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PREPARATION AND PROPERTIES OF COMPLEX SALT OF SULFILIMINE AND TCNQ

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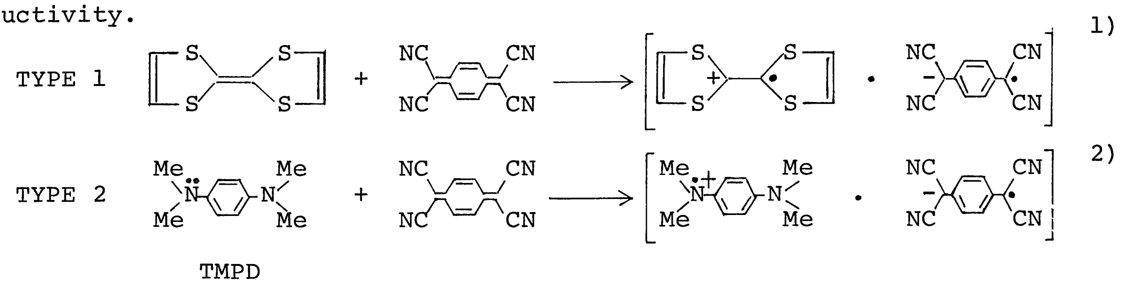
The interaction between sulfilimines and TCNQ in CH_2Cl_2 was examined. The interaction depended markedly upon the structure of the sulfilimines: the higher the basicity of the sulfilimine, the stronger the interaction observed. For the crystalline complex of S,S-dimethyl-N-p-nitrophenylsulfilimine—TCNQ, 1:1 structure of biradical-salt type was estimated by spectroscopic and chemical analyses.

It is well known that 7,7,8,8-tetracyanoquinodimethane(TCNQ) forms charge transfer complex salts by interaction with compounds which have an electron rich double bond(TYPE 1) or a lone pair(TYPE 2). Recently, much attention is being denoted to such charge transfer complexes in view of their characteristic electric-conductivity.



In analogy with two types of donors cited above, ylides would be expected to be another class of donor, because they have ylide and ylene structures in resonance such as $X^{+}-Y^{-} \leftrightarrow X=Y$. However, no complex salt of this type has been reported, except for the complex of $[X=Y\cdot M^{n+}X_n]$ type.3)

In the course of our study on sulfilimines, we have studied the interaction of them with TCNQ. We wish, in this paper, to describe the preparation and properties of sulfilimine-TCNQ charge transfer complexes.

$$\underset{\mathbf{1}}{R^1{}_2S=NR^2} \quad + \quad \text{TCNQ} \quad \longrightarrow \quad \underset{\mathbf{2}}{[R^1{}_2S=NR^2\cdot\ \text{TCNQ}]}$$

Interaction between sulfilimines and TCNQ in CH_2Cl_2

Equal amounts (by volume) of 0.01 M solutions of dichloromethane containing TCNQ and sulfilimine **1**[4] were mixed and allowed to stand at 20°C. The change in color of the mixed solution was observed. As shown in Table 1, the coloration (before mixing, most of the solutions have a light yellow or an orange color) depended markedly upon the structure of the sulfilimines. Thus, the sulfilimines, which have high basicity as **1i**, **1j**, and **1k**, showed such a strong interaction that marked color change (to deep violet) occurred at the moment of mixing of both solutions, and the ones, which have low basicity as **1a**, **1c**, **1d**, **1f**, **1h**, **1l**, and **1m**, showed no color change even on standing for a week.

The each colored solution showed absorptions at the similar range as $TCNQ^{\overline{\cdot}}$ (600-900 nm),[5] but the shapes were different from the latter. Judged from the color

Table 1. Interaction between sulfilimines and TCNQ

Sulfilimines (**1**) and Others	Color Change ‡	Vis. Absorption (nm)	Remarks
1a $Me_2S{=}NTs$	×	———	
1b $Me_2S{=}NC_6H_4NO_2$-4	○	849, 748, 625	Violet needle*
1c $Me_2S{=}NC_6H_3(NO_2)_2$-2,4	×	———	
1d $Me_2S{=}NC_6H_2(NO_2)_3$-2,4,6	×	———	
1e $Me_2S{=}NCOC_6H_5$	●		
1f $Me_2S{=}NCOC_6H_4NO_2$-4	×	———	
1g $(CH_2)_4S{=}NC_6H_4NO_2$-4	○	847, 746, 626	Violet needle*
1h $(C_6H_5)_2S{=}NTs$	×	———	
1i $(C_6H_5)_2S{=}NH$	◎	580	Blue powder**
1j $(C_6H_5)_2S{=}NC_6H_5$	◎	598	Violet needle**
1k $(C_6H_5)_2S{=}NC_6H_4CH_3$-4	◎	630, 582, 548	Violet ppt*
1l $(C_6H_5)_2S{=}NC_6H_3(NO_2)_2$-2,4	×	———	
1m $(C_6H_5)_2S{=}NC_6H_2(NO_2)_3$-2,4,6	×	———	
$Me_2S{=}CHCOC_6H_5$	◎	847, 747, 668	Violet ppt*
$Me_2S{=}C(CN)_2$	×	———	
$(C_6H_5)_3P{=}CHCOC_6H_5$	◎	853, 754, 692	Violet ppt*
$(4\text{-}CH_3C_6H_4)_2S{\rightarrow}O$	×	———	

