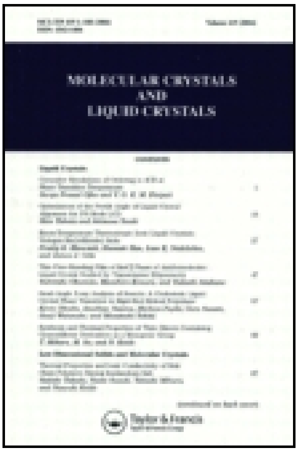

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: Y. Matsunaga & T. Yuri (1993): Mesomorphic Behavior of N,N′- Bis[4-(4-alkoxybenzoyloxy) benzylidenel- 3,3′-diaminodiphenylsulfones, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 237:1, 145-150

To link to this article: http://dx.doi.org/10.1080/10587259308030130

Mol. Cryst. Liq. Cryst., 1993, Vol. 237, pp. 145–150
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Printed in the United States of America

Mesomorphic Behavior of *N*,*N*′-Bis[4-(4-alkoxybenzoyloxy)benzylidene]-3,3′-diaminodiphenylsulfones

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(Received October 6, 1992; in final form December 8, 1992)

A new series of sulfur ligated siamese twin mesogens, *N*,*N*′-bis[4-(4-alkoxybenzoyloxy)benzylidene]-3,3′-diaminodiphenylsulfones has been studied for the thermotropic phase transition behavior. A stable or metastable nematic phase is exhibited by the methoxy to tetradecyloxy derivatives and a metastable smectic C phase by the dodecyloxy to octadecyloxy derivatives.

Keywords: siamese twin mesogens, nematic, smectic

INTRODUCTION

Studies on siamese twin mesogens were initiated by Griffin *et al.*[1] They bridged two *N*-(4-alkoxybenzylidene)-4-alkoxyaniline units by a methylene group at the 3-positions of the aniline moieties. The twins were capable of mesomorphic behavior only if the terminal groups are of sufficient length. A thermodynamically stable smectic C phase was observed for their twins when the octyl or decyl group was employed for the benzylidene moiety and the octyl, nonyl, or decyl group for the aniline moiety. Assuming the parallel orientation of the two molecular units, the authors discussed the geometrical arrangement possible for the twin molecule.

Then, Dehne *et al.* studied the compounds in which two methyl 4-(4-alkoxybenzoyloxy)benzoate or analogous units are joined by sulfur, sulphinyl, and sulfonyl groups, respectively.[2] Although all the compounds are similar in molecular structure, the mesomorphic properties are distinctly different from each other. The sulfides are not mesogenic at all, the sulfoxides show only a metastable nematic phase even when an alkyl group as long as octyl is employed, and the sulfones can show a stable nematic phase if the alkyl group is hexyl or longer. They carried out dielectric measurements on magnetically oriented samples and obtained the die-

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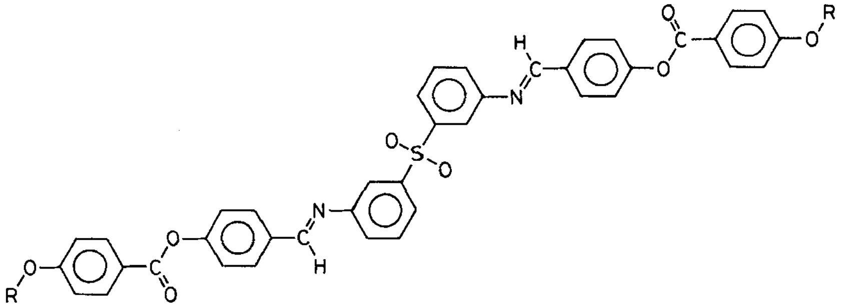
lectric constant explainable only if the two units in a twin molecule are arranged antiparallel to each other.

Recently, the molecular structure of 3,3′-sulfur-bis[methyl 4-(4-methylbenzoyloxy)benzoate] was examined by Baumeister *et al.* taking it as a model of sufur-ligated siamese twin mesogens.[3] The molecular geometry is far from common shapes for mesogenic compounds. The two substituted phenyl benzoate units are oriented antiparallel in conformity with the conformation proposed earlier. The substituted benzoate unit is, in most, extended and of nearly linear shape, but the plane of the 4-methylphenyl ring is almost perpendicular to that of the benzoate ring. Thus, the molecule is of the C_2 symmetry and gabled-roof-like. Our interests in mesogenic compounds with unconventional molecular structure[4,5] led us to examine the thermal behavior of *N*,*N*′-bis[4-(4-alkoxybenzoyloxy)benzylidene]-3,3′-diaminodiphenylsulfones in which the molecular unit carries only one terminal substituent.



