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# Physical Properties and Constitution of the 5,6: 11,12-Bis(epidithio)-naphthacene-Iodine Complexes (TTT-$I_n$)

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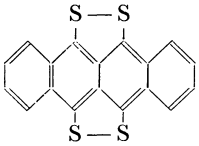
The electrical resistivity of the 5,6: 11,12-bis(epidithio)naphthacene(TTT)–iodine system was examined using polycrystalline compactions. The room-temperature resistivity reaches a minimum of 0.3 ohm cm at the composition of the well-studied metallic phase, TTT–$I_{1.5}$, and a shoulder as large as 200 ohm cm occurs at the composition of the other metallic phase, TTT–$I_{2.7}$. The apparent activation energy for semiconduction at the latter composition is as much as 0.13 eV, indicating some semiconductor behavior in directions other than the needle axis. The appearance of the latter phase is also manifested by a drastic increase in the Seebeck coefficient near this composition, which corresponds to a change in the amount of charge per TTT molecule from 0.68 to 0.85. The diffuse reflection spectra were recorded for TTT–$I_{1.53}$ and TTT–$I_{2.79}$. The resemblance between the spectrum of the iodine-rich complex and that of TTT–Br is noted.

It has been known for some time that 5,6: 11,12-bis(epidithio)naphthacene(TTT¹⁾) can produce highly



conducting ionic molecular complexes and also cation radical salts. The former group consists of the complexes with *o*-haloanils,²⁻⁴⁾ tetracyanoethylene,²,³⁾ tetracyanoquinodimethane,⁵⁻⁸⁾ and bis(1,2-ethylenedithiolato)nickel(II),⁹⁾ while the latter includes halides and thiocyanate.¹⁰⁾ Recently, there has been a great deal of interest in TTT–$I_{1.5}$, which is among the most conducting organic compounds so far developed.¹¹⁻¹⁴⁾ Here, we wish to report the electrical properties of TTT–$I_n$ as functions of the composition. Earlier, similar studies were made on the four semiconducting thiazine–iodine systems.¹⁵⁾ The location of electrical singularities was shown to be a powerful tool for elucidating the constitution of organic compound-iodine systems. For instance, we demonstrated that a shoulder in the resistivity-composition isotherm, a decrease in the activation energy for semiconduction by a factor of two, and a change in the sign of the Seebeck coefficient from negative to positive can be observed at a composition of two molecules of phenothiazine to five atoms of iodine and that the incorporation of a half mole of iodine to this compound gives rise to a resistivity minimum.

## Experimental

*Materials.* TTT was synthesized following the method reported by Marschalk and Stumm and recrystallized three times from trichlorobenzene.¹⁶⁾ Samples were prepared by grinding the weighed TTT and iodine or the weighed sample of a less iodine content and iodine in an agate mortar in the presence of a small amount of benzene. The iodine contents were determined by microanalysis. Two additional samples were prepared by the reaction between TTT and iodine in boiling nitrobenzene and benzene respectively. Their compositions were TTT–$I_{1.53}$ and TTT–$I_{2.79}$.

*Measurements.* The electrical resistivities and Seebeck coefficients of polycrystalline compactions were recorded as functions of the temperature from −120 to 20 °C by the procedures described in our previous paper.¹⁷⁾ The diffuse reflectance of samples diluted with sodium chloride was measured by means of a Beckman DK 2A spectroreflectometer in the range from 325 to 2500 nm. The reference was pure sodium chloride. The spectrum was then plotted using the Kubelka-Munk function.

## Results and Discussion

*Electrical Properties.* In Fig. 1, the logarithm of electrical resistivity at 20 °C is plotted against the number of iodine atoms per TTT molecule, *n*. Two shaded circles indicate that these samples were made by the reaction in boiling nitrobenzene or benzene; therefore, they were supposed to be more homogeneous than the others. It must be emphasized that the shaded circles fit in well to the resistivity-composition isotherm made with open circles. A minimum resistivity of about 0.3 ohm cm is found at $n=1.5$. Then the resistivity reaches a shoulder at $n=2.7$, the value being about 200 ohm cm. Although Buravov *et al.* have reported a phase corresponding to $n\simeq 1$,¹¹⁾ no singularity due to this phase could be detected in our isotherm. Kamaras

