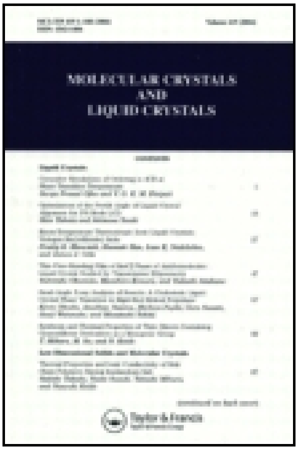

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The Reactions of Sulfilimines withTCNQ and their Characteristic Charge-Transfer Complexes as Products

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The Reactions of Sulfilimines with TCNQ and their Characteristic Charge-Transfer Complexes as Products

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The reactions of sulfilimines with TCNQ were undertaken to investigate the electronic structure of the sulfilimine. The reaction of ylide bond ($S=N$) of sulfilimine with the multiple bonds ($C=C$ or $C\equiv N$ of TCNQ does not occur, but new charge-transfer complexes were formed as products. The molar ratio of the sulfilimine and TCNQ in new charge-transfer complex I was 1:1.3. This ratio was determined by elemental analyses. The results of various thermal analyses indicated that these complexes do not have definite melting points. The reason for this result is that the sulfilimine is instabilized by the weakened ylide bond in the complex, because IR data showed that the electron transfer from ylide bond to TCNQ in the complex occurs and as a consequence, the bond strength of ylide bond is weakened. ESR measurements of various sulfilimine-TCNQ complexes were performed. It was also clarified from the measurements of conductivities that the behaviors of conductivity of new complexes are similar to those of typical charge-transfer complexes.

Keywords: Sulfilimine; TCNQ; charge-transfer complex

INTRODUCTION

Since the ylide has a ylide bond containing the heteroatoms, it has been known that the ylide shows the specific properties and reactions [2a–l]. In order to clarify these specific properties and reactivities, a variety of studies

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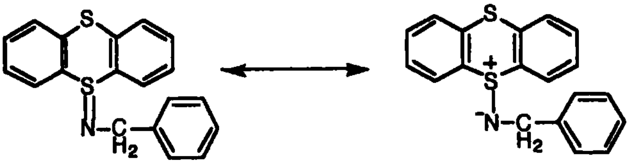
*Corresponding author.

on ylides have been conducted by many investigators and many interesting reactions have been found [3a–p]. A typical ylide reaction is characterized by the reaction of the ylide bond with the polarized bond such as carbonyl group. However, the effect of the bonding character of the ylide bond on the reaction remains to be solved. For example, one of the open questions of the sulfilimine is the bonding character of the S ═ N bond such as the effect of sulfur d-orbital which stabilizes the anionic nitrogen atom[4–5]. The reaction of the sulfilimine with TCNQ will provide some answers about this problem since the reaction products depend on the electron density on the anionic nitrogen of the sulfilimine.

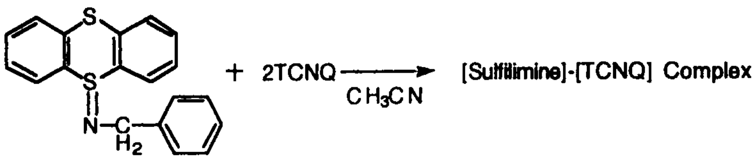
Several sulfilimines were synthesized and the reactions of these sulfilimines with TCNQ were conducted with the aim of obtaining information about this question. Since sulfilimine 1 does not have the stabilizing groups adjacent to the anionic nitrogen atom and the sulfur atom, the reaction products are expected to be affected directly by the bonding character of the S ═ N bond. The reaction of sulfilimine with TCNQ showed that the reaction of the S ═ N bond of sulfilimine with the multiple bond (C ═ C or C≡N) of TCNQ does not occur, but new charge-transfer complexes composed of the sulfilimine and TCNQ were formed. In order to clarify the properties of these new charge-transfer complexes, several physical measurements (UV-Visible, Infrared, ESR, and thermal analyses) were carried out. These results indicated the specific electronic structures of the charge-transfer complexes.



1a 1b

RESULTS AND DISCUSSION

The reaction of sulfilimine 1 and TCNQ was performed at room temperature. That is, the acetonitrile solution of sulfilimine 1 was added to the acetonitrile solution of TCNQ under argon. Though a pale yellow solution of reaction mixture immediately turned to green, the product was not isolated. After partial removal of solvent, this reaction mixture was stood for a week, and as a result, precipitates were formed. After filtration and dryness under a vacuum for 5 h, precipitates were obtained as black crystals. The spectroscopic analyses of this crystal showed that this was not the reaction products of the ylide bond of sulfilimine with the multiple bond of TCNQ, but the complex I as shown in below were formed [6].



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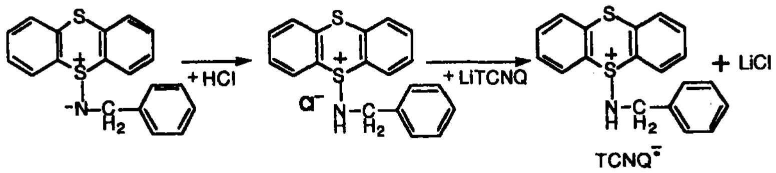
This product is a new charge-transfer complex composed of the sulfilimine and TCNQ. In order to prove the complex formation and to clarify the properties, several spectroscopic measurements were performed by using these crystals. In general, it has been known that the charge-transfer complexes are formed by partial electron transfer from the donor to the acceptor and their electronic structures are specific. Therefore, in order to clarify the electronic structures and properties of the sulfilimines in the complex, the spectra of infrared, UV-Visible, and ESR for these compounds were measured. Furthermore, in order to explore the effect of the ratio of electron transfer in sulfilimine-TCNQ charge-transfer complex I on its physical property, it is necessary to compare with the related compounds which have only TCNQ anion radical in the molecule. Hence, the simple salt 3 and complex salt 4 as shown in the following scheme were synthesized [21], and the data of physical measurements of these compounds were compared with those of complex I.