EXPERIMENTAL

4-(4-Alkoxybenzoyloxy)benzaldehydes were prepared by a reaction between 4-alkoxybenzoic acids with 4-hydroxybenzaldehyde in chloroform, following the procedure of Hassner and Alexanian.[6] The desired compounds were obtained by condensing the benzaldehyde derivatives with 3,3′-diaminodiphenylsulfone in boiling ethanol, adding a catalytic amount of glacial acetic acid. The products were purified by recrystallization from mixtures of ethanol and toluene until a sharp mesomorphic-isotropic transition was recorded on the DSC curve. For example, Found: C, 72.47; H, 6.27; N, 3.07%. Calcd for $C_{54}H_{56}N_2O_8S$ (the heptyloxy derivative): C, 72.62; H, 6.32; N, 3.14%.

The mesophases were identified by examination of their textures using a polarizing microscope in conjunction with a heated stage. The transition temperatures and associated enthalpies were determined by calorimetric curves recorded on a Rigaku Denki Thermoflex differential scanning calorimeter. A phase diagram was determined by the calorimetric curves of mixtures recorded at every ten mol%. The afore-mentioned phase assignment is supplemented by X-ray diffraction measurements.

RESULTS AND DISCUSSION

The thermodynamic data are summarized in Table I and the transition temperatures are plotted against the number of carbon atoms in the alkyl group in Figure 1. Here, K, S_C, N, and I denote the crystalline, smectic C, nematic, and isotropic phases, respectively. Note that all the compounds carrying methoxyl to octadecyloxyl groups are mesogenic. Griffin *et al.* remarked that the alkoxy chain of their twins has to be considerably longer than is usually necessary before a mesophase is seen. This contrast may be understood as indicating enhanced mesophase stability for our six-ring system relative to their four-ring system. It may be added that even the unit compound with the shortest alkoxyl group, *N*-[4-(4-methoxybenzoyloxy)-benzylidene]aniline is highly nematogenic and shows a solid-nematic transition at 129°C and a nematic-isotropic transition at 177°C.[7]

The mesophase exhibited by the methoxy to undecyloxy derivatives is highly

TABLE I

Transition temperatures (°C) and associated enthalpies (kJ mol^{-1}) of *N,N'*-bis[4-(4-alkoxybenzoyloxy)benzylidene]-3,3'-diaminodiphenylsulfones[a]

n[b]	K	S_C	N	I
1	. 218 (58)		[. 210 (2.1)][c]	.
2	. 202 (62)		. 213 (2.7)	.
3	. 205 (77)		[. 193 (2.6)][c]	.
4	. 206 (79)		[. 192 (2.8)][c]	.
5	. 181 (73)		. 188 (2.7)	.
6	. 161 (56)		. 175 (3.3)	.
7	. 148 (46)		. 166 (3.1)	.
8	. 151 (54)		. 161 (3.3)	.
9	. 156 (56)		[. 154 (3.0)][c]	.
10	. 162 (63)		[. 152 (3.4)][c]	.
11	. 160 (64)		[. 149 (3.2)][c]	.
12	. 156 (66)	[. 122 (1.3)][c]	[. 147 (3.6)][c]	.
14	. 142 (67)	[. 138 (2.8)][c]	. 143 (4.3)	.
16	. 151 (76)	[. 147 (12)][c]		.
18	. 151 (84)	[. 149 (14)][c]		.

[a] The latter quantities are in parentheses.

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

[c] Monotropic transition.

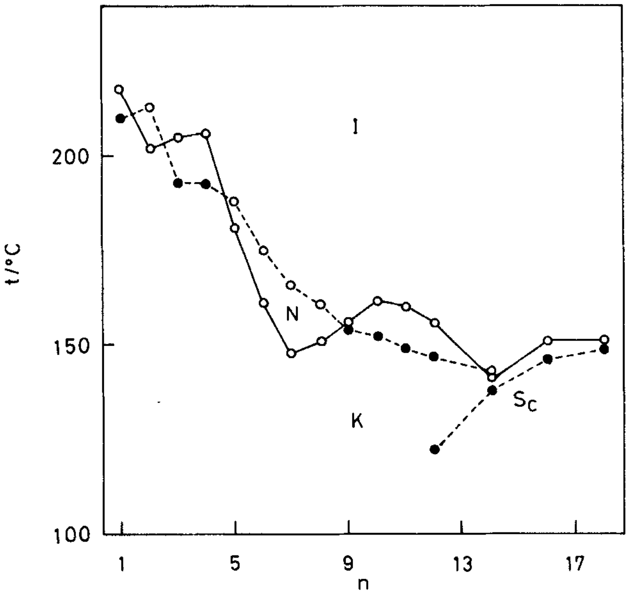


FIGURE 1 Plots of transition temperatures against the number of carbon atoms (n) in the alkyl group. The shaded circles represent monotropic transitions.

fluid and displays marble and/or schlieren textures under a crossed polarizing microscope, indicating that the phase is nematic in type. The magnitude of enthalpy changes at clearing point, 2.1 to 4.3 kJ mol^{-1} is typical for N-I transitions as compiled by Demus *et al.*[8] Of the fifteen compounds examined, those with $n = 2$, 5, 6, 7, 8, and 14 exhibited an enantiotropic transition. The temperature range of stable existence is 10 to 18°C.

