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Some New Organic Semiconductors: Thiazine-Iodine Complexes

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(15. II. 63)

Solid halogen complexes can be made from a variety of organic compounds with low ionization potentials. Some of them have been shown to exhibit resistivities many decades lower than the parent organic compounds. For instance, perylene, an aromatic hydrocarbon with five benzene rings, has a resistivity of 10^{17} ohm-cm. at room temperature¹⁾. The resistivity of the perylene-bromide complex is only 5 ohm-cm²) and that of the iodine complex 8 ohm-cm³). The former value is the lowest ever found in halogen complexes.

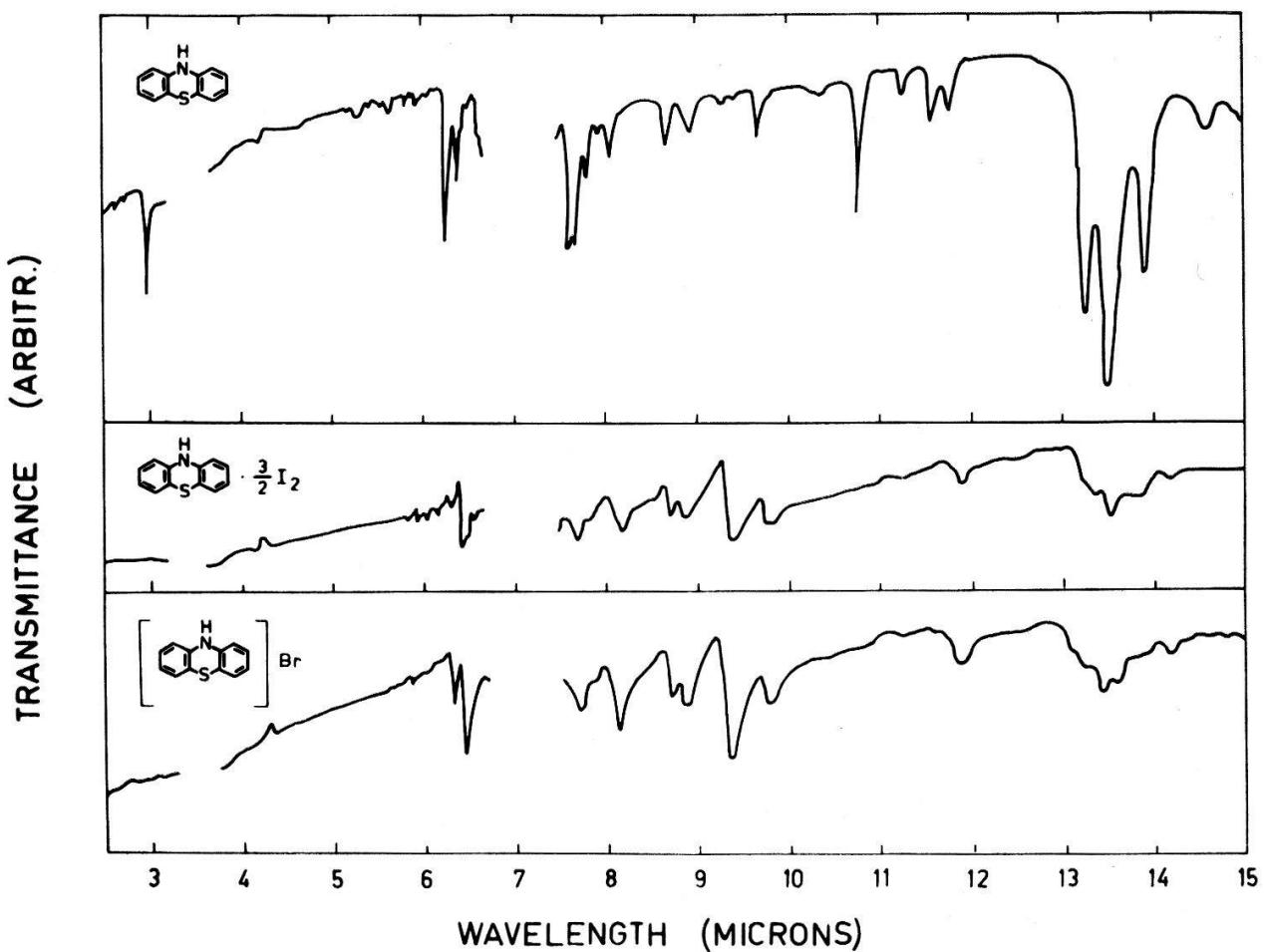
It is generally accepted that these halogen complexes are of the charge-transfer type. Briefly, in the ground state of a 1:1 complex *DA* the electron-donor *D* and the electron-acceptor *A* are weakly held together by non-bonding forces. The first excited singlet state is a dative state $D^+ A^-$ formed by the transfer of one electron from *D* to *A*. The resonance between the non-bonding state and the dative state is considered as essential for the stability of the complex⁴).

As thiazines are more easily available than polycyclic aromatic hydrocarbons and expected, on the basis of their chemical behaviour, to have low ionization potentials, we prepared their iodine complexes and measured the electrical resistivities. The complexes with phenothiazine, benzo(a)phenothiazine and benzo(c)phenothiazine were prepared by mixing of solutions of the components in benzene. For N-methyl-phenothiazine complex ether was used instead of benzene. Some crystals about $1 \times 2 \times 5$ mm³ of the last complex were grown by slow evaporation of the solution. These complexes dissociate into the components when dissolved in benzene so that the iodine content could be determined by titration against sodium thiosulfate. All of the complexes were found to consist of two molecules of thiazine and three of iodine. The resistivities of compressed polycrystalline samples of these complexes were measured by a four probe method. Since the N-methylphenothiazine complex melts at 71°C without decomposition, some samples were made by fusion. The resistivities obey the usual exponential law $\rho = \rho_0 \exp(E/k T)$ as found in most other organic semiconductors. The results of the electrical measurements on the complexes described here are as follows:

donor		ρ (20°C)	E
phenothiazine	pressed	20 ohm-cm	0.17 eV
N-methylphenothiazine	pressed	1.4	—
	fused	1.4	0.14
benzo(a)phenothiazine	pressed	20	0.19
benzo(c)phenothiazine	pressed	20	0.20

For comparison, we add that phenothiazine itself was reported to have values $\rho = 10^{11}$ ohm-cm and $E = 0.8$ eV⁵). Some measurements on crystals of the N-methyl-phenothiazine complex were attempted and values of the order of one ohm-cm obtained for the resistivity along the long axis. As seen in the above table, the iodine complexes with thiazines are as conductive as the iodine complex with large aromatic hydrocarbons. Moreover, the thiazine complexes were found to be more stable than the hydrocarbon complexes.

The fact that the complexes dissociate into the components when dissolved in benzene suggests the non-bonding character of the ground state of the complexes. However, as shown in Figure, the infrared spectrum of phenothiazine-iodine



Infrared spectra of phenothiazine, phenothiazine-iodine complex, and semiquinoid phenazathionium bromide.

complex is quite different from that of the parent organic compound, but identical with that of semiquinoid phenazathionium bromide. This observation indicates that in the solid state the ground state of the iodine complex is dative. Consequently, our phenothiazine-iodine complex may be characterized as semiquinoid phenazathionium triiodide or as iodine-adduct of the iodide. Finally we mention that the phenothiazine-iodine complex does not lose its semiconducting properties if part of the iodine is replaced by either chlorine or bromide: the iodine-adducts of semiquinoid phenazathionium chloride and bromide have resistivities of the order of 10 ohm-cm. The other thiazine complexes studied here are possibly of the same nature.

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