molecular crystals, however, in which molecular interactions is believed to be rather small, a question arises concerning the mechanism for charge transfer between molecules. This is the principal problem for the organic semiconductors.

From the chemical viewpoint, it should be also interesting to find the characteristic functions in molecular structures that can contribute to the electrical conductance. In this chapter, we shall present a survey of the chemical aspects of the organic semiconductors that have been investigated in our laboratory.

Polycyclic Aromatic Compounds

The typical examples for the compounds that possess semiconductive properties can be found in the polycyclic aromatic compounds.[1–4] The molecules of these compounds are made of a condensation of benzene rings, which consist of the conjugated double bonds; thus they are plane molecules and contain a large number of delocalized π electrons. The electrical resistivity of these compounds is dependent on the size of the molecule, and it decreases in a rather simple way as the molecular size becomes larger. Naphthalene and anthracene are electrical insulators with high values of resistivity. As the condensation of aromatic rings proceeds, the resistivity of the compound decreases. Thus, for instance, anthanthrene with six rings possesses 10^{19} ohm-cm, pyranthrene with eight rings possesses 10^{16} ohm-cm, and violanthrene with nine rings possesses 10^{14} ohm-cm. In the same way, the value of energy gap also decreases. This can be seen in Table 20.1.

It is believed that in aromatic-hydrocarbon molecules π electrons are capable of being excited readily, and their ionization potential decreases, whereas the electron affinity increases, as the molecular size becomes larger. Thus the electron transfer between molecules would be facilitated as the molecule becomes larger.

The largest aromatic molecule is the graphite molecule. The resistivity along the basal plane of graphite crystal is 10^{-5} ohm-cm, which is the same value as the resistivity of mercury. This is easily understood, since the basal plane is nothing other than the molecular plane of graphite, in which the π electrons can move freely. Whereas graphite possesses conductivity along the c axis of its