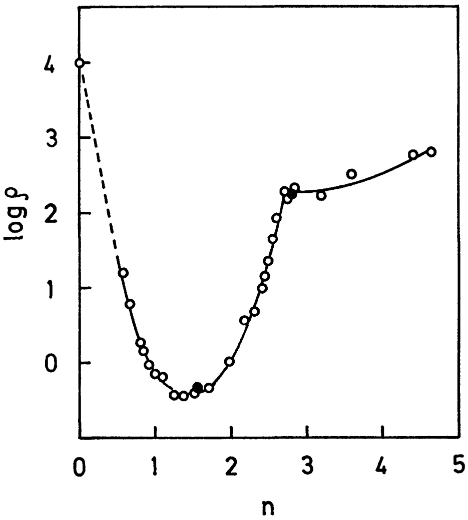


Fig. 1. Electrical resistivity at 20 °C plotted against the iodine content (*n* I atoms/TTT molecule).

*et al.* have noted that the phase can be obtained only occasionally, together with TTT and TTT–$I_{1.5}$;[13] therefore, the amount of TTT–I in our samples may be too small to show any singularity.

Now we wish to summarize briefly the electrical behavior of mixtures. If two coexisting phases are strictly stoichiometric and mechanically mixed without interaction, Lichtenecker's logarithmic mixing rule may apply for the resistivity.[18,19] The composition of a distinct compound may correspond to a minimum in the resistivity-composition isotherm when its resistivity is the lowest in the system or to an abrupt change in the slope when its resistivity is not the lowest. If the incorporation of a marked stoichiometric imbalance is conceivable for a phase, the electrical behavior may depend quite differently upon the composition. When additional carriers are introduced by the imbalance, the stoichiometric composition may be indicated by a maximum in the resistivity-composition isotherm. When the effect of an excess of one of the components on the resistivity is small or when the stoichiometric phase is incapable of existence, a shoulder may be observed instead of a maximum.

The composition of the well-studied TTT–$I_{1.5}$ phase has been reported to vary within narrow limits, from $n=1.50$ to 1.56;[14,20] therefore, the appearance of a resistivity minimum at this composition seems to be more likely than that of a maximum. Even if a maximum exists, the presently-observed resistivity values around $n=1.5$ arise essentially from contact between the crystals and are probably much larger than the maximum value. All the reported resistivity values along the needle axis are of the order of 0.001 ohm cm.[11–13] The electrical behavior found for the phase around $n=2.7$ is clearly of a nonstoichiometric type, and is in agreement with the observation made by Kamaras *et al.*, namely, the composition of their recrystallized samples ranges from $n=2.6$ to 2.9.[13] The sharp edge appearing in Fig. 1 shows that the ideal composition of this phase is $n=2.7$ and also that the incorporation of an excess of TTT considerably lowers the resistivity. This large effect seems to agree qualitatively with the observation by Kamaras *et al.* again. They have examined about twenty crystals in this phase and have found resistivity values along the needle axis scattered by a factor of 16. However, it must be added that the values in Fig. 1 are three orders of magnitude greater than the reported values, namely, from 0.01 to 0.2 ohm cm. This disagreement suggests that the anisotropy in the TTT–$I_{2.7}$ phase is anomalously large and is much larger than that in the TTT–$I_{1.5}$ phase.

The temperature dependence of the resistivity, $\rho$, follows the typical semiconductor behavior: $\rho=\rho_0 \exp (E_a/kT)$. The activation energy for semiconduction, $E_a$, thus obtained is plotted against $n$ in Fig. 2. As the single crystal resistivities measured along the needle axes in both the TTT–$I_{1.5}$ and TTT–$I_{2.7}$ phases are known to be metallic in the temperature range from 200 to 300 K, the activation energy observed with the polycrystalline compactions must be attributed to the activation energy for semiconduction in the directions other than the needle axis and, at least in part, to contact between the crystals. The small activation energy found near $n=1.5$ may be mostly due to the latter; however, the value as large as 0.13 eV found for the TTT–$I_{2.7}$ phase arises undoubtedly from the semiconductor behavior along the axes other than the needle axis.

