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# On the Magnetic Susceptibilities of Some Organic Sulfur Compounds\*

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## Synopsis

Magnetic susceptibilities of ten organic sulfur compounds have been measured by use of the Gouy balance, and the structures of these compounds are discussed. The compounds are tetramethylthiuram disulfide (I), tetramethylthiuram monosulfide (II), dixanthogene (III), sodium diethyldithiocarbamate (IV), sodium butyltrithiocarbonate (V), thiobenzophenone (VI), 2-mercaptobenzothiazole (VII), dibenzothiazolyl-2-disulfide (VIII), benzothiazolyl-*N'*-cyclohexylsulfenamide (IX) and trithioacetone (X).

They are found to be all diamagnetic. The atomic increment of double bond sulfur has been newly evaluated to be  $-11.1 \times 10^{-6}$  c.g.s.u., from the experimental values of compounds indicated by (IV, V) and (VI).

The six compounds (I, II, III, VII, VIII) and (IX) have all shown large diamagnetic exaltation, suggesting to have the molecular  $\pi$ -electron orbits. The compound X is found to have the single bond sulfur rather than the double bond sulfur, suggesting the cyclic structure.

## I. Foreword

There have been so far a few experimental data on magnetic susceptibilities of sulfur compounds. Although some efforts to systematize the relation between the measured value and the chemical structure have been found in the literature, the exact quantitative systematization has not yet been established.

Pascal<sup>(1)</sup>, for instance, obtained the value of  $-15 \times 10^{-6}$  c.g.s.u. as an atomic increment for magnetic susceptibility of single bond sulfur ( $-S-$ ), evaluated from  $(CH_3)_2S$  and  $(C_2H_5)_2S$ .

On the other hand, Clow and Thompson<sup>(2)</sup> studied the relation between chemical structure and magnetic susceptibility on the basis of quantitative relation between the actual value of magnetic susceptibility for organic sulfur compound and Pauling's<sup>(3)</sup> theoretical value of magnetic susceptibility for atoms or ions as well as the dipole moments of its compounds.

In their article, magnetic susceptibility for atoms or ions were evaluated from the residual charge of each atom constituting a molecule, and the difference

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(1) P. Pascal, Ann. Chim. Phys., 19 (1910), 5; 25 (1912), 289; 29 (1913), 218.

(2) A. Clow, J. M. C. Thompson, Trans. Faraday Soc., 33 (1937), 894.

(3) L. Pauling, Proc. Roy. Soc., A114 (1927), 191.

between its total sum and the measured value was regarded as the fall of diamagnetism due to chemical combination; the amount of fall of diamagnetism for similar chemical combination in different molecules was investigated and it was shown to be applicable to the same extent of usual additive law. But misinterpretation of the part of diamagnetic anisotropy due to  $\pi$  electrons in aromatic compounds leads to conclusion that it depends upon polarization between each carbon atom.

In another case, as in the case of Goehring's<sup>(4)</sup> data for  $N_4S_4$ , some single-bonded sulfur compounds showed further surplus diamagnetic exaltation; but chemical interpretation of this surplus value has not yet been quantitatively solved.

On the other hand, it has been known that, in some cases, disulfide in solution shows paramagnetism in certain temperature as is the case in the study of Selwood & Cutforth.<sup>(5)</sup>

In the present study some adequate compounds were chosen to evaluate the experimental value of  $\chi_{(SF)}$  concerning the double bond sulfur (S=); moderately large exaltation was often observed between measured and calculated values derived from the usual additive law on the basis of above value and  $\chi_{(-S-)}$  for single-bonded sulfur (-S-). In this connection, these sulfur compounds were thought to produce free radicals in certain conditions<sup>(5),(6)</sup> (solvent, temperature, etc.) and it is thought to be associated with the promotion of vulcanisation.<sup>(7)</sup>

## II. Experimental

### § 1. Materials

#### Group A

- I Tetramethylthiuram disulfide. ( $C_6H_{12}N_2S_4$ )
- II Tetramethylthiuram monosulfide. ( $C_6H_{12}N_2S_3$ )
- III Dixanthogene. ( $C_6H_{10}O_2S_4$ )
- IV Sodium diethyldithiocarbamate. ( $C_5H_{10}NS_2Na$ )
- V Sodium butyltrithiocarbonate. ( $C_5H_9S_2Na$ )
- VI Thiobenzophenone. ( $C_{12}H_{10}S$ )