We suppose that simple salt 3 is formed by full electron transfer from the donor to the acceptor because a positive charge localizes on the thianthrene moiety. A comparison of the properties of complex I with those of simple salt 3 and complex salt 4 is expected to provide some useful information about the properties of sulfilimine-TCNQ complexes.

Confirmation of Formation of Sulfilimine-TCNQ Charge-Transfer Complexes

The solid state infrared spectrum (4000 – 650 cm^{-1}) of complex I was different from the spectra of constituent neutral molecules as expected for



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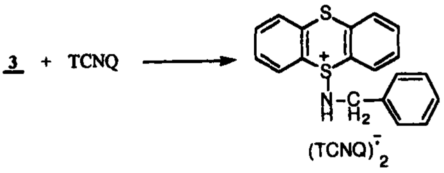

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charge-transfer complexes. All of the absorption bands were broadened compared to those of the constituent molecules, and the changes of the frequencies and intensities of the absorptions were observed. The CN stretching band of the complex was broadened and observed at 2177 cm^{-1}. These values are in the region where the CN stretching modes of the TCNQ anion radical usually appear (2200–2170 cm^{-1}) [7–8].

In general, it has been known that the molar ratio of the donor and TCNQ in the complex is presumed by the ratio of the intensity of the absorption at about 400 nm to that of TCNQ anion radical absorption (841 nm) [9–10]. For example, when a complex is composed of one molecule of the donor and two molecules of TCNQ, its ratio of the intensity of absorption at about 400 nm to that at 841 nm is much larger than that of the complex which is composed of one molecule of the donor and one molecule of TCNQ.

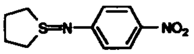
The UV-Visible data for sulfilimine-TCNQ charge-transfer complexes and related compounds are summarized in Table I, and the UV-Visible spectra of new complex I and complex salt 4 are shown in Figure 1 . The ratio of complex salt 4 containing two molecules of TCNQ was 5.2, and the ratio of simple salt 3 containing one molecule of TCNQ was 0.6 as shown in Table I.

These results of the UV-Visible measurements for simple salt 3 and complex salt 4 are in agreement with the results reported as described above [9–10]. Hence, it is possible to presume the approximate molar ratio of

TABLE I The Data of UV-Visible spectra of new Sulfilimine-TCNQ Charge-Transfer Complex **2** and related compounds in Acetonitrile

Compounds[a]	*UV-Visible absorption (nm)*						*The ratio of the intensity of TCNQ absorption* (–400 nm) *to that of TCNQ anion radical absorption* (841 nm)
Complex **I**[b]	254	391		679	741	841	9.4
Complex **II**[c]		391		679	741	841	5.0
Simple Salt **3**	252		416	679	741	841	0.6
Complex Salt **4**	251	390		679	741	841	5.2
LiTCNQ			416	679	741	841	0.7
Sulfilimine **1**	254						

a) The structures of these compounds are shown in the text.
b) sulfilimine **1** -$\mathrm{TCNQ}_{1.3}$
c) sulfilimine **5**-TCNQ_2 ref. 16



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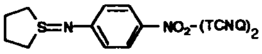

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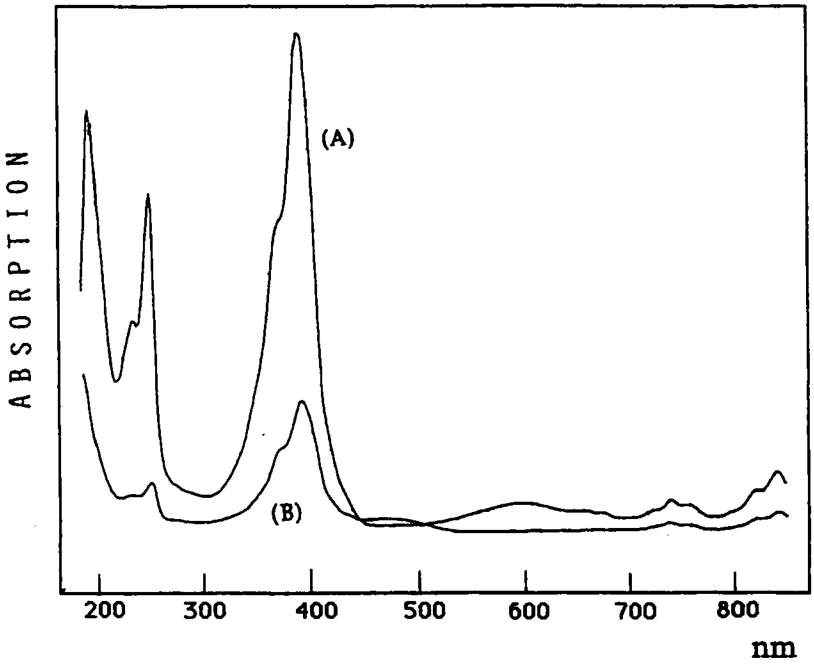
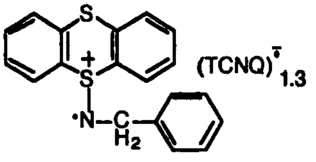


FIGURE 1 UV-Visible Spectra of new Sulfilimine-TCNQ Charge-Transfer Complex I and Complex salt 4 in acetonitrile (A); Complex I, (B); Complex salt 4.

