BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2381—2385 (1970)

Electrical and Optical Behaviour of Tetrathionaphthacene at High Pressures

Ichimin SHIROTANI, Kaoru KAWADA and Hiroo INOKUCHI

The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo

(Received February 14, 1970)

The temperature dependence of the electrical resistance and the absorption spectra for tetrathionaphthacene (T.T.N.) have been studied at high pressure. It has been found that the intrinsic conduction level, which does not correspond to the observed optical transition, is located about 2 eV above the valence band. The red shift of absorption peaks with the pressure was much smaller than the contraction of the intrinsic band gap. The existence of the intrinsic conduction level is supported by the fact that the minimum of the photoemission yield arising from electron-pair production is located about 2 eV above the threshold point. The band gap of 0.4—0.62 eV previously observed seems to correspond to an acceptor level formed by chemical impurities.

Certain types of impurities and imperfections drastically affect the electrical properties of organic semiconductors. Adsorbed oxygen, as one kind of impurity, is known to modify strongly the semi- and photo-conduction of organic crystals.[1,2] For example, the semiconduction of the quaterrylene[*1] film is especially sensitive to oxygen.[1] Under atmospheric circumstances, this compound is a p-type semiconductor due to an oxygen impurity level which lies 0.6 eV above the valence band. The intrinsic energy gap, observed under a high vacuum or at a high temperature, is 1.7 eV. The effect of the pressure on these energy gaps has already been studied.[3]

Tetrathionaphthacene (T.T.N.) has a low electrical resistivity, 10^4 Ωcm at room temperature. This observed value is very low when compared with others in the group of polycyclic aromatic semiconductors. Matsunaga has suggested that this anomalously low value is due to the presence of a small quantity of positive tetrathionaphthacene ions formed by oxidation with air.[4] However, no abrupt change in the electrical properties of this compound occurred when oxygen was adimitted to a sample stored in a high vacuum of 10^{-8} mmHg. Therefore, the effect of oxidation with air on the electrical resistivity may be disregard.[5] Though the activation energy and the electrical resistance of the microcrystals decrease with an increase in the pressure, these properties are not very sensitive to pres-

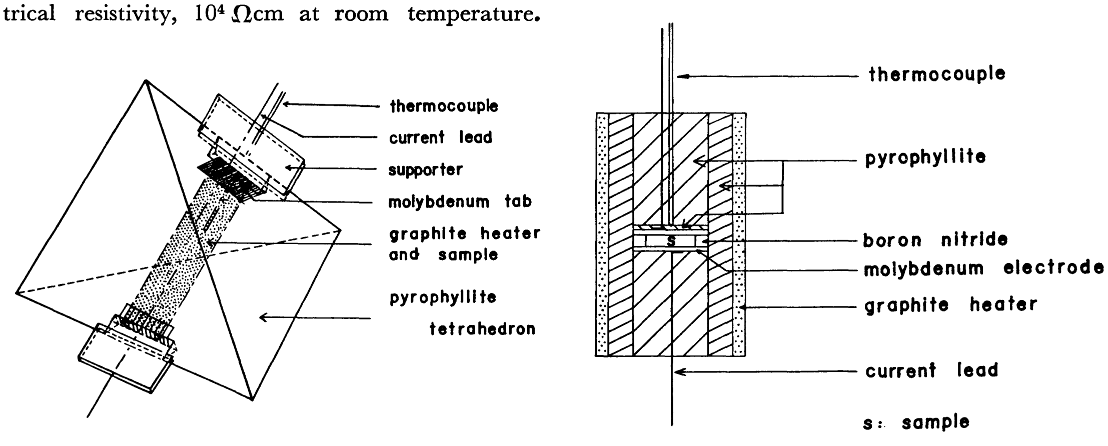

Fig. 1a, 1b. The sample assembly.

---

[1] Y. Maruyama and H. Inokuchi, This Bulletin, **39**, 1418 (1966).

[2] G. H. Heilmeier and S. E. Harrison, *Phys. Rev.*, **132**, 2010 (1963).

[*1] Eleven-membered aromatic hydrocarbons, $C_{40}H_{20}$.

[3] I. Shirotani, H. Inokuchi and S. Akimoto, This Bulletin, **40**, 2277 (1967).

[4] Y. Matsunaga, *J. Chem. Phys.*, **42**, 2248 (1965).

[5] H. Inokuchi, M. Kochi and Y. Harada, This Bulletin, **40**, 2695 (1967).

sure.[6] The anomalous electrical behaviour may arise from the chemical impurities. We have studied the temperature dependence of the electrical resistance of tetrathionaphthacene (T.T.N) at high pressures and have found the intrinsic energy gap, near 2 eV. In this report, the intrinsic conduction level of tetrathionaphthacene will be discussed.

