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Sulfilimine. II. IR, UV and NMR Spectroscopic Studies

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The physical properties of several *N*-*p*-tolylsulfonylsulfilimines were studied by means of infrared, ultraviolet and NMR spectroscopic determinations. Four characteristic infrared absorption bands due to both sulfonyl and sulfilimino groups are observed and those due to both N–S(IV) and N–S(VI) stretching vibrations appear at nearly the same positions and overlap with each other. The ultraviolet spectra suggest that the sulfilimino group is not an electron donor but an electron acceptor group when conjugated with a phenyl ring and could be used to measure the pK_a value of methyl-*p*-methoxyphenyl derivative. The NMR chemical shift of methyl protons attached to the S atom of *S*-methyl-*S*-*p*-tolyl derivative appears at 2.81 ppm, whereas the shifts of the corresponding sulfoxide and the sulfone groups appear at 2.69 and 3.04 ppm, respectively. From these results, it seems that the N–S(IV) bond of *N*-*p*-tolylsulfonylsulfilimine is of semipolar character while the charges on the S(IV) atom and the N atom are delocalized substantially with strong $d\pi$ conjugation into S(IV)–N–S(VI) bondings.

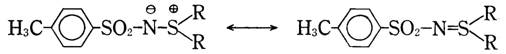
Sulfilimines have been known as sulfur-nitrogen ylides or ylenes. The *N*-acyl derivatives are especially well known compounds and their IR,[1] UV,[2] and X-ray data[3] have been accumulated in recent years.

The configuration of *N*-sulfonylsulfilimine is not established, though the S–N bond has been postulated from IR spectroscopic study[1] to have a double bond character. We have examined IR, UV and NMR spectra of various *N*-sulfonylsulfilimines. This paper will describe the new data and their relation to a preferable structure for *N*-sulfonylsulfilimine.

Results and Discussion

IR Spectra of *N*-*p*-Tolylsulfonylsulfilimines. The IR spectra of several *N*-*p*-tolylsulfonylsulfilimines are taken in KBr disks and shown in Table 1. All the sulfilimines have four strong characteristic IR absorption bands at around 930—980, 1070—1090, 1130—1140 and 1260—1280 cm^{-1} respectively (Fig. 1). The latter two bands, 1130—1140 and 1260—1280 cm^{-1} are well assigned to those of both symmetrical and asymmetrical stretching vibrations due to SO_2 group. The first band, 930—980 cm^{-1} has been assigned to the stretching vibration due to N–S(IV) group by Kucsman *et al.*,[1] though there are controversies in the assignment of the absorption of S–N stretching vibration.[4–6] The second band, 1070—1090 cm^{-1}, which appears in all arylsulfonamides was revealed by Tanaka *et al.* to be not of the S–N stretching absorption band from a study of the IR spectra of various sulfonamides, sulfonic acids, sulfones and other related compounds.[5]

N-*p*-Tolylsulfonylsulfilimine may be formulated by either the ylide structure, the ylene structure or by the resonance hybrid of both.



Ylide type Ylene type

Kucsman *et al.* favor the ylene structure on the basis of IR spectroscopic observations.[1] They argue that the $\bar{\nu}$ SO_2[*1] band in sulfilimine appears at a wave number considerably higher than that in sulfonate ($\bar{\nu}$ $SO_3 = 1120$ cm^{-1}) although it might

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1) A. Kucsman, I. Kapovits and F. Ruff, *Acta Chim. Acad. Sci. Hung.*, **40**, 75 (1964); A. Kucsman, I. Kapovits and F. Ruff, *Tetrahedron*, **22**, 1575 (1966).

2) A. Kucsman, F. Ruff and I. Kapovits, *Acta Chim. Acad. Sci. Hung.*, **50**, 325 (1966).

3) A. Kalman, *Acta Crystallogr.*, **22**, 501 (1967).

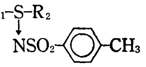
4) J. N. Baxter, J. Cymerman-Craig and J. B. Willis, *J. Chem. Soc.*, **1955**, 669; W. Augus, A. H. Leckie and J. I. Williams, *Trans. Faraday Soc.*, **34**, 793 (1938). The bands between 1070 and 1100 cm^{-1} were assigned to the S–N stretching vibration from a study of the Raman spectra of a veriety of sulfur-nitrogen compounds.

