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Anselm C. Griffin [a], Neal W. Buckley [a], William E. Hughes [b] & David L. Wertz [a]

[a] Departments of Chemistry, University of Southern Mississippi, Hattiesburg, MS, 39401

[b] Departments of Physics & Astronomy, University of Southern Mississippi, Hattiesburg, MS, 39401

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EFFECT OF MOLECULAR STRUCTURE ON MESOMORPHISM.11.[1] A SIAMESE TWIN LIQUID CRYSTAL HAVING TWO INDEPENDENTLY SMECTOGENIC CONFORMATIONS

ANSELM C. GRIFFIN,[a] NEAL W. BUCKLEY,[a] WILLIAM E. HUGHES[b] and DAVID L. WERTZ[a]
Departments of Chemistry[a] and Physics & Astronomy[b]
University of Southern Mississippi
Hattiesburg, MS 39401

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Abstract: Two different molecular conformations of a particular Siamese Twin liquid crystal can, independent of each other, give rise to a smectic C phase. X-ray diffraction results are presented from which it is concluded that there are two possible conformations of this molecule in the solid state and that different smectic C layer types can be formed by melting these different solid state conformations.

We wish to report that for a Siamese Twin[2] liquid crystalline Schiff's base we have obtained, by x-ray diffraction, the following results:

i. From a solvent precipitated sample (no previous thermal history) only a single small angle diffraction ring in the room temperature solid state is obtained. This ring is retained as the only small angle diffraction ring in the smectic C mesophase of this material. (see Table 1)

ii. From a melt solidified sample there is obtained at room temperature a single small angle diffraction ring which carries over as the only small angle diffraction ring in the smectic phase. This ring, however, is not the same as that in i above.

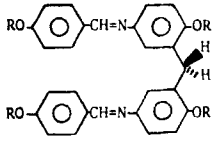
It is generally assumed[3-6] that distances corresponding to these small angle diffraction maxima correspond to the thickness of smectic layers. Compound 1 can therefore form two different types of layers in the smectic C phase dependent on the

solid phase from which the smectic phase was formed.

iii. A sample which had been heated as it was being packed into the quartz x-ray capillary tube exhibited two low angle diffraction rings in both the solid state and the smectic C mesophase. These rings were identical to those described above in i and ii.

Presumably the moderate heating interconverted some of the conformers.

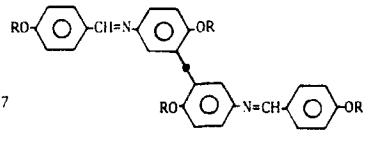
The compound under study is shown below in its two mesogenic conformations.



1a

$R=nC_{10}H_{21}$

$K113.5S_c131.5I$[7]



1b

Although we[7] previously considered only conformation 1a for these Twins, careful examination of space filling molecular models led us to conclude that conformation 1b is also stable and is compatible with mesomorphic behavior of the Twins. It can be seen from the Table that the 'half-Twin' mesogen (sample IV) has a single small angle diffraction maximum corresponding to 32 ± 3Å[8] which corresponds reasonably well with the molecular length of the compound as measured from space-filling models, (41Å). This extent of agreement is commonly found for smectic C materials. The Twin compound (samples I and III) also has a diffraction maximum corresponding to 32 ± 3Å, which is similar to that of the 'half Twin'. The other diffraction maximum of the Twin material (Samples I and II) corresponds to a distance of several Angstroms less, 23 ± 3Å. This was at first quite puzzling since conformation 1b has a fully stretched head-to-toe molecular length several Angstroms longer than that for 1a and conventional analysis leads one to expect a longer distance (greater layer thickness) to arise from conformation 1b.

Construction of molecular models for the mesophase with the requirement of a minimum of void space between molecules provided the solution. For molecules in

Table 1

X-ray Diffraction Maxima of Unoriented Powder Samples

Sample	Compound	Diffraction Maxima (Å)	Temp.	Conditions/ Comments
I	1a,b	32 ± 3[a,8] 23 ± 3[a,8] 5.0 ± 0.1[b,8]	125°C	Sample was briefly heated while being packed into capillary: then placed into heater; heated from 28° to 125°. Intensities of the two inner rings varies only slightly during prolonged heating at 125°.
II	1b	23 ± 3[a,8] 5.0 ± 0.1[b,8]	28°C	solvent precipitated sample; no prior thermal treatment.
	1b	23 ± 3[a,8] 5.0 ± 0.1[b,8]	122°C	same sample as above; placed in heater preset at 122°C. Five photographs were taken at 80 minute intervals during the 122°C regimen. The first one of the five showed a very weak maximum at 31Å. The later four showed no trace of the 31Å ring.
III	1a	32 ± 3[a,8] 5.0 ± 0.1[b,8]	28°C	melt solidfied sample
	1a	32 ± 3[a,8] 5.0 ± 0.1[b,8]	122°C	same sample as above; placed in heater preset at 122°C. Five photographs were taken at 80 minute intervals during the 122° regimen. All five were identical.
IV	See (c)	32 ± 3[a,8] 32 ± 3[a,8]	108°C Sc phase 109°C Sc phase	different samples

a) small angle maxima were converted into distances using the Bragg relation $n\lambda=2d\sin\theta$ where n=1

b) high angle maxima were converted into distances using $n\lambda=1.17(2d\sin\theta)$ taken after A. deVries, Pramana, supplement no.1, 93 (1975).