Experimental

A tetrahedral anvil-type high-pressure apparatus similar to those described by Hall was used for this study. The present apparatus consisted of four 250-mm hydraulic rams, with 20-mm triangular tungsten carbide anvils, which were driven together simultaneously on a pyrophyllite-tetrahedron sample assembly with an edge length of 25 mm. Figures 1 (a) and 1(b) illustrate the sample assembly used for the electrical-resistance measurements. The temperature was measured with a chromel-alumel thermocouple. A tublar graphite furnace was placed nearly at the centre of gravity of the pyrophyllite-tetrahedron and was used for heating the sample. The electric power was supplied to the graphite furnace through molybdenum tabs which made contact with the faces of a pair of anvils. The sharp changes in the electrical resistances of Bi(I—II, 26 kbar),[*2] Tl(II—III, 37 kbar), and Ba(I—II, 55 kbar) at their phase transitions were used to calibrate the pressure applied to the pyrophyllite-tetrahydron. The details of the high-pressure technique have already been reported.[7]

Tetrathionaphthacene ($C_{18}H_8S_4$) was provied by Matsunaga. This sulphur compound was purified by recrystallisation from trichlorobenzene and also by fractional sublimations (three times). The sample was studied as a powder which was fused into flat platelets by applied pressure.

The absorption spectra were measured by using a Shimazu SV-50A spectrophotometer. The thin tetrathionaphthacene film was grown on a glass plate by sublimation in a vacuum. The high-pressure optical cell has been described elsewhere.[3] A hydrostatic pressure up to 7 kbar was applied by means of a pressure-transmitting medium through a pressure-intensifier. The pressure was determined by a Harwood manganine resistance gauge and a Heise Bourdon tube gauge.

Results

Figure 2 shows the relation between the lograithm of the electrical resistance and the reciprocal temperature for the compressed tetrathionaphthacene at 30 kbar. For temperatures less than 340°C the impurity conduction was dominant. The temperature range of 340—400°C was the intrinsic conduction region. The sample seems to melt about 410°C. Above 430°C the electrical resistance of the compound increased slowly with an increase in the temperature; the chemical reaction must, then, occur. The behaviour of the curve was reproducible for temperatures below 400°C at high pressures.

Under 30 kbar the energy gap calculated from the temperature dependence of the conductivity over the temperature range of 300—613°K was 0.61 eV. This is assumed to be an extrinsic energy gap and is denoted as E_a. On the other hand, the energy gap from the temperature-conductivity relation, shown in Fig. 2, at 613—673°K was 1.62 eV at the same pressure. This energy gap, E_g, is considered of to be the intrinsic one. Figure 3 shows the plots of E_g and E_a as functions of the pressure. E_g decreased remarkably with an increase in the pressure. However, E_a was less affected by the pressure. If the relation between the energy gap and the applied pressure is assumed to be linear,[*3] the extrapolated value of intrinsic gap at atmospheric pressure is about 2 eV. Table 1 shows the values of E_g and E_a at high pressures. From Fig. 3, we can find that the values of E_a and E_g decrease with an increase in the pressure at the rates of:

$$\left(\frac{\mathrm{d}E_g}{\mathrm{d}p}\right)_T \cong -15\times10^{-3}\ \text{eV/kbar} \qquad (1)$$

and:

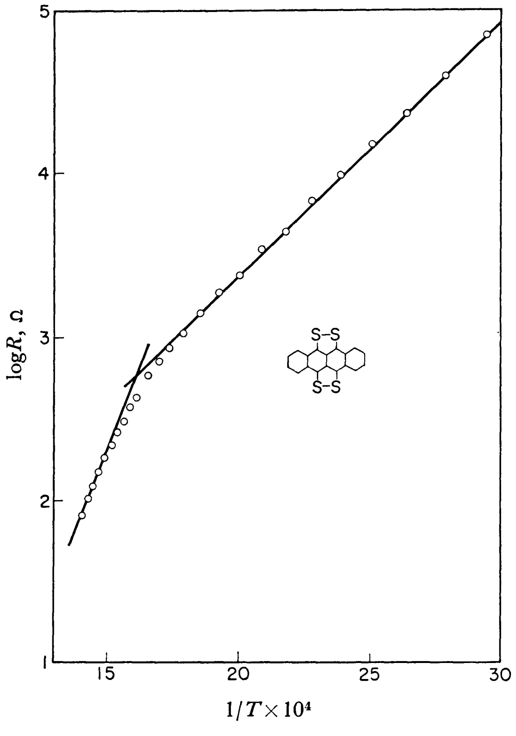

Fig. 2. The electrical resistance of tetrathionaphthacene as a function of temperature at 30 kbar.

