

4.4. SCATTERING FROM MESOMORPHIC STRUCTURES

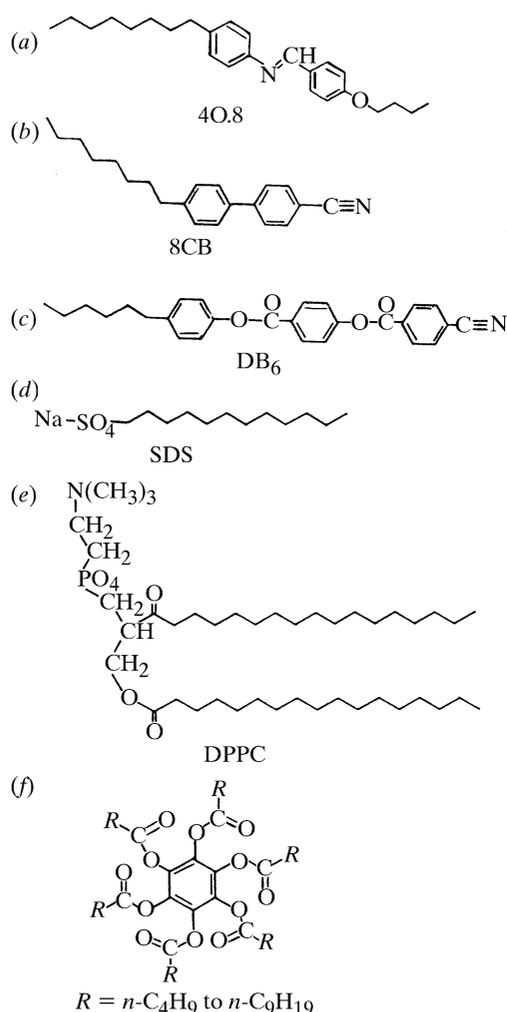


Fig. 4.4.1.3. Chemical formulae for some of the molecules that form thermotropic liquid crystals: (a) *N*-[4-(*n*-butyloxy)benzylidene]-4-*n*-octylaniline (4O.8), (b) 4'-*n*-octylbiphenyl-4-carbonitrile (8CB), (c) 4-hexylphenyl 4-(4-cyanobenzoyloxy)benzoate (DB₆); lyotropic liquid crystals: (d) sodium dodecyl sulfate, (e) 1,2-dipalmitoyl-L-phosphatidylcholine (DPPC); and a discotic liquid crystal: (f) benzenehexyl hexa-*n*-alkanoates.

that form thermotropic liquid-crystalline phases have hydrophilic and hydrophobic parts, the disparity in the affinity of these parts for either water or oil is much less and most of these molecules are relatively insoluble in water. These molecules are called thermotropic because their phase transformations are primarily studied only as a function of temperature. This is not to say that there are not numerous examples of interesting studies of the concentration dependence of phase diagrams involving mixtures of thermotropic liquid crystals.

Fig. 4.4.1.3 displays some common examples of molecules that form lyotropic and thermotropic phases. In spite of the above remarks, it is interesting to observe that different parts of typical thermotropic molecules do have some of the same features as the lyotropic molecules. For example, although the rod-like thermotropic molecules always have an alkane chain at one or both ends of a more rigid section, the chain lengths are rarely as long as those of the lyotropic molecules, and although the solubility of the parts of the thermotropic molecules, when separated, are not as disparate as those of the lyotropic molecules, they are definitely different. We suspect that this may account for the subtler features of the phase transformations between the mesomorphic phases to be discussed

below. On the other hand, the inhomogeneity of the molecule is probably not important for the nematic phase.

4.4.2. The nematic phase

The nematic phase is a fluid for which the molecules have long-range orientational order. The phase as well as its molecular origin can be most simply illustrated by treating the molecules as long thin rods. The orientation of each molecule can be described by a symmetric second-rank tensor $s_{i,j} = (n_i n_j - \delta_{i,j}/3)$, where \mathbf{n} is a unit vector along the axis of the rod (De Gennes, 1974). For disc-like molecules, such as that shown in Fig. 4.4.1.3(f), or for micellar nematic phases, \mathbf{n} is along the principal symmetry axis of either the molecule or the micelle (Lawson & Flautt, 1967). Since physical quantities such as the molecular polarizability, or the moment of inertia, transform as symmetric second-rank tensors, either one of these could be used as specific representations of the molecular orientational order. The macroscopic order, however, is given by the statistical average $S_{i,j} = \langle s_{i,j} \rangle = S(\langle n_i \rangle \langle n_j \rangle - \delta_{i,j}/3)$, where $\langle \mathbf{n} \rangle$ is a unit vector along the macroscopic symmetry axis and S is the order parameter of the nematic phase.

The microscopic origin of the phase can be understood in terms of steric constraints that occur on filling space with highly asymmetric objects such as long rods or flat discs. Maximizing the density requires some degree of short-range orientational order, and theoretical arguments can be invoked to demonstrate long-range order. Onsager presented quantitative arguments of this type to explain the nematic order observed in concentrated solutions of the long thin rods of tobacco mosaic viruses (Onsager, 1949; Lee & Meyer, 1986), and qualitatively similar ideas explain the nematic order for the shorter thermotropic molecules (Maier & Saupe, 1958, 1959).

The existence of nematic order can also be understood in terms of a phenomenological mean-field theory (De Gennes, 1969*b*, 1971; Fan & Stephen, 1970). If the free-energy difference ΔF between the isotropic and nematic phases can be expressed as an analytic function of the nematic order parameter $S_{i,j}$, one can expand $\Delta F(S_{i,j})$ as a power series in which the successive terms all transform as the identity representation of the point group of the isotropic phase, *i.e.* as scalars. The most general form is given by:

$$\Delta F(S_{i,j}) = \frac{A}{2} \sum_{ij} S_{ij} S_{ji} + \frac{B}{3} \sum_{ijk} S_{ij} S_{jk} S_{ki} + \frac{D}{4} \left| \sum_{ij} S_{ij} S_{ji} \right|^2 + \frac{D'}{4} \sum_{ijkl} S_{ij} S_{jk} S_{kl} S_{li}. \quad (4.4.2.1)$$

The usual mean-field treatment assumes that the coefficient of the leading term is of the form $A = a(T - T^*)$, where T is the absolute temperature and T^* is the temperature at which $A = 0$. Taking a , D and $D' > 0$, one can show that for either positive or negative values of B , but for sufficiently large T , the minimum value of $\Delta F = 0$ occurs for $S_{i,j} = 0$, corresponding to the isotropic phase. For $T < T^*$, ΔF can be minimized, at some negative value, for a nonzero $S_{i,j}$ corresponding to nematic order. The details of how this is derived for a tensorial order parameter can be found in the literature (De Gennes, 1974); however, the basic idea can be understood by treating $S_{i,j}$ as a scalar. If we write

$$\Delta F = \frac{1}{2} A S^2 + \frac{1}{3} B S^3 + \frac{1}{4} D S^4 = \left\{ \frac{A}{2} - \frac{B^2}{9D} \right\} S^2 + \frac{D}{4} \left(S + \frac{2B}{3D} \right)^2 \quad (4.4.2.2)$$

and if T_{NI} is defined by the condition $A = a(T_{NI} - T^*) = 2B^2/9D$, then $\Delta F = 0$ for both $S = 0$ and $S = -2B/3D$. This value for T_{NI}