5) D. H. Hadzi, *J. Chem. Soc.*, **1959**, 847; Y. Tanaka and Y. Tanaka, *Chem. Pharm. Bull.*, (Tokyo) **13**, 399, 858 (1965). The bands in the region near 900 cm^{-1} were assigned to the S–N stretching vibration.

6) H. J. Hofmann and K. R. Andress, *Naturwissenschaften*, **41**, 94 (1954); L. P. Bicelli, *Ann. Chim.*, **47**, 1380 (1957). It was suggested that the S–N frequency is at around 500 cm^{-1}.

[*1] $\bar{\nu}\ SO_2 = 1/2\ (\nu_s\ SO_2 + \nu_{as}\ SO_2)$.

TABLE 1. IR SPECTRUM OF *N*-*p*-TOLYLSULFONYLSULFILIMINE



R_1	R_2	Mp (°C)	$\nu_{(S-N)}$	$\nu_{s(SO_2)}$	$\nu_{as(SO_2)}$	
CH_3	CH_3	157—157.5	943	1129	1265	1088
$(CH_3)_2CH$	$(CH_3)_2CH$	117—118	961	1128	1260	1082
$CH_3(CH_2)_3$	$CH_3(CH_2)_3$	59—60	965	1132	1270	1083
$-(CH_2)_4-$		145—146	965	1132	1264	1079
$-(CH_2)_5-$		148—149	966	1123	1257	1081
CH_3	C_6H_5	129—130	930	1139	1280	1083
CH_3	p-$CH_3C_6H_4$	125—126	950	1133	1270	1088
CH_3	p-$CH_3OC_6H_4$	144.5—145	959	1139	1281	1085
CH_3	p-$NH_2C_6H_4$	206—207	933	1130	1250	1083
CH_3	p-ClC_6H_4	112—113	957	1130	1270	1080
CH_3	p-$NO_2C_6H_4$	162—163	958	1133	1275	1082
CH_3CH_2	C_6H_5	97—98	971	1135	1274	1082
$(CH_3)_2CH$	C_6H_5	115—116	936	1138	1275	1085
$(CH_3)_3C$	C_6H_5	101	955	1139	1277	1088
$C_6H_5CH_2$	C_6H_5	146—147	970	1136	1275	1087
$C_6H_5CH_2$	$C_6H_5CH_2$	190—191	983	1134	1275	1086
$C_6H_5(CH_2)_2$	C_6H_5	137—138	950	1132	1270	1086
C_6H_5	C_6H_5	111—112	950	1135	1280	1082
C_6H_5	p-$CH_3C_6H_4$	96—98	969	1133	1273	1082
C_6H_5	p-ClC_6H_4	89.5—90.5	969	1130	1273	1080
C_6H_5	p-$NO_2C_6H_4$	148—149	955	1135	1281	1084
p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	130—132	956	1131	1277	1073
p-$CH_3C_6H_4SO_2NH_2$			906	1155	1330	1096
$[p$-$CH_3C_6H_4SO_2NCl]^{\ominus}Na^{\oplus}$			929	1130	1246	1083

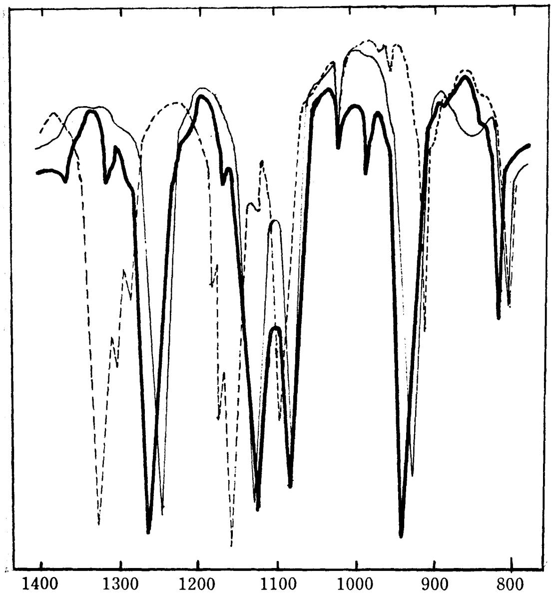


Fig. 1. IR spectra.

