Molecular Packing in Mesogenic Crystals

Aspects of molecular packing in crystals of homologous series of thermal mesogens are examined in relation to the type of liquid-crystalline or plastic-crystalline behavior shown by these compounds. The series examined are the \( p \)-alkylbenzoic and \( p \)-n-alkyloxycinnamic acids, and the \( p \)-nitrophenyl- \( p' \)-n-alkoxybenzoates, which yield liquid-crystalline phases; and the polychlorinated ferroenes, which show an alternation between normal melting and plastic-crystalline behavior dependent on their chlorine content.

The liquid crystal series show the sequence of phase transitions:

\[
\text{Crystal} \rightarrow [S_a] \text{ or } [S_c] \rightarrow \{N\} \rightarrow \text{Isotropic}
\]

Compounds in these series that do not yield liquid-crystalline phases have high packing efficiencies in the solid phase. Compounds yielding only a nematic phase have low packing efficiency deriving from steric incompatibilities between the aliphatic and aromatic components of the molecules. An anomalous instance of monotropic nematic behavior is shown to be associated with a particular crystal packing mode. Compounds yielding smectic phases all show some form of packing with two- or three-dimensional arrangements involving segregation of cores and chains.

In the chlorinated ferroenes, the observed structures all show packing modes in which the ferrocene molecules are arranged in stacks. Those members showing plastic-crystalline behavior have a net dipole moment normal to the stack axis, whereas those showing normal melting have a zero dipole normal to that axis.

\[ \text{C}_4\text{Hg-O(\biggarrow)}\text{CH=N-}\text{C}_4\text{Hg} \]

\[ \begin{align*}
40^\circ C & \supseteq S_G \supseteq S_B \supseteq S_A \supseteq N_0 \supseteq N \supseteq 1
\end{align*} \]

Average intermolecular distances, layer spacings and apparent molecular lengths (in case of nematic) have been determined in all the three smectic and nematic phases. Orientational order parameters of the aligned sample have been determined using the X-ray diffraction data and refractive index values. The \( <P_2> \) values determined from optical measurements agree with the Maier-Saupe theoretical values, but \( <P_2> \) and \( <P_4> \) determined from X-ray intensity measurements differ from theoretical values. Detailed discussions on this problem will be presented.