c) $C_{10}H_{21}O$-⟨○⟩-CH=N-⟨○⟩-$OC_{10}H_{21}$, 'half-Twin', K104S_c112I

conformation 1b the Twin is composed to two halves which are translationally skewed and give rise to the molecular shape depicted below. In order to pack molecules of this

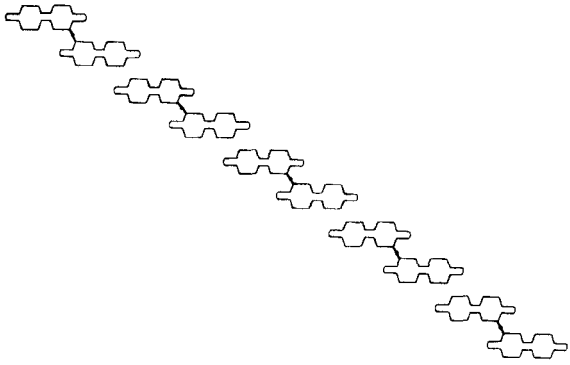


Figure 1. Molecular shape of conformation 1b.

shape into a parallel layered arrangement and at the same time introduce a minimum of void space, we propose the arrangement below. The distance between the resulting

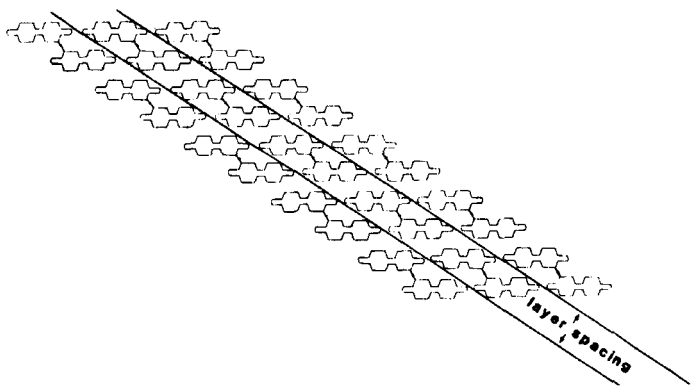


Figure 2. Smectic layers of molecules in conformation 1b.

layers is roughly 25Å depending on the exact conformation of the tails, corresponding to the heretofore unexplained 23Å distance found in the x-ray diffraction patterns of

samples I and II. Thus conformation 1b, having the greater head-to-toe molecular length, is responsible for the smaller x-ray diffraction distance. Conformation 1a, with its smaller molecular length, gives rise to smectic C layers having the greater associated distance (virtually identical to that of the 'half-Twin') due to the non-skewed allignment of component halves of the Twin molecule. The mesophase of sample I is, in our opinion, composed of two types of smectic layers segregated into domains of different layer thicknesses. Due to the extreme difficulty in interconverting conformations 1a and 1b (extremely non-planar conformers are involved) they are not able, on our time frame, to interconvert in the mesophase. Unless they are accidentally isoenergetic conformations, either 1a or 1b is more stable than the other. Our experiment does not directly allow the determination of which is the thermodynamically favored structure, but it is clear that one of the conformations is a 'kinetic' one. This finding of 'kinetic' mesophase structures substantiates the predictions made previously by one of us.[9] Preliminary x-ray diffraction results on other homologues in this series indicate similar behavior. The dependence of smectic structure on thermal history of the sample may also help explain the recent conflicting reports[10,11] of the small angle x-ray diffraction maxima of 4-pentyloxybenzylidene-4'-heptylaniline.

EXPERIMENTAL

All data were taken on a General Electric XRD-700 diffractometer using a transmission Polariod Laue cassette assembly installed on a vertically mounted CA-8S Cu-target tube operated at 45kV and 18mA. Polariod type 57 film was used, and the radiation was filtered prior to diffraction by a single layer of 0.0035 inch nickel foil. The sample-to-film distance was 15.49 ± .08cm.

The samples were contained in 1.5 mm quartz capillary tubes and mounted in a hot stage of our own design. The hot stage temperature was constant to ±0.5°C for the entire x-ray exposure time.

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