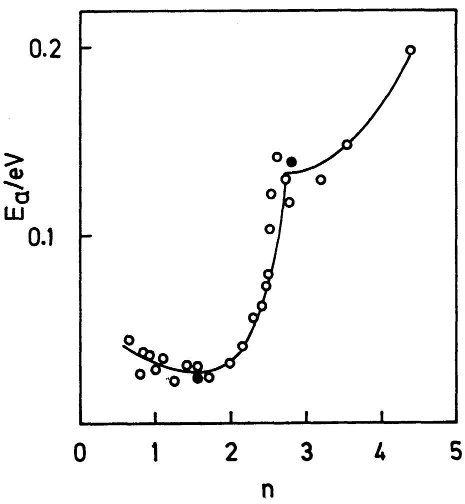


Fig. 2. Activation energy for semiconduction plotted against the iodine content.

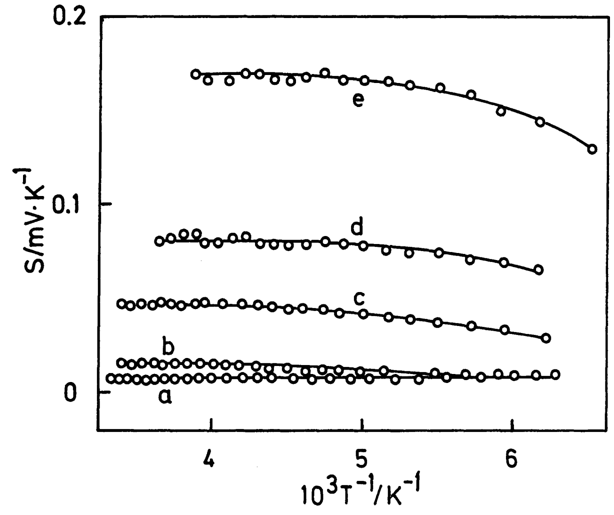


Fig. 3. Seebeck coefficient of the TTT–iodine complexes; a) $n=1.71$, b) 2.59, c) 2.84, d) 3.20, and e) 3.58.

The Seebeck coefficients of all the samples are positive throughout the examined temperature range, and tend to saturate at high temperatures (see Fig. 3). Similar behavior, but with the opposite sign, has been known to be characteristic of TCNQ salts with metallic conductivity.[21] According to the theory of Beni,[22] their Seebeck coefficients in the high temperature limit, $S(T\to\infty)$, are given by the equation,

$$S(T\to\infty) = -\frac{k}{|e|}\ln 2(1-\gamma)/\gamma,$$

where $\gamma$ is the carrier concentration defined by the ratio of the number of carriers to the number of sites, in other words, the amount of negative charge per TCNQ molecule. Following the proposal by Beni *et al.* that the above equation is the most direct way of

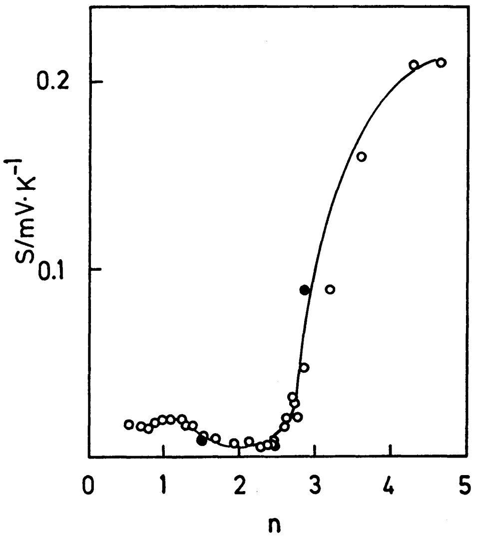


Fig. 4. Seebeck coefficient at −20 °C plotted against the iodine content.