---

6) I. Shirotani, H. Inokuchi and S. Minomura, *ibid.*, **39**, 386 (1966).

[*2] The phase transition from Bi(I) to Bi(II) occurres at 26 kbar.

7) S. Akimoto and H. Fujisawa, *J. Geophys. Res.*, **70**, 443, 1969 (1965).

[*3] For quaterrylene, E_g and E_a are proportional to the pressure, at least up to 50 kbar.

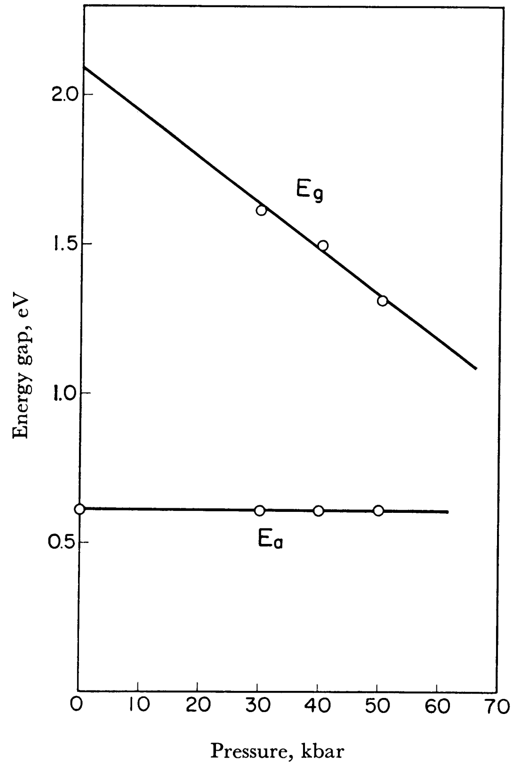

Fig. 3. The pressure dependence of the energy gaps.

$$\left(\frac{\mathrm{d}E_a}{\mathrm{d}p}\right)_T \cong 0 \quad \text{eV/kbar} \qquad (2)$$

It is interesting to note that the pressure dependence of E_g is larger than that of E_a. Similar behaviour has already been found in the quaterrylene crystal.[3]

Figure 4 shows the pressure dependence of the electrical resistance at room temperature and at 360°C. The electrical resistance in the extrinsic region was insensitive to pressure, but the intrinsic resistance rapidly decreased with an increase in the pressure. These phenomena, as is shown in Fig. 3, are due to the pressure depencence of the energy gaps. Since the mobility of the charge carrier in the crystal is not so sensitive to applied pressure, the large increase in the conductivity at high pressures is mostly due to the great increment in the concentration of the charge carriers.[6]

Table 1. THE PRESSURE DEPENDENCE OF THE THERMAL ENERGY GAPS OF TETRATHIONAPHTHACENE

Pressure (bar)	E_g (eV)	E_a (eV)
1	~2[a]	0.40—0.62[b]
30×10^3	1.62	0.61
40×10^3	1.50	0.61
50×10^3	1.32	0.61

a) extrapolated value from high pressure data.
b) Refs. 4 and 5.

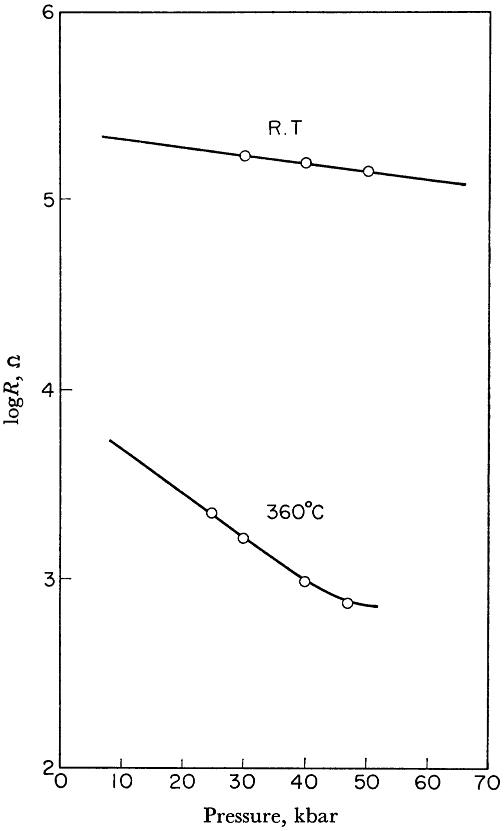

Fig. 4. The electrical resistivity of T.T.N. as a function of pressure at room temperature and at 360°C.