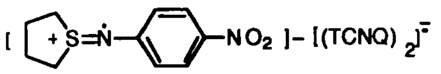
TCNQ to the sulfilimine in the complex by using the data of UV-Visible spectra. The ratio of new complex I was 9.4 as shown in Table I. This result proves that new charge-transfer complex I consists of one molecule of sulfilimine 1 and more than one molecule of TCNQ. Furthermore, in order to clarify the exact composition of complex I, the elemental analysis of complex I was performed, and the molar ratio of sulfilimine 1 to TCNQ in complex I was determined to be 1:1.3.



Sulfilimine 1 - TCNQ Complex I

These results prove that partial electron transfer from sulfilimine 1 to TCNQ in complex I does occur [9, 11–14, 25–27]. This properties of new charge-transfer complex I are still similar to that of TTF-TCNQ charge-transfer complex which has the high conductivity [15].

There is more evidence for the charge-transfer from the sulfilimine to TCNQ. For example, mass spectrum of complex II containing sulfilimine 5 showed parent peaks (m/e, 224 and 204) corresponding to sulfilimine and TCNQ, respectively; together with peaks arising from fragmentation of each compound [16]. This indicates that complex II is a molecular complex of the sulfilimine and TCNQ.



Sulfilimine 5 - TCNQ Complex II

The $\nu(C=O)$ streching bands of phosphorus ylide-TCNQ complexes showed a shift to higher frequencies, indicating an interaction between TCNQ and the ylide carbon (anionic carbon) of phosphorus ylide [17]. Similar results were also evident in Table IV, V, and VI (which will be later discussed).

It was reported that X-ray photoelectron spectra of sulfilimine 9-TCNQ charge-transfer complex IV and related compounds are measured, and the electron transfer from the ylidic nitrogen of sulfilimine to TCNQ occurs in complex IV [2j–k].

That is, the N 1s spectrum of the mixture of sulfilimine 9 and TCNQ showed a shoulder on the lower binding energy side of the CN peak and this shoulder was assigned to the ylidic nitrogen of sulfilimine 9. If there is not charge-transfer interaction, the peak of the ylidic nitrogen should be observed on the lower binding energy side of the cyano peak in complex IV. However, the shoulder assigned to the ylidic nitrogen was not observed in

TABLE II ESR Data of Sulfilimine-TCNQ Charge-Transfer Complexes I and II). Simple salt 3, and complex salt 4

Compounds	*g value (gauss)*	*line width (gauss)*	*resonance field (gauss)*
Complex I[a]	2.0031	1.7	3358
Complex II[b]	2.0037	1.4	3365
	2.0027		3366
Simple salt 3	2.0031	1.3	3358
Complex salt 4	2.0028	1.5	3355

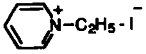
a) Sulfilimine 1 -TCNQ$_{1.3}$ b) Sulfilimine 5-TCNQ$_2$

TABLE III The Data of Charge-Transfer Complexes and related Compounds by DSC and TGA measurements

	1st Stage					*2nd Stage*			
	DSC		*TGA*	*DSC*		*TGA*	*DSC*		*TGA*
Compounds	*Temp* (°*C*)	ΔH^a (*KJ/mol*)	ΔW^b (%) (°*C*)	*Temp* (°*C*)	ΔH^a (*KJ/mol*)	ΔW^b (%) (°*C*)	*Temp* (°*C*)	ΔH^a (*KJ/mol*)	ΔW^b (%) (°*C*)
Phosphorus Ylide **8**	195	24	0	301	−216	29			
($Ph_3P=CHCOC_6H_4NO_2$)						(267−371)^c			
Sulfilimine **9**	166	18	0	197	−106	38			
($(CH_3)_2S=NC_6H_4NO_2$)						(178−288)^c			
Simple salt **11**^{d}	177	45	0	246	−40	14			
						(235−283)^c			
Complex **I**			11	236	−269	16			
(Sulfilimine **I** -$TCNQ_{1.3}$)			(173−198)^c			(199−245)^c			
Complex **III**				177	−92	8	252	−13	8
($Ph_3P=CHCOC_6H_4NO_2$-$TCNQ_2$)						(159−254)^c			(255−320)^c
Complex **IV**				145	−43	3	275	−127	12
($(CH_3)_2S=NC_6H_4NO_2$-$TCNQ_2$)						(142−194)^c			(195−269)^c

a) enthalpy b) loss of weight.

c) The figures in the parentheses are the range of the temperature (°C) during the loss of weight.

d) 

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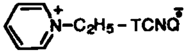

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TABLE IV Infrared Data of Sulfilimines and Sulfilimine-TCNQ Charge-Transfer Complexes

Compounds	*S = N streching band* *(cm^{-1})*
Sulfilimine 1	848
Complex I containing Sulfilimine 1	832
Sulfilimine 5 ($H_8C_4S=NC_6H_4NO_2$)	891
Complex II containing sulfilimine 5	810
Sulfilimine 9 ($(CH_3)_2S=NC_6H_4NO_2$)	885
Complex IV containing Sulfilimine 9	825

TABLE V Infrared Data of Phosphorus Ylides, their Salts, and Phosphorus Ylide-TCNQ Charge-Transfer Complexes

Compounds	*C = O streching band* *ν(C = O) (cm^{-1})*
$Ph_3P=CHCOC_6H_4NO_2$ 8[a]	1540
$Ph_3P=CHCOC_6H_4NO_2$-$TCNQ_2$ III[b]	1598
$Ph_3P^+-CH_2COC_6H_4NO_2)Br^-$ 14[a]	1689
$Ph_3P=CHCOPh$ 12[a]	1509
$Ph_3P=CHCOPh$-$TCNQ_2$ V[b]	1590
$(Ph_3P^+-CH_2COPh)Br^-$ 13[a]	1662

a) These data were published already, reference 21.
b) This work.

the N 1s spectrum of complex IV. Accordingly, the peak of the ylidic nitrogen of sulfilimine 9 shifts to the position of the peak of the cyano group of TCNQ due to the decrease in electron density caused by electron transfer [2k].

