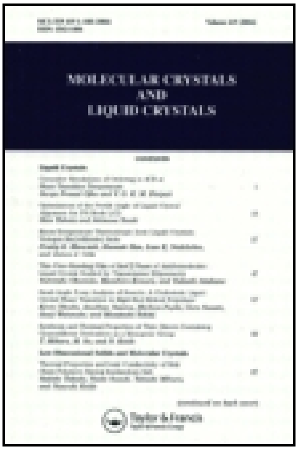

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Pressure-Temperature Phase Diagram of Some Tilted Smectic Phases

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PRESSURE-TEMPERATURE PHASE DIAGRAM OF SOME TILTED SMECTIC PHASES

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ABSTRACT

The pressure-temperature phase diagram of 4-(2′ methylbutyl)phenyl 4′-n-nonyloxybiphenyl-4-carboxylate (9OSI) has been determined by optical microscopy and found to be extremely linear. This compound exhibits smectics A,C,I,G′ and H′ phases. X-ray measurements on polycrystalline samples are also discussed.

We have measured the pressure-temperature phase diagram of a racemic composition of 9OSI (4-(2′-methylbutyl)phenyl 4′-n-nonyloxybiphenyl-4-carboxylate).[1] The molecular structure of this compound is shown inset in Fig. 1. It is of interest due to its large number of smectic phases in a convenient temperature range. At one atmosphere, 9OSI exhibits the following phase transitions:[2]

$$\text{solid} \xleftarrow{25^\circ C} \text{smectic H}' \xleftrightarrow{60^\circ C} \text{smectic G}' \xleftrightarrow{73.5^\circ C} \text{smectic I}$$

$$\xleftrightarrow{78.9^\circ C} \text{smectic C} \xleftrightarrow{134.1^\circ C} \text{smectic A} \xleftrightarrow{168^\circ C} \text{nematic} \xleftrightarrow{170.6^\circ C} \text{isotropic;}$$

melting point 82°.

The structure of the smectic A and C phases are well known. The smectic I phase[3] is one in which the molecules are tilted in the layers and arranged in a hexagonal array within each layer. The tilt direction in reciprocal space is toward the apex of the hexagon.[1–4] There is no long range positional order either within or between the layers, however, the phase does exhibit long range bond orientational order in 3-dimensions. The smectic I phase is immiscible with the smectic F phase[5] in which the tilt direction in reciprocal space is towards a hexagon side[4] and not the apex and which also lacks long range positional order. An example of the smectic F phase is given by TBPA (terephthalylidene-bis-4-n-pentylaniline)[4] which exhibits nematic and smectic A,C,F,G and H phases. In the smectic G and H phases[6], the direction of tilt relative to the hexagonal packing remains the same as in the smectic I or F phase but they are both crystalline in nature. However, G and H phases of differing relative tilt directions have not as yet been shown to be immiscible by conventional methods, consequently, they have been categorized as G′ and

$H'^{(2)}$ with a smectic I type tilt and G and H with a smectic F type tilt.