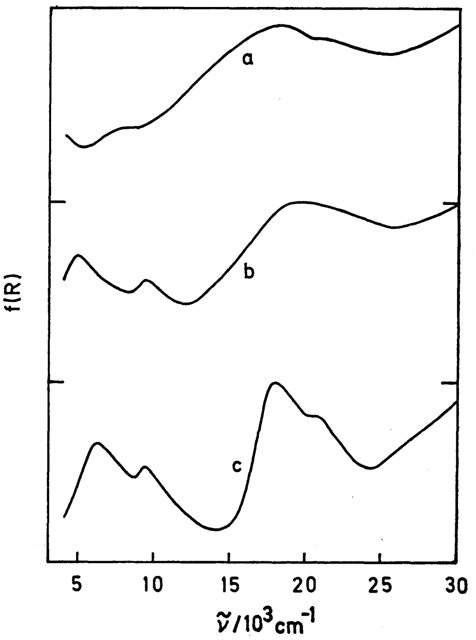


Fig. 5. Diffuse reflection spectra of a) TTT–$I_{1.53}$, b) TTT–$I_{2.79}$, and c) TTT–Br.

determining the value of $\gamma$,[23] we earlier found 0.52—0.55 for the high-conductivity 1 : 2 salts and 0.60—0.62 for the 2 : 3 salts by measurements on the polycrystalline compactions.[24] These values agree reasonably well with the expected ones, namely, 1/2 and 2/3. The high-temperature limit for the Seebeck coefficient is governed entirely by the entropy change per added carrier and is expected to be independent of the charge sign.[25] Consequently, the Beni equation may be employed for the estimation of the amount of positive charge per TTT molecule, because both TTT–$I_{1.5}$ and TTT–$I_{2.7}$ phases are known to be metallic. The positive coefficients are indicative of the $\gamma$ values larger than 2/3. The value estimated for the TTT–$I_{1.5}$ phase is 0.68 and that for the TTT–$I_{2.7}$ phase, 0.80—0.85. If all the iodine atoms in these phases exist as triiodide ions, the expected $\gamma$ values are 1/2 and 9/10 respectively. The $S(T\rightarrow\infty)$ value for the former $\gamma$ is −60 μV K$^{-1}$ and that for the latter is +130 μV K$^{-1}$. Thus, the estimated amount of charge per TTT molecule in the TTT–$I_{1.5}$ phase is significantly larger than the expected one. If one assumes that a part of the iodine is in the form of iodide ions, $I^-$, and that $\gamma=2/3$ for the sake of simplicity, the constitution at $n=1.5$ may be expressed by the formula: $(TTT^+)_{2/3}(TTT^0)_{1/3}(I_3^-)_{5/12}(I^-)_{1/4}$. The abrupt increase of the Seebeck coefficient in a narrow range of $n=2.6$ to 3.0 shown in Fig. 4 corresponds to the change of $\gamma$ from 0.68 to 0.85. The temperature-dependence of the Seebeck coefficient in the range above $n=3$ is similar to that below $n=3$. Tentatively applying the Beni equation to the range near $n=3$, it is concluded that the TTT molecule does not attain a unit positive charge even at the highest iodine content. Therefore, the TTT–$I_{2.7}$ phase may contain a higher polyiodide ion, possibly a pentaiodide ion, or an iodine molecule in addition to the triiodide ion.

*Electronic Spectra.* In Fig. 5, the Kubelka-Munk plots of diffuse reflectance are presented for samples TTT–$I_{1.53}$ and TTT–$I_{2.79}$. Each spectrum in the region below $10\times10^3$ cm$^{-1}$ consists of two peaks; however, their locations are markedly dependent on the composition. The TTT–$I_{1.5}$ phase shows one peak below $4\times10^3$ cm$^{-1}$, the limit of the spectroreflectometer employed, and the other at about $7.5\times10^3$ cm$^{-1}$, while the TTT–$I_{2.7}$ phase shows peaks at $4.8\times10^3$ and $9.4\times10^3$ cm$^{-1}$. The presence of two peaks in the infrared region is characteristic of solid TTT cation radical salts.[26] For comparison, the spectrum of TTT–Br taken from our previous work is added to Fig. 5. This bromide has been reported to exhibit a resistivity of 50 ohm cm at 25 °C by Perez-Albuerne *et al.*[10] Here, the peaks are located at $6.2\times10^3$, $9.5\times10^3$, and $18.0\times10^3$ cm$^{-1}$, with a shoulder at $20\times10^3$ cm$^{-1}$. As the appearance of such low-energy absorption bands attributable to electronic transitions are common to low-resistivity organic compounds, it is strange that no absorption has been noted below $10\times10^3$ cm$^{-1}$ in the spectra of samples TTT–$I_{1.6}$ and TTT–$I_{2.8}$ presented by Kamaras *et al.*[13] Although the lowest energy band in the TTT–$I_{2.7}$ phase is shifted a little to the lower-energy side compared with that in the TTT–Br, the close resemblance in the spectral features of these two may be noted. In agreement with the high $\gamma$ value estimated on the basis of the Seebeck coefficient, this resemblance suggests that the major fraction of TTT molecules is in the form of monopositive ions. The strong peak with a shoulder in the visible region shown by the solid TTT–Br is the cause of the dark red color and characterizes the TTT$^+$ ion. However, this peak cannot be identified in the spectra of black-colored TTT–$I_{1.53}$ and TTT–$I_{2.79}$ because of overlap with strong absorption bands due to triiodide and/or polyiodide ion.

