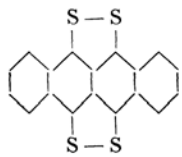
Electrical Properties of Tetrathiotetracene

Hiroo INOKUCHI, Masakatsu KOCHI and Yoshiya HARADA

The Institute for Solid State Physics, The University of Tokyo, Azabu, Tokyo

(Received April 18, 1967)

Recently, Matsunaga has reported that tetrathiotetracene (I) has a low electric resistance; he suggested that this anomalously low value is due to the presence of a small quantity of positive tetrathiotetracene ions formed by oxidation with air.[1] On the other hands, from the formation of molecular complexes between many kinds of electron acceptors and tetrathiotetracene, we can understand that this compound is a powerful electron donor.[1]



(I)

In this paper, we will report on the electrical resistivity of the solid state and also the ionization potential of the compound, as ascertained by means of vacuum ultraviolet spectrophotometry.

The tetrathiotetracene compound, provided kindly by Matsunaga, was purified through vacuum sublimations and recrystallizations. The surface-type cell of the dark-green thin film and also the sandwich-type cell were prepared by means of vacuum sublimation at 10^{-6} mmHg. The electrical resistances of these cells and the polycrystalline sample compressed at 290 kg/cm^2 in a poly-tetrafluorethylene cylinder were observed by the potential drop method.

TABLE 1. THE ELECTRICAL RESISTIVITY OF TETRATHIOTETRACENE

Specimen	ρ^*_{15} (Ωcm)	$\Delta\varepsilon^*$(eV)	Electrode
Surface-type	1.3×10^{6}	0.57	Al
Sandwich-type	4.2×10^{10}	0.41	Ag
Compressed	8.5×10^{3}	0.44	Cu
Matsunaga's (Ref. 1)	10^{4}	0.46	—

$^*\rho_{15}=\rho_0\exp(\Delta\varepsilon/2k\times288\ (°K))$.

The observed values of the electrical resistivity are quite low in the group of polycyclic aromatic semiconductors, as is shown in Table 1.

The discrepancy of band gaps ($\Delta\varepsilon$) among the observed values may originate from an anisotropy of the crystal structure, especially of the contribution of sulphur atoms in the tetrathiotetracene molecule.

The photoemissive current from the thin tetrathiotetracene film deposited on a polished copper plate was measured with a Cary 31 vibrating-reed electrometer under an illumination of monochromatized light from a hydrogen lamp. The details of the experimental procedure have already been reported.[2]

Through the observation, the threshold value of photoemission was found at around 272 mμ, 4.56 eV; this value corresponds to the ionization potential. This value is lower than those of similar polycyclic aromatic hydrocarbons; for instance, the value for tetracene ($C_{18}H_{12}$) is 5.28 eV, and that for quaterrylene ($C_{40}H_{20}$), 4.74 eV, while it is 4.73 eV for colloidal graphite.

For the polycyclic aromatic hydrocarbons, we have found that an abrupt change in the electrical properties occurrs when oxygen is admitted to samples stored in a high vacuum of 10^{-8} mmHg.[3,4] Following a similar procedure, we observed a change in the electrical conductivity when oxygen was introduced into a high vacuum surface-type cell, in which tetrathiotetracene has been evaporated onto the surface-type electrodes at 10^{-8} mmHg. The change, however, was not very large; 10^7 Ωcm decreased at that high vacuum to 1×10^6Ωcm. Therefore, we can neglect practically the effect of oxidation with air on the electrical resistivity.

From the preliminary results of X-ray analysis, we found that the molecules are packed closely.

1) Y. Matsunaga, *J. Chem. Phys.*, **42**, 2248 (1965).

2) Y. Harada and H. Inokuchi, This Bulletin, **39**, 1443 (1966).

3) Y. Maruyama and H. Inokuchi, *ibid.*, **39**, 1418 (1966).

4) H. Inokuchi, N. Matsubara, Y. Maruyama and E. Clar, *Nature*, **205**, 64 (1965).

The high electronic conduction in the crystal may take place *via* the sulphur atoms.

We have already found that aromatic polysulphides, the reaction products between polycyclic aromatic compounds and sulphur, have a fairly high electrical conductivity; for instance, anthracene polysulphide ($(C_{14}H_{10})S_6$) has a value of $1.0\times10^4\Omega$cm, while that of violanthrone ($(C_{34}H_{16}O_2)S_{10}$) is $4.0\times10^2\ \Omega$cm.[5] The conduction mechanism in the polysulphides may be similar to that of tetrathiotetracene.

The authors wish to thank Professor Y. Matsunaga, Hokkaido University, for his gift of the chemical.

5) H. Akamatu, Y. Maruyama, M. Kinoshita and H. Inokuchi, Symposium on Carbon III-1-1, Tokyo, (1964).