#### Group B

- VII 2-Mercaptobenzothiazole. ( $C_7H_5NS_2$ )
- VIII Dibenzothiazolyl-2-disulfide. ( $C_{14}H_8N_2S_4$ )
- IX Benzothiazolyl-N'-cyclohexylsulfenamide ( $C_{13}H_{16}N_2S_2$ )

#### Group C

- X Trithioacetone. ( $C_9H_{18}S_3$ )

### § 2. Purification of the Sample

Compound (I) was prepared from commercial product (directly from factory)

(4) M. Goehring, Chem. Ber., **80** (1947), 122.

(5) P. W. Selwood, H. G. Cutforth, J. A. C. S., **70** (1948), 278.

(6) H. P. Koch, J. Chem. Soc., (1949), 401.

(7) Advances in Colloid Science Vol. II.

recrystallized twice from purified chloroform, washed with anhydrous ether and dried over phosphorus pentoxide in a vacuum desiccator; mp. 155°C.

Compound (II) was also a commercial product recrystallized twice from purified chloroform, washed with anhydrous ether and dried over phosphorus pentoxide in vacuum desiccator; mp. 108°C, yellow.

Chloroform used in above purification was such that had been redistilled after drying with phosphorus pentoxide, and ether was such that was redistilled after dehydration by metallic sodium.

Compound (IV) was Merck product itself.

Compounds (III), (V), (VI) and (X) were kindly synthesized and offered by Assistant Prof. Tarô Yamazaki, Research Institute of Ore Dressing and Refining, Tôhoku University; (V) and (VI) were recrystallized from petroleum ether after synthesis and (VI) was recrystallized from petroleum ether after vacuum distillation (137~138°/2 mm Hg) and crystallization under cooling by liquid air; blue colored, mp. 47°C.

Treatment of compound (VI) was conducted in the atmosphere of carbon dioxide to prevent as much as possible oxidation and stored over phosphorus pentoxide in a vacuum desiccator.

Compound (VII) was a commercial product recrystallized from the mixture of purified alcohol and benzene (1:2); slightly yellow crystals of mp. 178°C.

Compound (VIII) was a commercial product recrystallized twice from hot benzene; faintly light-yellowed, almost white crystals, mp. 179°C.

Compound (IX) was a commercial product recrystallized twice from purified methanol; mp. 105°C, colorless.

Benzene used in above purification was a commercial special grade reagent washed with sulfuric acid until no coloration, washed with distilled water, washed with sodium bicarbonate solution, dehydrated with metallic sodium and then brought to distillation; alcohol was dehydrated by quick lime and then further dehydrated by metallic calcium.

Compound (X) was synthesized in the same way as Kamihara<sup>(8)</sup> and after dehydrating distillation it was solidified in liquid air; mp. 24°C.

### § 3. Measurement of Magnetic Susceptibility

Magnetic susceptibility was measured by Gouy's method, in which lidded silica measuring tube of about 5 mm in outside diameter, of about 3 mm in inside diameter, of about 0.6 ml. in volume and of 2.6~3.5 g in weight was hanged by silica fiber of about 0.5 mm in diameter from the arm of a semimicrobalance and was adjusted to bring it about the center of electromagnetic poles installed underneath<sup>(9)</sup>.

The surface of magnetic pole was about 8 mm in diameter, the distance between two poles were 10.5 mm and maximum intensity of magnetic field at

(8) S. Kambara, J. Industr. Chem. of Japan, 54 (1951), 673.

(9) G. Hazato, et al. Sci. Rep. RITU, A5 (1953), 278.

the center was about 1000 Gauss when electric current of 9 A was applied through it.

Three measuring tubes were as those shown in the following table.