In addition to the nematic phase, the dodecyloxy and tetradecyloxy derivatives exhibit a metastable smectic phase. This phase displays also a schlieren texture. No nematic phase but the smectic phase of the same type is observable for the higher homologous members. The above-mentioned texture and large enthalpy changes at the smectic-isotropic transition, 12 and 14 kJ mol^{-1}, are indicative of the C type.

In order to support the identification of mesophases, the phase diagram of a binary system consisting of the dodecyloxy derivative and the corresponding unit compound, *N*-[4-(4-dodecyloxybenzoyloxy)benzylidene]aniline was examined. The latter compound melts at 111°C. The smectic phase appearing by melting is transformed into a nematic phase at 126°C and then into an isotropic liquid at 135°C. As is shown in Figure 2, the eutectic point is located at 95°C and about 95 mol% of the unit compound. The N-I transition curve connecting the monotropic transition of the twin and the enantiotropic one of the unit compound is met by the freezing point curve of the former compound at 140°C and 60 mol%. As the N-I transition temperature is practically independent of the composition around this intersection, no horizontal line arising from this point is detectable. The S-N transition temperature of the twin is rapidly depressed by the addition of the unit compound and is no longer observable at 20 mol%. On the other hand, the S-N

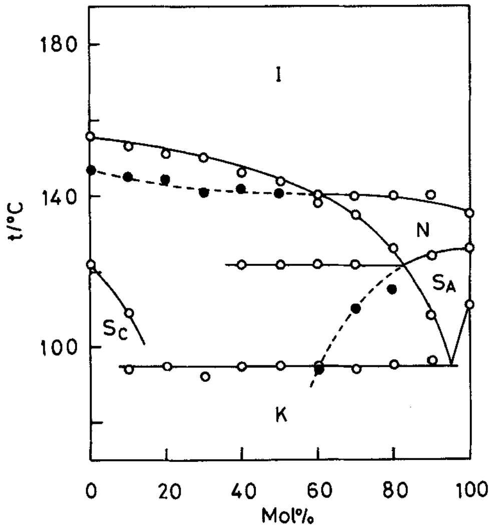


FIGURE 2 Phase diagram of the binary system consisting of the dodecyloxy derivative and *N*-[4-(4-dodecyloxybenzoyloxy)benzylidene]aniline. The latter compound is located on the right hand-side. The shaded circles represent monotropic transitions.

transition curve of the unit compound meets the freezing point curve of the twin at 122°C and 83 mol% and the horizontal line separating between the smectic and nematic phases both with the coexisting solid twin can be seen down to 40 mol%. The X-ray diffraction measurement of the smectic phase exhibited by the unit compound revealed that the layer spacing is 3.42 nm in agreement with the calculated molecular length of 3.46 nm. Therefore, the phase must be of the smectic A_1 type. On the other hand, the dodecyloxy derivative yields a spacing of 4.06 nm, suggesting that the smectic phase is of the A_d type if it is not of the C type. The presence of a miscibility gap between the smectic phases given by these two compounds favors our afore-mentioned assignment though this observation alone cannot be conclusive evidence that the smectic phase is of the C type because the smectic A_1 and A_d phases are known to be not necessarily miscible with each other.[9]

The X-ray diffraction patterns indicate the absence of in-plane order and the layer spacings (*d*/nm) are approximated by $d = 1.96 + 0.174n$, where n is the number of carbon atoms in the alkyl group. The length, 1.96 nm, which is the projection along the layer normal of the molecular core, is almost the same as the length of a unit molecular core. The increment per carbon atom exceeds markedly that for the most extended configuration of a single alkyl group, indicating the presence of the groups extended outwards in both directions to the layer boundaries. Unless the alkyl groups are interdigitated and/or conformationally disordered, their mean tilt angle may be about 46°.

The parallel arrangement of the two units in a twin molecule leads to a partial-bilayer structure which is foreseeable only when the alkyl group is tilted by 46° relative to the long axis of the molecular core. Such a model contradicts our observation that the smectic layer spacing observed for the unit compound agrees well with the molecular length, and it does not seem plausible.

The tilt angle of the molecular core may be as large as 60° if the two units in a twin molecule are in an antiparallel arrangement. The smectic C phase in the present series first appears when $n = 12$; therefore, the tilt angle of the whole molecule may be reduced to about 50°. This value seems to be reasonable since the present smectic C phase belongs to the subgroup which goes directly over into a nematic or isotropic phase.[10]

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