

tric field gradients (19-20). The quadrupole splitting, $\Delta\nu$, for an unoriented lamellar dispersion is directly proportional to the order parameter S

$$\Delta\nu = \frac{3}{4} \chi |S|$$

where χ is the quadrupole coupling constant and S is the order parameter associated with a C-D bond.

For molecules deuterated in different positions, a spectrum will result that comprises a series of splittings centered about a central frequency. The difference in the degree of order in the molecule is reflected in the size of the order parameters and may be expressed as an order profile for which S_i is considered as a function of position in the molecule.

The location between the hydrocarbon chains of the lipids gives an order parameter of about 0.1 to 0.2 for groups attached to a long-chain compound. Compounds located between the methyl group layers show order parameters approximately one-tenth of this value (21).

The NMR spectrum of perdeuterated palmitic acid is a good example. The central peak (Fig. 3.7) is from palmitic acid localized between the central methyl group layers. These palmitic acid molecules show little order, their motion is essentially isotropic. The series of split signals arise from palmitic acid being located in the organized amphiphilic layer. The order parameter for the latter is about 0.15.

This layered structure and its order have the most profound influence on the transport properties of lipids and water.

C. Transport in Layered Structures

The diffusion in liquid crystals is highly anisotropic (22-25). The essential information for the problem of transport across the stratum corneum is that the diffusion *parallel* to the layers is fast; the same magnitude as in a liquid. Conversely, perpendicularly to the layers the diffusion is one or two magnitudes lower.

A layered structure, such as that in the lipid part of the stratum corneum, is not a perfectly organized array of layers parallel to the skin surface but, instead, a series of dislocations always occur as shown schematically in Figure 3.8. Hence, the pertinent diffusion coefficient is the gross one for a partially organized lamellar structure.

The permeability of water through reconstituted stratum corneum was determined earlier (5). The method lends itself to investiga-