Vibrational spectroscopy has proven to be very useful for studying charge transfer compounds, since their charge distributions can often be probed by monitoring vibrational frequency shifts. For example, it was reported that the Raman spectrum of the charge-transfer complex containing TCNQ as a acceptor gives the information about the degree of the electron transfer from the donor to TCNQ [18a–b]. Therefore, the Raman spectra of complex II and LiTCNQ were measured. The absorptions of complex II and LiTCNQ assigned to TCNQ moiety were 1422 and 1455 cm^{-1}, respectively. The absorption assigned to TCNQ itself was 1385 cm^{-1}. The degree of electron transfer from sulfilimine 5 to TCNQ in complex II can be estimated from these values and its value (ρ) is 0.53. This fact suggests that the TCNQ molecule in the complex II is not a typical anion radical.

Consequently, the evidences by results of mass spectroscopy, XPS measurements, IR data of ν(C = O and S = N), Raman spectroscopy, and elemental analysis show that the charge-transfer complexes are formed by the reaction of sulfilimine and TCNQ.

Analyses of Magnetic Properties of Charge-Transfer Complexes by ESR Measurements

In order to examine the magnetic properties of complex I, the ESR data of charge-transfer complex I was compared with those of simple salt 3 containing only an anion radical of TCNQ and complex salt 4.

As shown in Table II , the g value, line width, and resonance field of simple salt 3 are different from those of complex salt 4. These results seem to be caused by the fact that simple salt 3 consists of one molecule of the salt of sulfilimine 1 and one molecule of TCNQ, and complex salt 4 consists of one molecule of the salt of sulfilimine 1 and two molecules of TCNQ.

In order to clarify the magnetic properties of charge-transfer complexes I and II which are composed of one molecule of sulfilimine and more than one molecule of TCNQ, the g values of complexes I and II were compared with that of complex salt 4 in which $(TCNQ)_2$ has an anion radical.

The g value of complex I was 2.0031, and that of complex II were 2.0027 and 2.0037. The g value of complex salt 4 was 2.0028 and was different from those of complexes I and II .

The line width of complex salt 4 was 1.5 gauss, while the line width of charge-transfer complexes I and II were 1.7 and 1.4, respectively. It is believed that the difference of these g values arise from the effect of the neighboring molecule on TCNQ or the difference of crystal structure of charge-transfer complexes containing TCNQ.

The peak shape of the ESR spectrum of complex II was different from that of complex I. That is, complex II showed unsymmetric peaks as shown in Figure 2 [19]. On the other hand, the peak shape of complex I showed a singlet and a symmetric peak. The ESR spectra of charge-transfer complexes with unsymmetric peaks were reported by Yamamoto [21], Matsunaga [19], and Kinoshita [20]. However, they did not report the detailed explanation for unsymmetric structures [21, 19]. Thus, it is very difficult to explain the reason why the shape of these spectra are different from each other.

In summary, since these results of complexes I and II were similar to those of LiTCNQ, these results indicated the existence of TCNQ anion radical. But, it could not be proven that the cation radical derived from sulfilimine contributes to ESR spectra, and this reason can not be well explained.

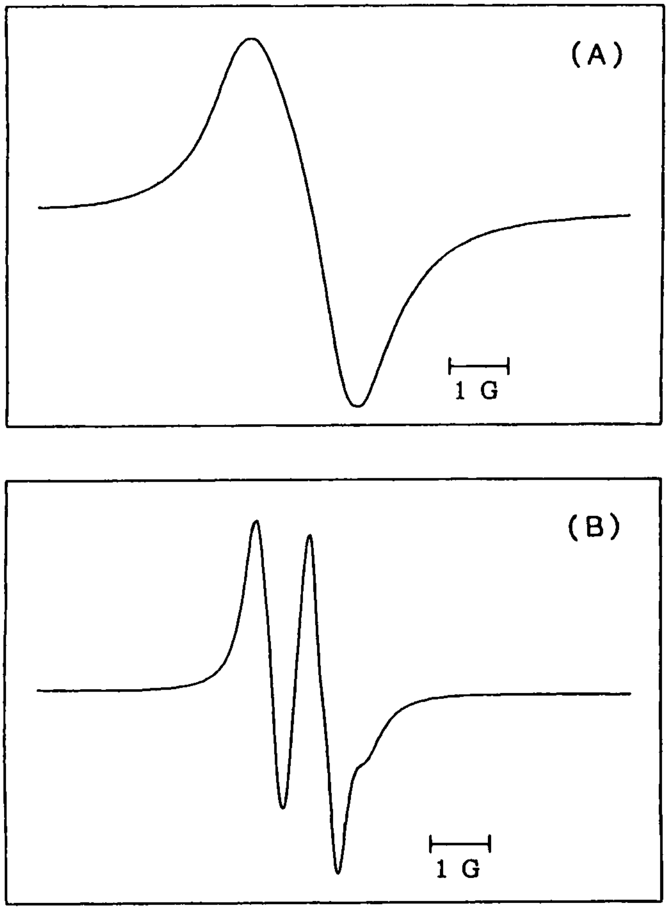


FIGURE 2 ESR Spectra of Sulfilimine-TCNQ Charge-Transfer Complexes (A); Complex I, (B); Complex II. The resonance field of Complex I is 3358 ±5 (gauss). The resonance field of Complex II is 3366 ±5 (gauss).

