

stable. The resistivity of this complex decreases as the iodine content increases, and the minimum value is attained at the composition of one molecule of violanthrene and two of iodine, i.e. when the mole ratio is two, the resistivity is about 40 Ωcm at room temperature with the energy gap of 0.15 eV. Beyond this composition, the resistivity begins to increase. It seems that up to the mole ratio of two, the iodine content is insufficient to make the addition compound with all molecules of violanthrene, while beyond this composition, excess iodine molecules are present in some state which is unfavorable for electrical conduction.

The magnetic susceptibility-composition curve shows a large discrepancy from the additive law, that is, a depression in diamagnetism is observed²². The curve has again a minimum value at a mole ratio of two, where the depression from the additive law exceeds about 35%. Beyond this composition, the susceptibility approaches the additive law. This suggests again the existence of a molecular compound made of one violanthrene and two iodine molecules.

From the investigation²³ of the equilibrium isotherm of the violanthrene-iodine system, it is concluded that this system can be seen as the solid-solution between molecular compound and excess hydrocarbon molecules or excess iodine molecules. The molecular compound consists approximately of one violanthrene and two iodine molecules. However, in reality, it does not have a stoichiometric composition and it is better to say that the molecular compound is expressed by violanthrene-2I₂ as the idealized formula.

X-ray diffraction has revealed that this system is completely amorphous. However, after applying the radial distribution analysis to the diffraction profile, we have obtained some essential features of the structure. For

instance, iodine molecules do not dissociate into atoms nor ions, but the atomic distance in the iodine molecule extends to 2.85 Å from the normal value of 2.67 Å. This might be due to the increase in the ionic character of the iodine molecule in the complex formation. Secondly, four or five iodine molecules aggregate together making a small group in a two-dimensional arrangement.

All of the observed results suggest that in this molecular compound, four iodine molecules are sandwiched between two neighboring violanthrene molecules, corresponding to the idealized formula of violanthrene-2I₂. A plain molecule of violanthrene has just such an area as can be occupied by four or five iodine molecules.

In contrast to the violanthrene-iodine complex, the complex between perylene and iodine shows a sharp X-ray diffraction pattern. The crystalline structure is not yet known. However, the composition of this complex is in the ratio of two perylene molecules to three iodine molecules. This means probably that two perylene molecules sandwich three iodine molecules between them, as the perylene molecule is smaller than the violanthrene molecule.

These sandwich type structures are similar to the structure of well-known graphite complexes. Probably, the same kind of electronic structure takes place in these cases, and this gives rise to more movable electrons which can transfer from molecule to molecule.

It is generally believed that the intermolecular force in a molecular crystal of organic compound is mainly the van der Waals type of force. However, if electrons can transfer from a molecule to the neighboring molecule, this means that there is an additional coupling between them to the non-bond structure. The wave function for a couple of molecules, for instance *A* and *B*, can be expressed as,

$$\Psi = a\Psi_0(A.B) + b\Psi_1(A^+-B^-) \quad (3)$$

²² Y. Matsunaga, *Bull. Chem. Soc. Japan* **28**, 495 (1955).

²³ H. Akamatu, Y. Matsunaga and H. Kuroda, *Bull. Chem. Soc. Japan* (in press).

where Ψ_0 is a non-bond structure such as the van der Waals type, and Ψ_1 is a dative structure between A , the electron donor, and B , the acceptor. This results in a gain of resonance energy, and Mulliken²⁴ called the attractive force due to such a resonance as the intermolecular charge transfer force.

It is well known that, for instance, in a benzene solution of iodine, a molecular compound is formed between benzene as donor and iodine as acceptor. In the excited state, the similar type of resonance as in Eq. 3 with Ψ 's involving excited states of A and B molecules must be considered. The very intense absorption of the iodine solution in benzene is explained as the optical transition to such an excited state, in which the contribution from the dative structure is predominant.

The formation of the semiconductive complexes is probably due to a similar force as in the case of benzene-iodine molecular compound. However, there is a noteworthy difference between those two cases. Such a small molecule as benzene or naphthalene forms only a loose molecular compound with iodine in a dissolved state, so the charge transfer may be located only within each molecular compound.

On the other hand, in semiconductive complexes molecular compounds are formed in the solid state, and they are packed together closely, so the charge transfer may not be limited within each molecular compound, but spread out rather widely to neighboring compounds. Even the stoichiometric 1:1 corresponding relationship is not necessarily fulfilled. In such a case, the molecular orbital for any one molecule might overlap with those of more than one of its neighbors. This means that the bond character between hydrocarbon and halogen molecules should be shifted to the metal-like bond with highly

delocalized electrons, which can transfer between molecules and can drift as an electrical current under the influence of applied field.

In Eq. 3, the contribution from the dative structure is important when molecule A is a strong donor with low ionization energy, and B is a strong acceptor with large electron affinity. This condition is usually fulfilled between unlike molecular entities, as in the case of molecular compound between aromatic hydrocarbon as donor and halogen as acceptor. However, in the case where A and B are of the same type, the resonance with an additional term $c\Psi_2(A-B^+)$ can contribute in the same amount as the second term in Eq. 3. This is only important in the case where A and B are identical in donor and acceptor powers. This is the case of graphite, as pointed out by Mulliken. However, in polycyclic aromatic compounds this condition is nearly fulfilled, especially in compounds with large molecules. Because, in this series of compounds, as the molecule becomes bigger, the ionization energy becomes lower, the electron affinity becomes larger and the difference between those two quantities approaches to zero²⁵. This means that they are good electron donors and simultaneously good acceptors. Therefore, not only in the case of molecular compounds with halogens, but also in the case of a pure state, the contribution from the charge transfer force should play an important role for the inter-molecular force in polycyclic aromatic compounds.

The remarkable conductivity which is found in the molecular compounds strongly suggests that the electronic conduction in organic compounds may be closely related to the "charge transfer mechanism" of the inter-molecular interaction.

²⁴ R. S. Mulliken, *J. Amer. Chem. Soc.* **74**, 811 (1952); *J. Phys. Chem.* **56**, 801 (1952).

²⁵ N. S. Hush and J. A. Pople, *Trans. Faraday Soc.* **51**, 600 (1955).