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## References

1) As the trivial name, tetrathiotetracene given by C. Marschalk and C. Stumm (Ref. 16) has been widely used; TTT is the abbreviation in accord with those in the references.

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

3) Y. Okamoto, S. Shah, and Y. Matsunaga, *J. Chem. Phys.*, **43**, 1904 (1965).

4) E. Krikorian and R. J. Sneed, *J. Appl. Phys.*, **40**, 2306 (1969).

5) J. H. Perlstein, J. P. Ferraris, V. V. Walatka, Jr., D. O. Cowan, and G. A. Candela, *A. I. P. Conf. Proc. Magnetism Magenetic Materials*, **10**, 1494 (1972).

6) O. N. Eremenko, M. L. Khidekel, D. N. Fedutin, and E. B. Yagubskii, *Izv. Akad. Nauk, Ser. Khim.*, **1972**, 984.

7) P. Delhaès, S. Flandrois, G. Keryer, and P. Dupuis, *Mat. Res. Bull.*, **10**, 825 (1975).

8) R. C. Wheland and J. L. Gilson, *J. Am. Chem. Soc.*, **98**, 3916 (1976).

9) L. V. Interrante, J. W. Bray, H. R. Hart, Jr., J. S. Kasper, P. A. Piacente, and G. D. Watkins, *J. Am. Chem. Soc.*, **99**, 3523 (1977).

10) E. A. Perez-Albuerne, H. Johnson, Jr., and D. J. Trevoy, *J. Chem. Phys.*, **55**, 1547 (1971).

11) L. I. Buravov, G. I. Zvereva, V. F. Kaminskii, L. P. Rosenberg, M. L. Khidekel, R. P. Shibaeva, I. F. Shchegolev, and E. B. Yagubskii, *J. Chem. Soc., Chem. Commun.*, **1976**, 720.

12) L. C. Isett and E. A. Perez-Albuerne, *Solid State Commun.*, **21**, 433 (1977).

13) K. Kamaras, K. Ritvay-Emandity, G. Mihaly, and G. Grüner, *Solid State Commun.*, **24**, 93 (1977).

14) V. F. Kaminskii, M. L. Khidekel, R. B. Lyubovskii, I. F. Shchegolev, R. P. Shibaeva, E. B. Yagubskii, A. V. Zvarykina, and G. L. Zvereva, *Phys. Status Solidi* (*A*), **44**, 77 (1977).

15) S. Doi, T. Inabe, and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **50**, 837 (1977).

16) C. Marschalk and C. Stumm, *Bull. Soc. Chim. Fr.*, **1948**, 418.

17) K. Kan and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **45**, 2096 (1972).

18) K. Lichtenecker, *Z. Elektrochem.*, **40**, 11 (1934).

19) K. Ulbert, *Aust. J. Chem.*, **23**, 1347 (1970).

20) D. L. Smith and H. R. Luss, *Acta Crystallogr.*, *Sect. B*, **33**, 1744 (1977).

21) L. I. Buravov, D. N. Fedutin, and I. F. Shchegolev, *Soviet Phys. JETP*, **32**, 612 (1971).

22) G. Beni, *Phys. Rev. B*, **10**, 2186 (1974).

23) G. Beni, J. F. Kwak, and P. M. Chaikin, *Solid State Commun.*, **17**, 1549 (1975).

24) Y. Matsunaga and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **49**, 2713 (1976).

25) P. M. Chaikin and G. Beni, *Phys. Rev. B*, **13**, 647 (1976).

26) Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **45**, 770 (1972).