

RE-ENTRANT NEMATIC PHASE IN PURE COMPOUNDS AT ATMOSPHERIC PRESSURE

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CLADIS<sup>1</sup> discovered that binary mixtures of certain mesogenic cyano-compounds exhibit the following interesting sequence of phase transitions on cooling: isotropic → nematic → smectic A → nematic. The second nematic phase, which occurs at a lower temperature than the smectic phase is called the 're-entrant nematic' phase (in analogy with similar 're-entrant' phases observed in superconductors, He-3, etc.). More recently, Cladis *et al.*<sup>2,3</sup> also observed the re-entrant nematic phase in pure cyano-compounds at elevated pressures. Beyond a certain pressure, the smectic phase disappears altogether, implying that it occurs only in a relatively small area in the P-T phase diagram.

All these compounds have a highly polar cyano-group attached to one end of the molecule, which results in strong antiparallel correlations between neighbouring molecules<sup>4</sup>. This, in turn, leads to a bilayer structure with interdigitated molecules in each bilayer<sup>5</sup>. As the temperature and pressure are varied, the molecular packing is altered slightly, and the resulting subtle changes in the bilayer structure appear to be responsible for the occurrence of the re-entrant nematic phase. Up to now, this phase has only been observed either in mixtures<sup>1,6</sup> or at high pressures in single component systems<sup>2,3</sup>.

We have now observed, for the first time, the re-entrant nematic phase in three pure compounds at

atmospheric pressure. The compounds were recently synthesized in our laboratory<sup>7,8</sup>. The molecular structures are shown in Fig. 1.

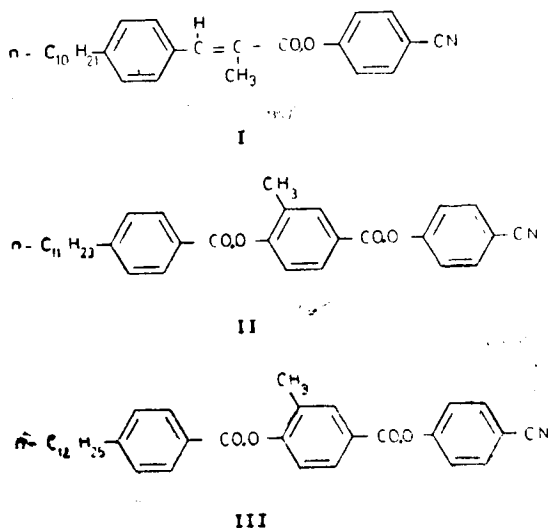


FIG. 1. Molecular structures of (I) *trans-p-n*-decyloxy-*a*-methyl-*p'*-cyanophenyl cinnamate, (II) 4-cyano-phenyl-3-methyl-4 (4-*n*-undecyl benzyloxy) benzoate and (III) 4-cyano-phenyl-3-methyl-4 (4-*n*-dodecylbenzyloxy) benzoate.

TABLE I

	Heating		Cooling	
Compound I	solid-nematic nematic-isotropic	62.8° C 73.5° C	isotropic-nematic nematic-smectic A smectic A-re-entrant nematic re-entrant nematic-solid	73.5° C 56.8° C 32.5° C ~32° C
Compound II	solid-smectic A smectic A-nematic nematic-isotropic	103° C 127° C 152.5° C	isotropic-nematic nematic-smectic A smectic A-re-entrant nematic re-entrant nematic-solid	152.5° C 127° C (14.7 J/mole) 78.5° C (15.4 J/mole) ~65° C
Compound III	solid-smectic A smectic A-nematic nematic-isotropic	102° C 138.5° C 148° C	isotropic-nematic nematic-smectic A smectic A-re-entrant nematic re-entrant nematic-solid	148° C 138.5° C (255 J/mole) 59.8° C (46.4 J/mole) ~56° C

In the case of compound I the crystal, on heating, melts directly to the (normal) nematic phase. In the other two cases, it melts to the smectic A phase, which then goes over to the nematic phase at a higher temperature. On cooling, the normal nematic phase transforms first to the smectic A phase, which on super-cooling gives the re-entrant nematic phase, metastable with respect to the crystalline phase (see Table I). The re-entrant nematic phase was identified by the typical schlieren textures, mobility of the phase when the cover slip is displaced, and by its miscibility with other nematic compounds.

In compound I, the re-entrant phase occurs just before solidification (at  $\sim 32.5^\circ\text{C}$ ) on cooling the smectic A phase very rapidly. In fact in ref. 7, the phase was reported to be a smectic phase exhibiting a schlieren texture, but we have now confirmed by miscibility studies that it is indeed the re-entrant nematic phase. In compounds II and III, the re-entrant nematic phase is formed more readily and the crystallisation occurs well below the smectic A-re-entrant nematic transition point (see Table I), even when the sample is cooled relatively slowly. The transition points could be determined on a Mettler hot stage (Model FP 52), as well as from thermograms taken on a differential scanning calorimeter (Perkin-Elmer, Model DSC-II). It is interesting to note that

heat is liberated at both the nematic-smectic A and smectic A-re-entrant nematic phase transitions. Comparing the data on the compounds II and III (Table I) it is seen that both these transitions are somewhat stronger, involving larger heats of transition, for the higher homologue, viz., compound III. Further details about the phase transitions in these compounds and some mixtures will be discussed elsewhere.

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