Figure 5 shows the electronic absorption spectra of the evaporated film and of the benzene solution of tetrathionaphthacene. The absorption band of film at 600—850 mμ may correspond to the 550—750 mμ peaks in the solution-state spectrum. Three absorption peaks of the film showed a red shift with

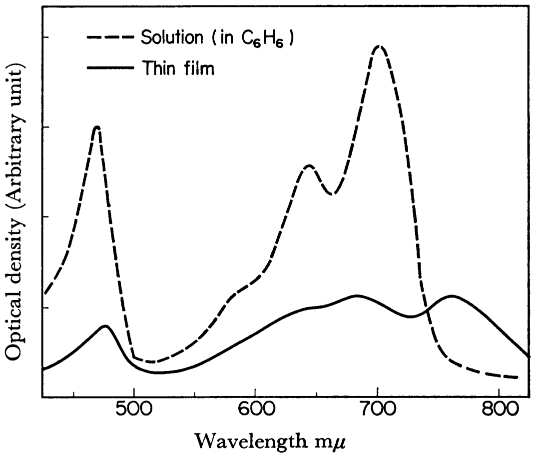

Fig. 5. The absorption spectra of T.T.N.
——— thin film ---- solution (in C_6H_6)

TABLE 2. THE RED SHIFT OF THE OPTICAL ABSORPTION PEAK FOR TETRATHIONAPHTHACENE AND NAPHTHACENE

Compound	Absorption peak mμ	Shift per unit of pressure 10^{-3} eV/kbar
Tetrathionapthacene	476	− 2.2
	680	− 2.6
	763	− 4
Naphthacene	471	− 9.4
	521	−13.4

an increase in the pressure. Table 2 illustrates the average rate of the red shift of the absorption spectra for T.T.N. and naphthacene. The values of the pressure shift for T.T.N. were much smaller than that of ordinary aromatic hydrocarbons.[8] The energy shift was approximately proportional to the applied pressure. The small red shift of T.T.N. should be noted.

Discussion

The pressure coefficient for the optical-energy gaps of such inorganic semiconductors as silicon and germanium agrees with the value determined by measuring the intrinsic resistivity as a function of the pressure.[9] In the case of the molecular crystal, similar behaviour has been observed in the absorption spectra of quaterrylene ($C_{40}H_{20}$); the rate of the red shift of the peak at 760 mμ which corresponds to the absorption peak in the solution-state spectrum, agrees approximately with that of the contraction of the thermal-energy gap. This behaviour may be useful in analyzing the mechanism of the carrier generation in quaterrylene crystal.[3]

The absorption peaks in the 575—700 mμ region observed in the benzene solution spectrum may be due to the lowest-singlet excitation of the tetrathionaphthacene molecule. The crystalline spectrum of T.T.N. corresponds to the spectrum of the free molecule, though a spectral red shift and broadening were observed. The 630, 680, and 760 mμ peaks in the film spectrum may form an exciton band arising from this lowest molecular excitation. As has been stated earlier, it was found, from the temperature dependence of the electrical resistance that the intrinsic energy gap was about 2 eV. This thermal-energy gap did not correspond with the absorption band of the T.T.N. evaporated film. As is shown in Eq. (1) and in Table 2, the red shift of the absorption peaks was very small compared with the contraction of the thermal-band gap. This suggests that the absorption band observed on evaporated film is the singlet-exciton state.

The photoconductance of anthracene crystals in the ultraviolet region (250—400 mμ) has also been investigated.[10,11] Castro and Hornig observed a peak in the photocurrent at 280 mμ which does not correspond to any known optical transition.[10] The magnitude of the 280 mμ electron photocurrent was relatively insensitive to the condition of the crystal surface. Therefore, they pointed out that the intrinsic conduction band is located in anthracene at about 4.4 eV. In the case of the tetrathionaphthacene crystal, the study of the photocurrent spectral-response curve was very difficult because of the large dark conductivity.[12] However, if the photocurrent curve can be investigated, the peak of the photoconductivity may be located near 2 eV.