‡Color changed to green within 10 min (◎), 1-2 hr (○), and a day (●). No color change in a week (×). * Complex salts liberated from the solutions. ** Complex salts obtained after evaporation of the solvent.

change with respect to time, the order of donating effects of the substituents on nitrogen atom is presumed as follows:

$$\mathrm{H,\ Ar} \gg \mathrm{C_6H_4NO_2\text{-}4} > \mathrm{COC_6H_5} \gg \mathrm{Ts,\ COC_6H_4NO_2\text{-}4,\ C_6H_3(NO_2)_2\text{-}2,4,\ C_6H_2(NO_2)_3\text{-}2,4,6}$$

For comparison, the interaction of S-C and P-C ylides, and sulfoxide with TCNQ were also examined, in which only the ylides of phenacyl type showed color changes and formed unstable precipitates (as shown in Table 1).

Preparation and characterization of complex salt from sulfilimine and TCNQ

A solution of 0.5 mmol of dimethyl-N-p-nitrophenylsulfilimine (1b) and 0.5 mmol of TCNQ in 20 ml of CH_2Cl_2 was allowed to stand at room temperature. The color of the solution turned to green from an initial light yellow and the intensity of the green color increased with time. After standing for a week, the resulting violet needles were collected by filtration, washed with CH_2Cl_2-ether several times, and dried in vacuum. The needles decomposed at about 165°C. Elementary analysis showed the needles to be the 1:1 complex(2b) of 1b and TCNQ: Found (calculated for $C_{20}H_{14}N_6O_2S$) (%); C 59.88(59.68), H 3.39(3.51), N 21.15(20.85). The IR spectrum was markedly different from that of a superimposition of each component. Compared to 1b, the absorption band at 880 cm^{-1} ($\nu_{S=N}$) disappeared and the band at 1290 cm^{-1} (ν_{NO_2}) shifted to 1335 cm^{-1}. Moreover, compared to TCNQ, the band at 860 cm^{-1} (based on the quino- form) disappeared and the band at 2200 cm^{-1} (ν_{CN}) shifted to 2170 cm^{-1}. The electronic spectrum of 2b in THF, as shown in Fig. 1, has absorption in the range 600-1000 nm. The spectral figure is markedly different from those observed for other types of TCNQ-complex salts such as $[\mathrm{Me_2\overset{+}{S}\text{-}NHC_6H_4NO_2\text{-}4\ TCNQ^{\overline{\bullet}}}]$ (3)[6] and $[\mathrm{n\text{-}Bu_4N^{+}\ TCNQ^{\overline{\bullet}}}]$ (4).[7] The ESR spectrum of the complex salt 2b in THF showed three asymmetrically distributed lines at 25°C, which differed from the broad singlet line of the complex salts, $[\mathrm{M^{+}\cdot TCNQ^{\overline{\bullet}}}]$,[8] 3, and 4 as shown in Fig. 2. The former is similar to the spectrum of the biradical complex salt $[\mathrm{TMPD^{\overset{+}{\bullet}}\cdot TCNQ^{\overline{\bullet}}}]$ prepared form $[\mathrm{TMPD^{\overset{+}{\bullet}}\cdot ClO_4^{-}}]$ and $[\mathrm{Li^{+}\cdot TCNQ^{\overline{\bullet}}}]$ by M. Kinoshita.[2b]

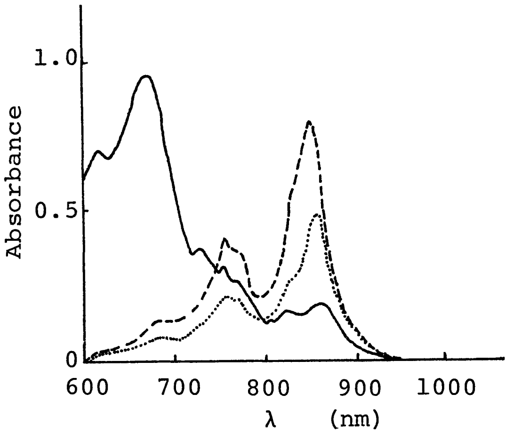


Fig. 1. Visible spectra (20°C, THF) of 2b (2.4×10^{-4}M) (——), 3 (1.7×10^{-5}M) (---), and 4 (1×10^{-5}M) (·······).