No.	Outside diameter	Inside diameter	Length	Weight	The average of $\Delta W_V$
1	4.4 mm	3.0 mm	125 mm	2.6 g	0.00392
2	4.5 mm	3.0 mm	125 mm	3.5 g	0.00536
3	4.7 mm	3.0 mm	125 mm	3.0 g	0.00444

In the above,  $\Delta W_V$  shows force of restitution for empty containers. Samples were taken in this tube about 0.4~0.2 ml. and from  $\Delta W_S$ , force of restitution for above,  $W_S$ , weight of the sample,  $\Delta W_W$ , force of restitution for water of the same volume as respective samples and  $W_W$ , weight of the water,  $\chi_g$  was calculated according to the following equation.

$$10^6 \times \chi_g = -0.72 \times \frac{\Delta W_S}{W_S} \times \frac{W_W}{\Delta W_W}$$

### III. Measured values

Table 1

Group A

Samples	Temperature	$-\chi_{\text{mol}} \times 10^6$	$\Delta W_S$	$W_S$
I	18°	139.0	0.00241	0.41710
	21°	142.1	0.00222	0.36914
II	18°	118.5	0.00300	0.53708
	18°	118.3	0.00237	0.39462
III	23.5°	138.5	0.00192	0.33498
	23°	137.2	0.00224	0.45814
IV	20°	98.3	0.00210	0.35546
	20°	99.6	0.00226	0.36380
V	26°	104.5	0.00089	0.06048
VI	24°	118.0	0.00336	0.52140
	24.5°	118.1	0.00248	0.38882

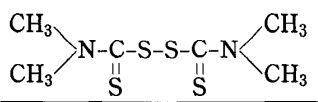
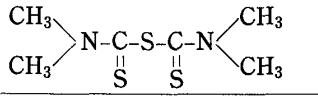
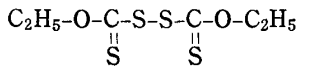
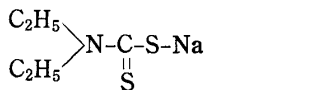
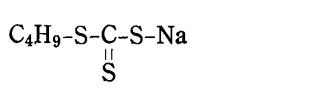
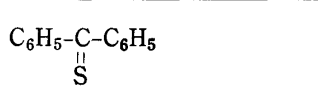
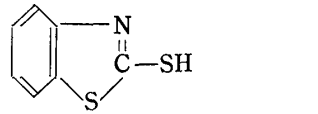
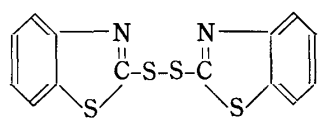
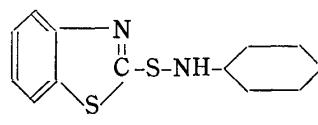
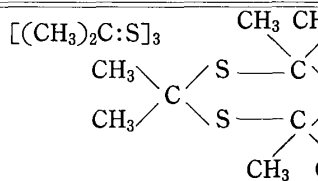
Group B

VII	20°	99.4	0.00294	0.38852
VIII	22°	186.4	0.00187	0.32503
	20°	189.0	0.00187	0.32148
IX	22°	166.4	0.00235	0.35461

Group C

X	28.5°	156.9	0.00294	0.41036
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Table 2

Sample		Observed value	Calculated value	Excess
Group A				
I		140.6	121.0 Ia 115.4 Ib, Ic	19.6 25.2
II		118.4	106.0 IIa 106.2 IIb, c, d, e, f	12.4 12.2
III		137.3	121.2 IIIa 115.6 IIIb, c	16.6 22.2
IV		99.2		
V		104.5		
VI		118.1		
Group B				
VII		99.4	86.4	13.0
VIII		189.0	166.9	22.1
IX		166.4	153.2	13.2
Group C				
X		156.9	151.3 S(F) 139.3 S(F)	

Diamagnetic coefficient  $\chi_A$  of each element used for above calculation and corrected value  $\chi_\pi$  for increase of diamagnetism by  $\pi$  electron are shown in Table 3, in which S(F) was calculated from the measured value of compound (IV), (V) and (VI) as in the following way.

In the case of compound (IV) :—

$$\sum\chi_A = 4C_{(F)} + C_{(F)} + 10H + (>N-) + (-S^\ominus) + (Na^\oplus) + S_{(F)}$$

$$-99.2 = -88.2 + S_{(F)}$$

$$\therefore S_{(F)} = -11.0 \times 10^{-6}$$

In the case of compound (V) :—

$$\sum\chi_A = 4C_{(F)} + C_{(F)} + 9H + (-S-) + (-S^\ominus) + (Na^\oplus)$$

$$-104.5 = -88.8 + S_{(F)}$$

$$\therefore S_{(F)} = -5.7 \times 10^{-6}$$

This compound is very hygroscopic and probably for that reason, the value was low. But considering experimental error, the value as above may be approvable.