The Thermal Properties of the Charge-Transfer Complexes

The analysis of thermal properties of new charge-transfer complexes by thermal measurements is necessary in order to clarify the detailed electronic structures of ylide and TCNQ in new charge-transfer complexes, because the bonding energy obtained by thermal analysis is affected by the electronic structure of molecule.

The measurements of DSC and TGA of new complex I were carried out. In order to compare the thermal properties of complex I with those of ylides and other complexes, the related compounds such as $Ph_3P=CHCOC_6H_4NO_2$-$TCNQ_2$ (complex III), $(CH_3)_2S=NC_6H_4NO_2$-$TCNQ_2$ (complex IV) [21] and pyridinium salt-TCNQ (simple salt 11) were prepared and their thermal measurements were also performed (Tab. III).

The thermal process may be largely divided into two stages; that is, the 1st stage is in a lower temperature range and includes a melting point, and the 2nd stage is in a higher temperature range and consists mainly of a decomposition process. As shown in Table III , the melting points of phosphorus ylide 8 and sulfilimine 9 were 195°C and 166°C, respectively, and the enthalpies of melting points of phosphorus ylide 8 and sulfilimine 9 were +24 KJ/mol and +18KJ/mol, respectively. The melting point and the enthalpy of phosphorus ylide 8 were much higher than those of sulfilimine 9.

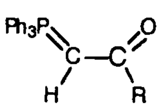
These results are reasonable since it has been known that these thermal properties are in proportion to the molecular weight. In fact, the molecular weight of ylide 8 and sulfilimine 9 are 425 and 198, and the order of increase is in agreement with the order of molecular weight of the ylide. Since the ylide bond has two canonical structures such as Ia and Ib, the ylide is stabilized by these resonances. However, when a charge-transfer complex is formed by partial electron transfer from the ylide bond to TCNQ, it is expected that the resonance contributing to the stability of the ylide does not occur, and as a result, its stability related to the bonding energy decreases and the decomposition temperature of the complex also decreases. In fact, though the DSC data of the ylides showed definite melting points, the melting points of their charge-transfer complexes I, III, and IV were not observed as shown in Table III , and the exothermic behaviors were observed over a wide region. For example, though phosphorus ylide 8 had a melting point at 195°C, charge-transfer complex III containing phosphorus ylide 8 decomposed at 177°C, which is lower than the melting point of phosphorus ylide 8.

A reason why these thermal behaviors occurred is believed to be that the bond strength of ylide bond is weakened by the formation of the complex accompanied with the electron transfer from the ylide to TCNQ. The decrease of the bond strength of ylide bond in the complex can be confirmed by Ir measurements. That is, the infrared absorptions of the ylide bonds (S=N bonds) of sulfilimine 1 and its charge-transfer complex I were 848 and 832 cm^{-1}, as listed in Table IV; the formation of the charge-transfer complex gave lower shift of 16 cm^{-1}. The absorptions (S=N) of sulfilimine 9 and its complex IV were 885 and 825 cm^{-1}, respectively, and the absorptions (S=N) of sulfilimine 5 containing tetrahydrothiophene and its complex **II** were 891 and 810 cm^{-1}, respectively. This fact suggests the relationship between thermal stability and the ratio of change of $\nu(S=N)$. In the case of complex **I**, the shift of $\nu(S=N)$ accompanied by the formation of charge-transfer complex is 16 cm^{-1}, and the ratio of instabilization is small, and the decomposition temperature is very high (236°C). In the case of Complex **IV**, the shift of $\nu(S=N)$ is 60 cm^{-1}, and this large difference suggests that the degree of instability of $S=N$ bond is very large. The thermal properties showed the same tendency; this complex **IV** decomposes at 145°C.

As is stated above, these results are a definite evidence that an electron on the nitrogen atom in the ylide bond ($S=N$) is partially transferred to TCNQ with the formation of the charge-transfer complex and the character of the double bond in the $S=N$ bond decreases. The decrease of electron density of the nitrogen atom in charge-transfer complex was also confirmed by XPS measurements [2k].

The changes in the infrared spectrum with the formation of the sulfilimine-TCNQ charge-transfer complex were also observed in other charge-transfer complexes containing the other ylide. The results of the absorptions of $\nu(C=O)$ for the phosphorus ylide, its phosphonium salt, and the phosphorus ylide-TCNQ charge-transfer complex are summarized in Table V [2l]. For example, the absorptions of $\nu(C=O)$ for phosphorus ylide **12**, its salt **13**, and phosphorus ylide-TCNQ charge-transfer complex **V** were 1509, 1662, and 1590 cm^{-1}, respectively. The same tendency was also observed in the case of other phosphorus ylide **8**. These results indicate that, since an electron of carbon atom in the ylide bond is transferred to TCNQ partially with the formation of the charge-transfer complex, the contribution of the canonical structure (c) decreases and the absorption of $\nu(C=O)$ for the complex shifts to the range of a higher wave number. This electron transfer from the ylidic carbon (C^-) to TCNQ also means the decrease of the bond strength of ylide bond ($P=C$), because the contribution of canonical structure (a) decreases.