The photoemission from polycyclic aromatic crystals in the vacuum ultraviolet region has also been studied.[13] Figure 6 shows the spectral distri-

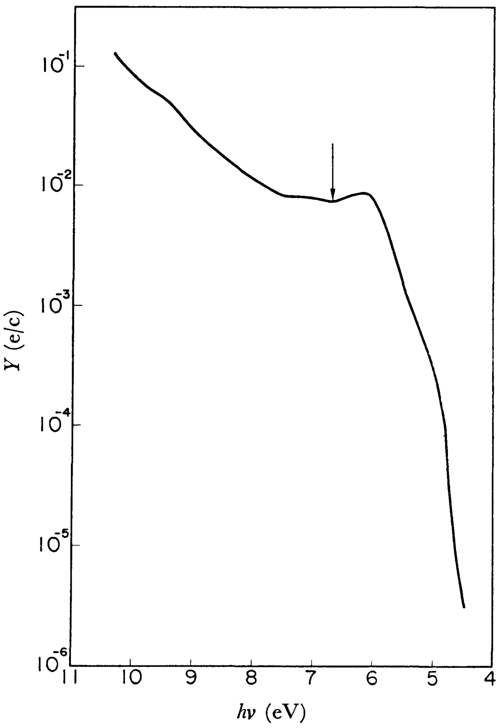

Fig. 6. Spectral distribution of the photoemission yield for T.T.N; arrow indicates the energy minimum produced from pair production scattering.

---

[8] H. Ohigashi, I. Shirotani, H. Inokuchi and S. Minomura, *J. Chem. Phys.*, **43**, 314 (1965).

[9] W. Paul and D. M. Warschauer, *J. Phys. Chem. Solids.*, **5**, 89 (1958).

[10] G. Castro and J. F. Hornig, *J. Chem. Phys.*, **43**, 1459 (1965).

[11] R. F. Chaiken and D. R. Kearns, *ibid.*, **45**, 3966 (1966).

[12] M. Kochi, private communication.

[13] Y. Harada and H. Inokuchi, This Bulletin, **39**, 1443 (1966); M. Kochi, Y. Harada and H. Inokuchi, *ibid.*, **40**, 531 (1967).

bution of the photoemission yield for T.T.N. The decrease in the yield has a minimum around 2 eV above the threshold of 4.55 eV. Kochi *et al.* have suggested[14] that this decrease in the photoemission yield arises from pair-production scattering*[4] and that the threshold near 2 eV for the pair production for T.T.N. corresponds to the intrinsic-band gap. This experimental result supports the idea that the energy gap obtained from conductivity measurements under high pressure, above 2 eV, is an intrinsic one.

The inner heat of the sublimation of T.T.N. is about 36 kcal/mol. As is shown in Table 3, the sublimation energy for T.T.N. ($C_{18}S_4H_8$) and four aromatic hydrocarbons of 22 carbons is of the same order.[15] These results show that the cohesive energy of the sulphur compound is not much larger than that of aromatic hydrocarbons. The spectral red shift of the crystalline T.T.N. relative to the solution spectrum was quite small; further, the energy shift was not so sensitive to the pressure. In view of these points, the molecular interaction between T.T.N. seems to be weak. However, the electrical resistivity of this compound is quite low under atmospheric pressure. The anomalous electrical behaviour arises from the chemical impurities. Judging the photoemission data,[13] the band gap of 0.4—0.62 eV previously observed[4,5] seems to correspond to an acceptor level formed by the impurity.

Table 3. The heats of sublimation of tetrathionaphthacene and five aromatic hydrocardons

Compound	Molecular formulae	Molecular weight	ΔH kcal/mol
Benzo[*g,h,i*]perylene	$C_{22}H_{12}$	276	30.0[a]
3,4-Benztetraphene	$C_{22}H_{14}$	278	32.6[a]
1,2,5,6-Dibenzo-anthracene	$C_{22}H_{14}$	278	33.9[a]
Pentacene	$C_{22}H_{14}$	278	37.7[a]
Picene	$C_{22}H_{14}$	278	33.5[a]
Tetrathionaphthacene	$C_{18}H_8S_4$	352	36.1[b]

a) Ref. 15.
b) N. Wakayama, private communication.

The authors would like to thank Dr. M. Kochi for his useful discussions and Professor Y. Matsunaga for his gift of the chemical. Their thanks are also due to Professor S. Akimoto and Dr. M. Nishikawa for their valuable advice and kind assistance throughout this work.

---

14) M. Kochi, Y. Harada, T. Hirooka and H. Inokuchi, Technical Report of ISSP, Series A, No. 358 (1969).

*[4] "Pair production" means the process in which the primary electron with energy E excites the second one with energy E_0 to conduction band and loses the minimum energy equal to the band gap, ΔE.

15) N. Wakayama and H. Inokuchi, This Bulletin, **40**, 2267 (1967).