In the case of (VI) :—

$$\sum\chi_A = 13C_{(F)} + 10H + S_{(F)} + 2\chi_{\pi\text{Benzene}}$$

$$-118.1 = -107.6 + S_{(F)}$$

$$\therefore S_{(F)} = -10.5 \times 10^{-6}$$

This value coincide tolerably with that in the case of (IV).

For  $\chi_{\pi\text{Indene}}$  the measured value<sup>(10)</sup> of  $-84.76 \times 10^{-6}$  was used.

$$\sum\chi_A = 8C_{(F)} + C_{(F)} + 8H = -56.32$$

$$-84.76 = -56.32 + \chi_{\pi\text{Indene}}$$

$$\therefore \chi_{\pi\text{Indene}} = -28.44 \times 10^{-6}$$


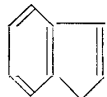
In the above,  $\chi_{\pi\text{Indene}}$  means the degree of contribution of diamagnetism which depends upon  $\pi$  electron belonging to indene nucleus for its circulation in indene nucleus.

In other words, as indene molecule has a plane structure,  $\chi_{\pi\text{Indene}}$  may be interpreted to mean the degree of magnetic anisotropy as a result of above. On the contrary,  $\sum\chi_A$  may be taken as the isotropic part.

This idea of magnetic anisotropy is incompatible fundamentally with the idea of Clow & Thompson<sup>(2)</sup> who considered that diamagnetism increases as a result of polarization between the carbon atoms in aromatic compound.

Next, =N- was calculated<sup>(11)</sup> by subtracting the part of molecular anisotropy as a result of  $\pi$  electron from the measured value on pyridine; and the value for "ion" type such as  $-S^\ominus$  and the under-mentioned in Table 3 was calculated

Table 3

	$\chi_A \times 10^6$
C	- 6.00
C(F)	- 3.36
>C- $\ominus$	-10.05
H	- 2.93
>N-	- 1.54
=N-	- 0.88
-S-	-15.0
S(F)	-11.0
=S- $\ominus$	-16.85
=S- $\oplus$	- 6.37
-S $\ominus$	-20.8
-O-	- 4.61
Na $\oplus$	- 9.2
$\chi_{\pi}$ 	-17.33
$\chi_{\pi}$ 	-28.44

(10) S. S. Bhatnagar, K. K. Mathur, "Physical Principle and Application of magnetochemistry." (1935), 80.

(11) G. Hazato, private communication.

with reference to the Angus's<sup>(12)</sup> value which means increase or decrease in magnetic susceptibility of atom owing to ionisation. Magnetic susceptibility of sulfur by Angus is as follows.

$(\chi_A \times 10^6)$	
$S^\ominus$	25.18
$S^\circ$	19.33
$S^\oplus$	14.70

$\left. \begin{array}{l} 25.18 \\ 19.33 \\ 14.70 \end{array} \right\} \begin{array}{l} 5.83 \\ 4.63 \end{array}$

and  $-S^\ominus$  was calculated by adding 5.83, a difference between  $S^\ominus$  and  $S^\circ$ , to Pascal's value.

$$-S^\ominus = -15.0 - 5.85 = -20.8$$

$$\text{similarly } =S-\oplus = (=S) + 4.63 = -6.37$$

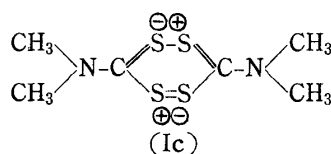
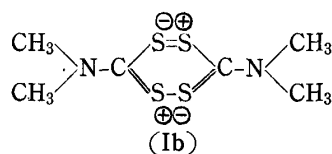
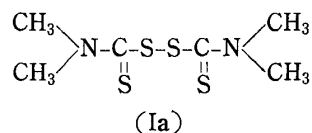
$$=S-\ominus = (=S) - 5.85 = -16.85$$

And so forth, values for  $>N^\ominus$ ,  $-C-\ominus$  and  $S^{\oplus\oplus}$  are also likewise obtainable.