As mentioned above, it was clarified from the data of the infrared spectrum that the electron transfer from the ylide to TCNQ occurs when the



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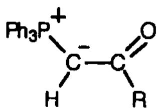

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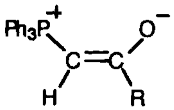
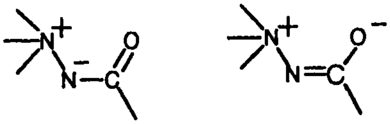


(c)

ylide-TCNQ charge-transfer complex is formed. A similar effect of electron transfer was also observed in the formation reaction of ylide-metal complexes [22]. For example, the results of $\nu(C{=}O)$ for aminimide **15** $[(p\text{-}O_2NC_6H_4CH_2)Me_2N^+N^-COMe]$ and its Pd complex **VI** $[PdCl_2\{(p\text{-}O_2NC_6H_4CH_2)Me_2N^+N^-COMe\}_2]$ are summarized in Table VI [22]. The absorptions of $\nu(C{=}O)$ for aminimide **15** and its Pd complex **VI** were 1580 and 1610 cm^{-1}, respectively. The same tendency was also observed in the case of other aminimides. Aminimide has the resonance structures (a) and (b) as shown in the following scheme. Since the donation of electron on the ylidic nitrogen of aminimide to palladium atom occurs with the formation of the complex, the contribution of canonical structure (b) decreases, and then, the absorptions of $\nu(C{=}O)$ for aminimide-Pd complexes shifted to the higher wave number.



(a) (b)

It was proved from the data of infrared spectrum that the bond strength of ylide bond is weakened by the formation of ylide-TCNQ charge-transfer complex. Therefore, it is considered that the cleavage of the weakened ylide bond in the complex takes place before the melting of the complex and as a consequence, the melting points of these complexes are not observed.

Spectroscopic results in this study provide important information about the bonding character of the $S{=}N$ bond of sulfilimines. If the sulfur-

TABLE VI Infrared Data of Aminimides, their Salts, and their Pd Complexes[a]

Compounds	*C = O streching band* $\nu(C{=}O)$ (cm^{-1})
$(p-O_2NC_6H_4CH_2)Me_2N^+N^-COMe$ **15**	1580
$[PdCl_2\{(p-O_2NC_6H_4CH_2)Me_2N^+N^-COMe\}_2]$ **IV**	1610
$[(p-O_2NC_6H_4CH_2)Me_2N^+NHCOMe]Br^-$ **16**	1690
$(PhCH_2)Me_2N^+N^-COPh$ **17**	1570
$[PdCl_2\{(PhCH_2)Me_2N^+N^-COPh\}_2]$ **VII**	1620
$[(PhCH_2)Me_2N^+NHCOPh]Br^-$ **18**	1700

a) These data were published already. reference 22 nitrogen bond in ylide bond is weak, the sulfilimine will be decomposed by the donation of electron of the sulfur-nitrogen bond to TCNQ. However, the stable sulfilimine-TCNQ charge-transfer complexes were isolated. Thus, this suggests that the sulfur-nitrogen bond of the sulfilimine is very stable. The results of the thermal analyses also suggest that sulfur-nitrogen bond is very strong and the contribution of canonical structure **1a** containing sulfur d-orbital aids to the stability of the sulfilimine.

In summary, the characteristics of thermal properties of ylide-TCNQ charge-transfer complexes are that the thermal decomposition of the complex occurs before melting and the melting point is not observed. As a reason the ylide in the complex is instabilized by electron transfer from the ylide to TCNQ.

The Conductivities of New Sulfilimine-TCNQ Complexes

In order to investigate the relationship between the electronic structures of new sulfilimine-TCNQ charge-transfer complexes and their properties, the conductivities of new complexes, simple salt and complex salt were measured. This result is summarized in Table VII.

The conductivity of charge-transfer complex **II** containing sulfilimine **5** was $\sigma = 2.0 \times 10^{-4}$ $\mathrm{Scm^{-1}}$ and this value was in the range of the conductivity of a semiconductor [16]. From the result of an X-ray crystal structure determination, it has been already clarified that sulfilimine **5** does not have the planarity in the molecular structure [5]. Since it has been reported that the packing of donor molecule in the charge-transfer complex is an important factor to have high conductivity [23–26], the nonplanarity of sulfilimine **5** seems to be one of explanations for the low conductivity of complex **II**.

In order to prove the relationship between the conductivity and the degree of electron transfer in the complex, the conductivities of simple salt **3** and complex salt **4** were measured. The conductivities of simple salt **3** and

TABLE VII Conductivites of new Sulfilimine-TCNQ Charge-Transfer Complexes, Simple Salt, and Complex Salt

Compounds	*Conductivity* (Scm^{-1})
Complex **I**	1.0×10^{-5}
Complex **II**	2.0×10^{-4}
Simple salt **3**	5.0×10^{-8}
Complex salt **4**	3.0×10^{-6}

complex salt 4 were $\sigma = 5.0 \times 10^{-8}$ and 3.0×10^{-6} Scm^{-1}, respectively. Moreover, the conductivities of simple salt 3 and complex salt 4 were lower than that ($\sigma = 1.0 \times 10^{-5}$ Scm^{-1}) of sulfilimine-TCNQ charge-transfer complex I.

As is stated in the section of ESR measurements, the results of Raman spectrum measurement of complex II indicated the partial electron transfer ($\rho = 0.53$). Thus, the results for compounds I, II, 3, and 5 indicate that the conductivities of sulfilimine-TCNQ charge-transfer complex I and II, which are formed by partial electron transfer, are higher than those of simple salt 3 formed by full electron transfer from donor to acceptor. It has been reported that the partial electron transfer in charge-transfer complex is an important factor to have high conductivity [9, 11–14, 26–27]. Therefore, it was proved that the behaviors of conductivity of sulfilimine-TCNQ charge-transfer complexes are similar to those of other charge-transfer complexes.