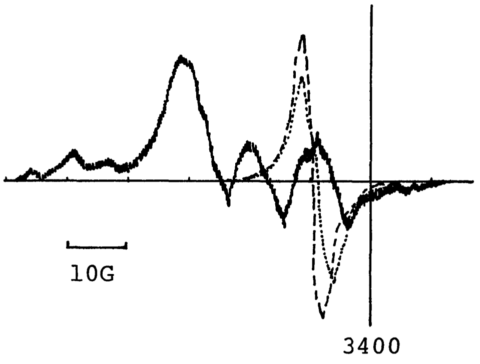
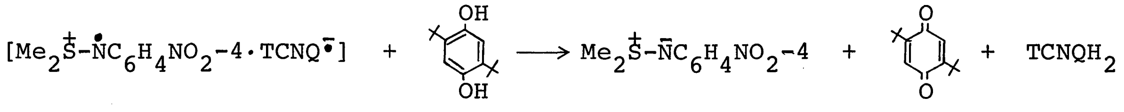


Fig. 2. ESR spectra (25°C, THF) of 2b (——), 3 (---), and 4 (·······).

On the bases of the results described above, the reasonable structure of the complex salt 2b is considered to be a biradical-salt form (2B). Moreover, this was confirmed by a chemical reaction.

The reaction between the complex salt 2B and 2,5-di-t-butylhydroquinone in equimolar amounts in THF was carried out. By thin layer chromatography of the resulting mixture, 2,5-di-t-butyl-p-benzoquinone (5) (silica gel-hexane), and also 1a and $TCNQH_2$ (6) (silica gel-THF) were identified, respectively. Actually 5 was obtained from the reaction mixture in 70% yield.



2B 1b 5 6

Electrical properties of the complex salt 2b

The specific resistance of the complex salt 2b measured by four probe method is 5×10^4 ohm cm, which corresponds to one-thousandth of the values of sulfilimine 1b (7×10^7 ohm cm) and TCNQ (6×10^7 ohm cm). This complex salt did not show photoconductivity. However, it showed semi-conductivity with the activation energy of conductivity of 0.27 eV (175~285°K).

References and Notes

1) S.B. Coleman, M.J. Cohen, D.J. Sandman, F.G. Yamagishi, A.F. Garito, and A.J. Heeger, Solid State Commun., 12, 1125 (1973).

2) (a) R. Foster and T. Thomson,Jr., Trans. Farady Soc., 59, 296 (1963).
(b) M. Kinoshita and H. Akamatsu, Nature, 207, 291 (1965).

3) For example, G. Natsubayashi, M. Toriuchi, and T. Tanaka, Chemistry Letters, 1973, 985.

4) The various sulfilimines used were prepared as follows:

(i) R^1=alkyl, aryl, R^2=tosyl; $R^1{}_2S + NaClTs \longrightarrow R^1{}_2S{=}NTs$

(ii) R^1=alkyl, R^2=aryl, acyl; $R^1{}_2S{\to}O + H_2NR^2 \xrightarrow{DMF-P_2O_5} \xrightarrow{Base} R^1{}_2S{=}NR^2$

(iii) R^1=aryl, R^2=H; $Ar^1{}_2S{=}NTs \xrightarrow{conc.H_2SO_4} \xrightarrow{NaH} Ar^1{}_2S{=}NH$

(iv) $R^1=R^2$=aryl; (a) $Ar^1{}_2S{=}NH + Ar^2X \xrightarrow{Base} Ar^1{}_2S{=}NAr^2$

(b) $Ar^1{}_2S{=}NBr + Ar^2Li \longrightarrow Ar^1{}_2S{=}NAr^2$

5) L.R. Merby, R.J. Harder, W.R. Hertler, W. Mahler, R.E. Benson, and W.E. Mochel, J. Amer. Chem. Soc., 84, 3374 (1962).

6) The preparation was carried out as follows:

$1b \xrightarrow{HCl} [Me_2\overset{+}{S}\text{-}NHC_6H_4NO_2\text{-}4]Cl^- \xrightarrow{[Li^+ \cdot TCNQ^{\bar{\bullet}}]} 3$

7) The preparation was carried out as the reference 5).

8) (a) P.H. Rieger, I. Berger, W.H. Reimuth, and G.K. Fraenkel, J. Amer. Chem. Soc., 85, 683 (1963).
(b) P.H.H. Fischer and C.A. McDowell, J. Amer. Chem. Soc., 85, 2695 (1963).

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