#### § 4. Discussion for the results

As for the representative compounds (I), (II) and (III) in group A in Table 2,  $\sum\chi_{A(I)}$ ,  $\sum\chi_{A(II)}$  and  $\sum\chi_{A(III)}$  were calculated using Table 3 and the results are listed in the column of calculated value in Table 2. By comparing these values with that measured, it is perceptible that the measured values always show remarkable exaltation in diamagnetism. Such diamagnetic exaltation usually occurs in molecule in the case as (i)  $\pi$  electron is in the state rather polarised (or internal ionic state<sup>(13)</sup>) than double-bonded or (ii) diamagnetism is given caused by  $\pi$  electron orbit shown as  $\chi_{\pi\text{Benzene}}$  or  $\chi_{\pi\text{Indene}}$  or (i) together with (ii) are both existing.

According to this way of consideration and from the exaltation of A group compounds (I), (II) and (III) in Table 2, such polarised cyclic structure as in the followings can be thought of, besides hitherto accustomed structural formula of (Ia), (IIa) and (IIIa) in Fig. 1. In this suggestion, if "energy" necessary for internal ionisation of S-S and S-C bonds is far smaller than "resonance energy" in above mentioned structural formula, this cyclic structure is stable and is thought possible to exist.



(12) W. R. Angus, J. Farquharson, Proc. Roy. Soc., **A136** (1932), 569, 579.

(13) F. W. Gray, J. H. Cruickshank, Trans. Faraday Soc., **31** (1935), 1491.



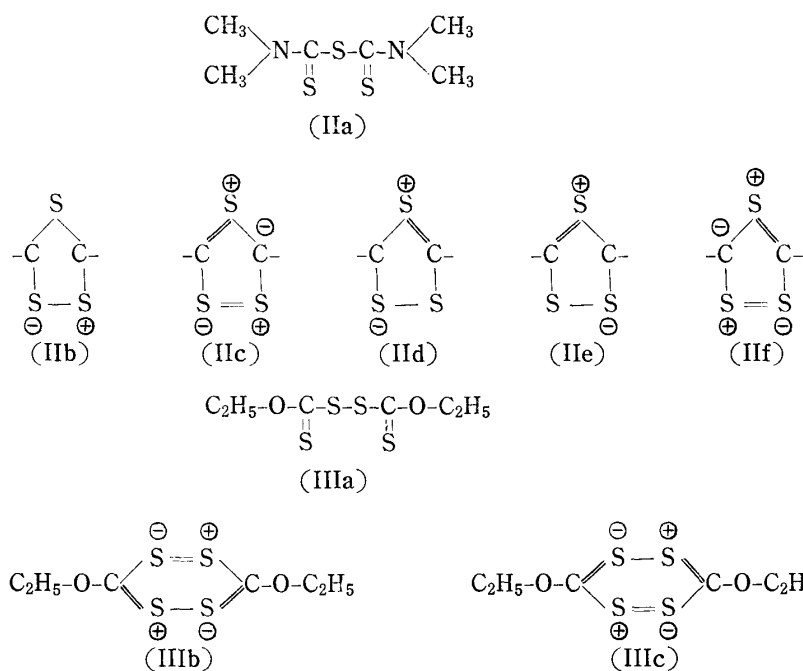


Fig. 1

As for the value for isotropic part of (Ib) or (Ic)

$$\chi_{(Ib)} = \chi_{(Ic)} = -115.4 \times 10^{-6}$$

This value shows further decrease in diamagnetism in comparison with double-bonded  $\chi_{(Ia)} = -121 \times 10^6$  and the actually measured value shows far larger diamagnetism. Therefore, the structure of compound (I) can not be completely explained only by intramolecular polarisation in the theory of Koch<sup>(6)</sup> and Clow & Thompson<sup>(2)</sup>. In the same manner for compound (II), the value for isotropic part is

$$\chi_{(IIb)} = \chi_{(IId)} = \chi_{(IIe)} = -107.1 \times 10^{-6}$$

and  $\chi_{(IIc)} = \chi_{(IIf)} = -105.2 \times 10^{-6}$

and in this case the analogous thing as (I) may be said.

