyclohexanone, and cycloheptanone are about 0.75, 0.78, and 0.81 nm, respectively. The difference in the breadth between the 1,4-phenylene and cyclohexanone rings is well compared with that associated with the introduction of a

TABLE III

Transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) of 2,7-bis(4-alkoxybenzylidene)cycloheptanones[a]

n[b]	K		S_C		N		I
1	.	128 (32)			[.	115 (0.9)][c]	.
2	.	133 (38)			.	141 (1.7)	.
3	.	142 (41)					.
4	.	113 (47)			.	115 (1.5)	.
5	.	101 (41)			.	101 (1.3)	.
6	.	92 (54)			.	104 (1.6)	.
7	.	85 (57)			.	98 (1.5)	.
8	.	85 (46)			.	101 (2.1)	.
9	.	89 (57)			.	98 (2.3)	.
10	.	87 (53)			.	99 (3.2)	.
12	.	88 (66)	.	102 (8.5)			.
14	.	94 (73)	.	98 (12)			.
16	.	96 (91)	.	98 (14)			.

a The latter quantities are in parentheses.

b The number of carbon atoms in the alkyl group.

c The transition is monotropic.

bromine atom as a lateral substituent to a phenyl or phenylene group. Such a broadening of the molecule is well known to result in the lowering of melting and clearing points because of the decreased intermolecular interactions.[11] For example, the N-I transition temperature of bis(4-hexyloxybenzylidene)-1,4-phenylenediamine is depressed from 245°C to 183°C by the chlorination at the 3-position of the central phenylene ring. Furthermore, the substitution eliminates the smectic phase appearing in the butoxy to heptyloxy homologues.[12] Thus, the above-mentioned tendencies may be explained, at least qualitatively, by the increase of the size of the central cycloalkanone moiety alone.

However, there is another factor to be considered; that is the effect of molecular geometry. Although the molecular cores of the cyclopentanone and cyclohexanone derivatives were established by structural analyses to be essentially linear,[6,7] the terminal C—O bonds are not towards each other in the same direction. The molecular models suggest that the angle between these bonds would be about 135° in the cyclopentanone derivatives, about 160° in the cyclohexanone derivatives, and about 170° in the cycloheptanone derivatives. Earlier, we examined the phase diagram of a binary system in order to estimate virtual N-I and S_A-N/I transition

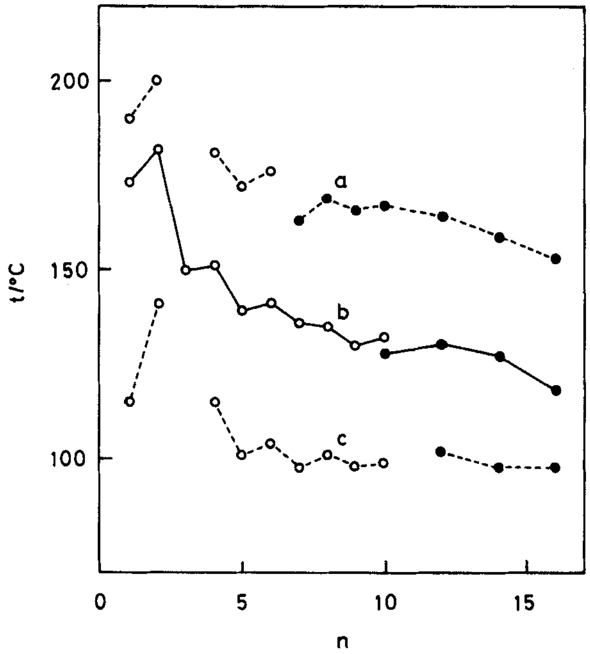


FIGURE 1 Plots of N-I (○) and S_C-N/I (●) transition temperatures against the number of carbon atoms (n) in the alkyl group. (a) cyclopentanone, (b) cyclohexanone, and (c) cycloheptanone derivatives.

temperatures of 4-[3-(4-dodecyloxybenzoyloxy)benzylideneamino]azobenzene and suggested that molecules with an obtuse-angled configuration tend to be smectogenic rather than nematogenic.[8] Indeed, our work on 1,3-phenylene bis[4-(4-alkoxyphenyliminomethyl)benzoates] revealed that the only mesophase exhibited by all the methoxy to hexadecyloxy homologues is of the smectic C type.[10] Consequently, the increase in the angle between the two terminal C—O bonds by the increase in the size of the central cycloalkanone moiety may account for the observed decrease of the incidence in a smectic C phase.

In order to explain the above-mentioned two characteristic features, whether these two factors are simultaneously operating in the present compounds or not may be judged by the consideration of values of the N-I transition temperatures. According to Vorländer's work, the mesophase appearing in bis[4-(4-ethoxyphenylazo)phenyl]terephthalate, a linear five-ring system, is thermodynamically so stable that the clearing point is higher than 322°C and not observable because of the thermal decomposition.[13] On the other hand, the isophthalate melts at 260°C, producing a mesophase stable only up to 266°C. The clearing point of the hexyloxy homologue in the cyclopentane series is lower by 69°C than that of the aforementioned linear 1,4-phenylenediamine derivative and the temperature range of the stable existence of the nematic phase is as narrow as 2°C. These observations are in conformity with our proposition that the molecule of the cyclopentanone derivative is appreciably bent. On going from the cyclopentanone derivative to the cyclohexanone derivative, the molecular linearity is significantly improved, whereas the molecular breadth is definitely increased. As a result, the nematic phase becomes thermodynamically stable in a broader temperature range, even though the clearing point is markedly depressed. The broadening effect is dominant when the cyclohexanone moiety is replaced by a cycloheptanone moiety. So, the clearing point is further lowered and the temperature range of stable existence of the nematic phase is again diminished.

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