CONCLUSION

As is stated above, the decrease of electron density on the ylidic nitrogen by electron transfer weakens dπ-pπ interaction of S$=$N bond of sulfilimine in the sulfilimine-TCNQ complex. As a consequence, the sulfilimine in the complex is instabilized and the complex decomposes before the melting point of sulfilimine itself. In reverse, this indicates that the dπ-pπ interaction of sulfur d orbital is an important factor to stabilize the sulfur-nitrogen bond of sulfilimine. This result would provide the great deal of knowledge to the chemistry of sulfilimines.

The characteristics of new sulfilimine-TCNQ charge-transfer complexes are as follows.

(1) The reactions of the sulfilimines with TCNQ at room temperature gave new charge-transfer complexes. These complexes would be expected as stable reaction intermediates of the cation type.

(2) These new sulfilimine-TCNQ charge-transfer complexes were composed of one molecule of the sulfilimine and more than one molecule of TCNQ.

(3) From the results of thermal measurements (DSC and TGA), it was clarified that these complexes do not have definite melting points. This reason is that the ylide bond is weakened with the formation of the ylide-TCNQ complexes and the ylide is decomposed before melting.

EXPERIMENTAL SECTION

Instruments

Nmr spectra of all the samples were measured by a JEOL GX270 Spectrometer. Infrared spectra were recorded on a Hitachi 260-10 spectrometer with KBr method. UV-Visible spectra were recorded on a Hitachi 340 Recording spectrometer. ESR spectra were recorded on a JEOL FE3X spectrometer. Differential Scanning Calorimetry (DSC) was performed by a PERKIN ELMER Model DSC-2, and Thermogravimetric Analysis (TGA) was performed by a Shimazu Thermal Analyzer DT-30.

Methods

The measurements of the conductivities are as follows. A hole with a defined radius was cut into a Teflon sheet. The powder of the samples was put into the hole and then, the pellets were made by the press. After measuring the thicknesses, silver paste was put on both sides of the pellets. The resistivities of the compounds were measured by the galvanometer.

Reagents

Chloroform, acetone, and diethyl ether were commercially available from WAKO PURE Chemical Co. and used without further purification. Aqueous perchloric acid ($HClO_4$) was obtained from YONEZAWA Chemical Co. TCNQ (Tetracyanoquinodimethane) was obtained from KANTO Chemical Co. and was purified by several sublimations. Acetic anhydride was obtained from YONEZAWA Chemical Co. and was purified by distillation just before use. Dry acetonitrile was prepared by distillation over phosphorus pentoxide. Dry benzene was prepared by distillation over CaH_2. Thianthrene was purified by several recrystallizations.

Preparation of Thianthrene Cation Radical Perchlorate 6 [28–29]

To a solution of 1.5 g (6.9 mmol) thianthrene in 90 ml dry benzene was added 3 ml of 70% perchloric acid. The aqueous layer of the added acid became blue and remained undissolved in the benzene. The mixture was magnetically stirred for 10 minutes and then was added dropwise to 45 ml of acetic anhydride at 0°C over 1 h. The mixture was allowed to stand for 4 h and filtered, and purple black crystals were formed. These crystals were washed with dry benzene until the benzene was colorless, giving 1.75 g

(80%) of compound 6 after drying under a vacuum. UVλmax (CH_3CN) 540 nm.

Reaction of Thianthrene Cation Radical Perchlorate 6 with Benzylamine [28–29]

A solution of benzylamine in dry acetonitrile was added dropwise to a solution of 1.75 g (5.54 mmol) thianthrene perchlorate 6 in 150 ml dry acetonitrile under nitrogen gas until the solution was colorless. The solvent of the resulting solution was removed on a rotary evaporator, and the residue was taken up in a small amount of acetone and chromatographed on a column of silica-gel (C-200). After the elution with petroleum ether and diethyl ether, the elution by the mixture solution of diethyl ether and acetone (1:1) was performed again. The orange crystals were gained after evaporation of the solvent. The yield of compound 7 was 0.47 g (20%). ^{1}H NMR ($(CD_3)_2CO$) δ 8.16 (2H, d of d), 7.81–7.57 (6H, m, arom), 7.23–7.06 (5H, m, C_6H_5), 6.86-6.48 (1H, br, s, -NH), 4.10 (2H, s, -CH_2-).

Preparation of Sulfilimine 1 [29]

To a solution of 0.47 g (1.11 mmol) compound 7 in ethanol (40 ml) was added dropwise to 2% NaOH solution until the solution became pH = 7. The resulting solution was poured into water. Then, the mixture was extracted with diethyl ether at several times and the combined organic layer was dried (Na_2SO_4) and the diethyl ether was evaporated on a rotary evaporator to give sulfilimine 1. The yield was 0.15 g (42%). This procedure was also repeated for the preparation of other compounds, ^{1}H NMR ($(CD_3)_2CO$) δ 7.97 (2H, d of d) 7.65–7.21 (11H, m, arom), 4.23 (2H, s, -CH_2-); UVλmax (CH_3CN) 254 nm; IR (KBr) 3062, 2919, 2850, 1720, 1599, 1570, 1491, 1440, 1282, 1118, 1074, 1028, 848, 750, 695 cm^{-1}. All spectroscopic data of this compound 1 was consistent with those previously reported [29].