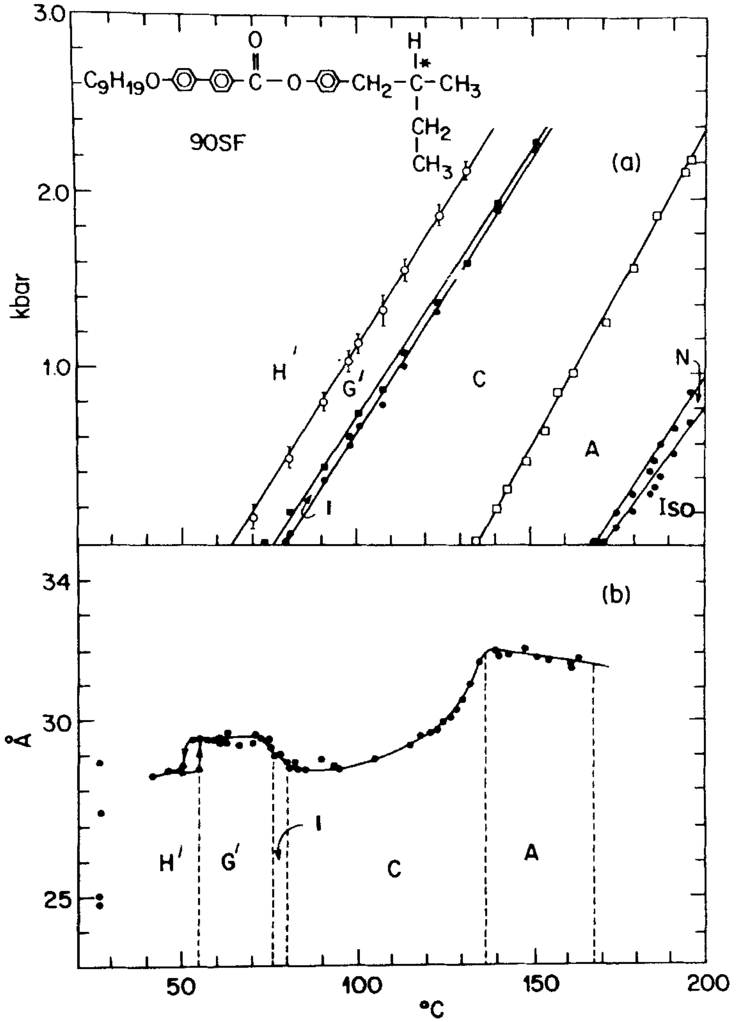

Fig. 1. (a) P-T phase diagram of 9OSI. b) Measured layer spacing at one atmosphere. The points on the left are the lengths observed in the solid phase.

Fig. 1(a) shows the pressure-temperature phase diagram of 9OSI found using a pressure bomb especially designed for the optical microscope.[7] The most striking feature of the phase diagram is the straightness of the transition lines. Also, note the apparent increase in stability of the smectic A phase relative to the smectic C phase with increasing pressure. This seems to be a characteristic of smectic A phases exhibited by ester compounds with two symmetrically disposed chains.[8–10] This may be due to the strong short-range repulsive interactions of the lone pairs of electrons of the oxygen atoms of the ester and alkoxy functional groups.

Another characteristic of the oxy esters is their tendency to form ordered orthogonal smectic phases in which there is an absence of long-range positional ordering of the molecules, but in which there is a long-range correlation of the orientation of the hexagonal net. These phases are known as hexatic B.[11,12] However, in the case of the analogous tilted smectic I and F phases, esters predominantly exhibit smectic I phases in preference to smectic F phases whereas smectic F phases appear to be preferred by compounds containing a Schiff's base linkage.[5] It should be noted, however, that some Schiff's bases do exhibit smectic I phases.[13]

The A-C and C-I transition lines in Fig. 1(a) project to an A-C-I triple point at 13.7 kbars and 517°C.

Table I The parameters of Fig. 1(a). T_0 is the zero pressure intercept.

Transition	dP/dT(kbar/°C)	T_0(°C)
N-Iso	37.7	170.6
N-A	33.4	168.0
A-C	27.9	134.3
C-I	32.0	79.2
I-G′	33.2	75.8
G′–H′	31.7	63.8

The slopes and zero pressure intercepts of the lines in Fig. 1a are shown in Table I. The almost parallel nature of the I, G and H transition lines with the N-A line is remarkable. In particular, the temperature range of the smectic I phase is relatively short and relatively constant with pressure.

Fig. 1(b) shows that the layer spacing changes continuously throughout the smectic I range of 9OSI. This may be different from the behavior of the smectic I phase of 8OSI[4] (4-(2′ methylbutyl)phenyl 4′-n-octyloxybiphenyl -4-carboxylate) where the layer spacing seems rather constant throughout the I phase and, correspondingly, may even have decreased somewhat in the F phase of TBPA.

We define a tilt angle, θ, as being

$$\cos\theta = d_x/d_A$$

where d_A is the longest layer spacing observed in the A phase and d_x is the layer spacing observed in the smectic X phase where X = C, I, G′ or H′. Fully extended, in its all *trans* conformation, 9OSI is 35Å long. The longest observed smectic A layering is 32Å. The relatively large difference between the fully extended all *trans* conformation and the observed smectic A layer spacing also seems to be a characteristic of compounds with an ester function. From Fig. 1(b), we see that the tilt angle increases continuously throughout the smectic C phase reaching a saturated value of 27.5°. The tilt then remains fairly constant for the rest of the C phase and begins to decrease with the onset of hexagonal ordering in the smectic I phase. It continues its decrease throughout the smectic I phase and the start of the smectic G′ phase levelling off about 5°C below the smectic G′-I transition with a tilt of ~23°. The onset of the H′ phase is signalled by an abrupt change in tilt back to the previously observed saturated value in the C phase of 27.5°. A relatively large hysteresis (for a liquid crystal-liquid crystal transition) was observed at the smectic G′ - smectic H′ transition.

CONCLUSION

We have studied the behavior as a function of pressure of the liquid crystal phases of 9OSI. Consistent with other ester compounds, its smectic A phase is piezo-resistant. We have found that under pressure the smectic I, G′ and H′ phases of this compound behave remarkably alike. A detailed study of the layer spacing as a function of temperature at one atmosphere revealed that the tilt angle saturated in both the C and G phases and increased continuously through out the I phase. The smectic H′ phase was characterized by the saturated G′ phase tilt abruptly switching, with hysteresis, to the value of the saturated C phase tilt.

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[13] e.g. TBDA (terephthalylidene-bis-4-n-decylaniline) exhibits both I and F phases but, to-date, we don't know of any esters which exhibit smectic F phases.