In both cases of (I) and (II), the difference between the measured value and the value for above isotropic part shows also the diamagnetic contribution owing to the motion of  $\pi$  electron in molecular orbit and this value is proportional to  $\chi_{\pi}$  in the following formula.

$$\chi_{\pi} = -\frac{Ne^2}{4mc^2} \sum_n r_{\pi}^2 \dots \dots \dots (1)$$

$r_{\pi}$  in the above formula means a radius of circumscribed circle for six-membered cyclic structure in (Ib, c) and (IIIb, c), and for five-membered cyclic structure in (IIIb) and the under-mentioned.  $n$  is the number of  $\pi$  electron in question and  $n=6$  in both cases.

Accordingly from (1), the following proportional relation will be established.

$$\frac{\chi_{\pi(I)}}{\chi_{\pi(II)}} \propto \frac{r_{\pi^2(I)}}{r_{\pi^2(II)}}, \quad \frac{\chi_{\pi(III)}}{\chi_{\pi(II)}} \propto \frac{r_{\pi^2(III)}}{r_{\pi^2(II)}} \dots \dots \dots (2)$$

The respective value of left side was actually calculated from the difference between the measured value and the isotropic part.

$$\frac{140.6-115.4}{118.4-106.2} = 2.07, \quad \frac{137.8-115.6}{118.4-106.2} = 1.82 \dots \dots \dots (3)$$

Right side in this equation must be 1.38 from genuinely geometrical consideration. While good coincidence could not be observed between this theoretical value and the measured value in (3), the respective value of  $\chi_{\pi(I)}$  and  $\chi_{\pi(III)}$  in (2) and (3) are essentially equal. Therefore contributions to  $\chi_{\pi}$  by six-membered structure shown in (I) and (III) in Fig. 1 are almost alike in both cases and formula (1) appears to be satisfied with both values. However, the difference in  $\chi_{\pi}$  as well as its character of six-membered ring of this type and of five-membered ring in (II) Fig. 1 may be more correctly interpreted to be unable to express in a simple classic formula as (I).

Exaltation in compounds (VII), (VIII) and (IX) in Group B, Table 2 expresses contribution of diamagnetism due to  $\pi$  electron orbit in benzene as well as in the neighbouring five-membered ring. In their recent work on thio-thiophthen, from X-ray analysis, Bezzi et al.<sup>(14)</sup> have proposed a dynamical formula for this compound suggesting a new type of aromatic system. The structure of this type also suggests to have the usual diamagnetic anisotropy due to  $\pi$ -electron orbit in its molecule.

As for compound (X) in Group C, Table 2, a value of 151.8 will be obtained on the assumption that it has cyclic structure containing single bond and a value of 139.8 will be obtained if calculated as double-bonded ( $S_{(F)}$ ). Thus the former structure ought to be supported, since it is closer to the measured value and in this case no circulation of electron is thought to occur.

### Summary

In this study the followings were elucidated. In sulfur compounds possessing single and double bond which have been taken as straight paraffinic compounds up to now, resonance structure of  $\pi$  electron as "benzene" nucleus or unsaturated five membered ring ("cyclopentadiene" series) is conceivable. The real existence have been established by measuring molecular diamagnetism. Hence these sulfur compounds have resonance structure of several kinds and possibility of ready polarisation in molecule was suggested. But, cyclic structure without circulation of  $\pi$  electron may also exist in some cases.

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(14) S. Bezzi, M. Mammi, C. Garbuglio, *Nature*, **182** (1958), 247.

Tôhoku University, for every convenience they offered during the course of investigation. Acknowledgment is also made to Assistant Prof. T. Isobe in that laboratory, and to Mr. S. Katagiri in Special Postgraduate Course of Chemistry, the Faculty of Science, Tôhoku University for their assistance in measuring magnetic susceptibility and to Miss Ch. Iwanaga for her assistance in experiments. My sincere thanks are offered to Assistant Prof. T. Yamazaki, Research Institute in Ore Dressing and Refining, Tôhoku University for his kind gift of several kinds of synthesized organic sulfur compounds. Best thanks are also due to Prof. T. Toriumi, The Chief of the Chemical Research Institute of Non-Aqueous Solutions, Tôhoku University and to Kawaguchi Chemical Industry Co. Ltd. for the permission to publish these papers.