Preparation of Simple Salt 3 and Complex Salt 4

To a solution of 0.077 g (0.24 mmol) sulfilimine 1 in ethanol (20 ml) was added a small amount of ca 5% HCl solution and the mixture was stirred at room temperature for 3 h. The solvent of the resulting solution was removed by a rotary evaporator and the hydrochloride salt of sulfilimine 1 was obtained. This product 2 (Hydrochloric salt of sulfilimine 1) was dried in a vacuum. To the solution of this compound 2 (0.085 g) in acetonitrile (20 ml) under argon was added 0.0507 g (0.24 mmol) LiTCNQ in acetonitrile (30 ml) and the mixture was stirred at room temperature for 2 h. The resulting solution was concentrated under reduced pressure. After filtration to separte lithium chloride, the removal of the solvent and the dryness in a vacuum affords 0.10 g (79%) simple salt 3. UVλmax (CH_3CN) 252, 416, 679, 741, 841 nm; IR (KBr) 3400, 2346, 2192, 1642, 1552, 1538, 1505, 1434, 1324, 1246, 1174, 1115, 1095, 756, 742 cm^{-1}.

To the solution of 0.039 g (0.074 mmol) simple salt 3 in acetonitrile (25 ml) under argon was added 0.0161 g (0.074 mmol) TCNQ in acetonitrile (15 ml) and the mixture was stirred at room temperature for 6 h. The removal of solvent and the dryness in a vacuum affords 0.042 g (78%) of complex salt 4. UV λ_{max} (CH_3CN) 251, 390, 679, 741, 841 nm; IR (KBr) 3400, 3054, 2337, 2194 (CN), 1572, 1542, 1506, 1438, 1351, 1338, 1180, 864, 762, 750 cm^{-1}.

Reaction of Sulfilimine 1 with TCNQ

To a solution of 0.0364 g (0.11 mmol) sulfilimine 1 in acetonitrile (20 ml) was added 0.0449g (0.22 mmol) TCNQ in acetonitrile (35 ml) under argon and the mixture was stirred under argon gas at room temperature for 1 week. The resulting solution was concentrated by a rotary evaporator and stood in a refrigerator for 1 week [16]. As a consequence, black crystals were obtained as precipitates. After filtration, the dryness in a vacuum for 5 h affords 0.009 g (11%) of black charge-transfer complex I. UVλmax (CH_3CN) 254, 391, 606, 579, 741, 841 nm; IR (KBr) 3469, 3044, 2177, 1592, 1436, 1428, 1340, 1168, 1100, 860, 832, 760, 750, 693 cm^{-1}; Anal. Calcd for Sulfilimine 1-(TCNQ)$_{1.3}$: C, 70.81; H, 3.47; N, 14.83. Found: C, 70.50; H, 3.94; N, 14.96.

The synthetic method of sulfilimine 5-TCNQ charge-transfer complex II was published [16].

Reaction of Phosphorus ylide 8 with TCNQ

To a solution of 0.0596 g (0.14 mmol) phosphorus ylide 8 in acetonitrile (25 ml) was added 0.572 g (0.28 mmol) TCNQ in acetonitrile (35 ml) under argon and the mixture was stirred under argon gas at room temperature for 1 week. The resulting solution was concentrated by a rotary evaporator and stood in a refrigerator for 1 week. After filtration, the dryness in a vacuum affords 0.018 g (15%) of charge-transfer complex III. UVλmax (CH_3CN)

391, 679, 741, 841 nm; IR (KBr) 2178, 1685, 1598, 1547, 1525, 1505, 1438, 1344, 1322, 1189, 1104, 1000, 865, 736, 711, 679 cm^{-1}.

Reaction of Phosphorus ylide 12 with TCNQ

To a solution of 0.0533 g (0.14 mmol) phosphorus ylide 12 in acetonitrile (25 ml) was added 0.0572 g (0.28 mmol) TCNQ in acetonitrile (35 ml) under argon and the mixture was stirred under argon gas at room temperature for 1 week. The solvent of reaction mixture was reduced by a rotary evaporator and stood in a refrigerator for 1 week. After filtration, the dryness in a vacuum affords 0.011g (10%) of charge-transfer complex V. UVλmax (CH_3CN) 391, 679, 741, 841 nm; IR (KBr) 2178, 1710, 1590, 1555, 1496, 1434, 1350, 1317, 1176, 1102, 997, 828, 748, 720, 686, cm^{-1}.

Reaction of Sulfilimine 9 with TCNQ

To a solution of 0.0436 g (0.22 mmol) sulfilimine 9 in acetonitrile (20 ml) was added 0.0902 g (0.44 mmol) TCNQ in acetonitrile (50 ml) under argon and the mixture was stirred under argon gas at room temperature for 1 week. The resulting solution was concentrated by a rotary evaporator and stood in a refrigerator for 1 week [21]. After filtration, the dryness in a vacuum affords 0.016 g (12%) of charge-transfer complex IV. UVλmax (CH_3CN) 392, 679, 741, 841 nm; IR (KBr) 3050, 2178, 1612, 1528, 1500, 1445, 1347, 1321, 1201, 1113, 863, 825, 766, 741, 700 cm^{-1}.

Preparation of Simple salt 11

To a solution of 0.2468 g (1.05 mmol) pyridinium salt 10 in acetonitrile (40 ml) under argon was added 0.2216 g (1.05 mmol) LiTCNQ in acetonitrile (90 ml) and the mixture was stirred at room temperature for 4 h. The resulting solution was concentrated under reduced pressure. After filtration to separate lithium chloride, the removal of the solvent and the dryness in a vacuum affords 0.27 g (82%) simple salt 11. IR (KBr) 3428, 2194, 2178, 1639, 1576, 1511, 1493, 1367, 1335, 1182, 825, 714, 688 cm^{-1}.

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