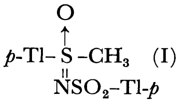
—— p-$CH_3C_6H_4SO_2N^{\ominus}$-$S^{\oplus}(CH_3)_2$
—— $[p$-$CH_3C_6H_4SO_2NCl]^{\ominus}Na^{\oplus}$
------ p-$CH_3C_6H_4SO_2NH_2$

be predicted that both SO_2 bands in the system $-SO_2-N^{\ominus}-$ and $-SO_2-O^{\ominus}$ would appear in the same region. A shift of 40—50 cm^{-1} towared a lower wave number of $\bar{\nu}$ SO_2 band in sulfilimine than that in sulfonamide or sulfone is also too small to be ascribed to the ylide structure.

However, a comparison of the two systems may not be appropriate and the shift of 40—50 cm^{-1} toward the lower wave number of SO_2 band is too large to be caused only by the electronic effect of sulfilimino group. We examined the IR spectra of sodium *N*-chloro-*p*-tolylsulfonylsulfonamide (chloramine T) which is considered to have the system $-SO_2-N^{\ominus}-$. IR spectra of *p*-tolylsulfonamide, chloramine T and *S*,*S*-dimethyl-*N*-*p*-tolylsulfonylsulfilimine are shown in Fig. 1. Chloramine T has four characteristic intense bands at 1255 ($\nu_{as}SO_2$), 1130 (ν_sSO_2), 1083 and 929 cm^{-1}. The whole spectrum does not resemble that of the sulfonamide but is very similar to that of sulfilimine except for the band at 929 cm^{-1} which is less intense than that of *S*,*S*-dimethyl-*N*-*p*-tolylsulfonylsulfilimine at 943 cm^{-1}.

The characteristic IR absorption bands of several sulfilimines, chloramine T and other related compounds are listed in Table 2. The values of $\bar{\nu}$ SO_2 of sulfilimines (1190—1210 cm^{-1}) are similar to the value of chloramine T anion (1193 cm^{-1}) but different from that of sulfonamide (1243 cm^{-1}) and

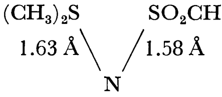
TABLE 2. IR SPECTRA OF SULFILIMINE $\overset{R_1}{\underset{R_2}{S}} \rightarrow NTs$ AND RELATED COMPOUNDS

R_1	R_2	$\nu_{(S-N)}$	$\nu_{s(SO_2)}$	$\nu_{as(SO_2)}$	—	$\bar{\nu}_{(SO_2)}$
CH_3	CH_3	943	1129	1265	1088	1197
CH_3	C_6H_5	930	1139	1280	1083	1210
CH_3	p-$CH_3C_6H_4$	950	1133	1270	1088	1201
CH_3	p-$NH_2C_6H_4$	933	1130	1250	1083	1190
C_6H_5	C_6H_5	950	1135	1280	1082	1208
p-Tl-SO_2-NH_2		906	1155	1330	1096	1243
$[p$-Tl-SO_2-NCl$]^{\ominus}Na^{\oplus}$		929	1130	1255	1086	1193
Alkyl-aryl-sulfone[8]		—	1160—1150	1334—1325	—	1238—1247
 p-Tl-$\overset{\overset{O}{\uparrow}}{\underset{\underset{NSO_2\text{-}Tl\text{-}p}{\Vert}}{S}}$-$CH_3$ (I)		—	1150	1312	—	1231

sulfones (1238—1247 cm^{-1}). The value of $\bar{\nu}$ SO_2 of sulfoximine (I) produced by the oxidation of sulfilimine is close to that of sulfonamide but not to that of sulfilimine or chloramine T. This fact seems to be supported by the S=N double bond character of sulfoximine.[7]

The results suggest that sulfilimine and chloramine T anion have similar electronic environments around the SO_2 group, and N-p-tolylsulfonyl sulfilimine would be represented better by the ylide structure than by the ylene structure.

Recently, an X-ray crystallographic study of S,S-dimethyl-N-methylsulfonylsulfilimine has revealed that the bond length of N–S(IV) and N–S(VI) are 1.63 and 1.58 Å respectively,[3] which are normal values for N–S distance of sulfonamide such as N-phenylmethanesulfonamide[9] or sulfamide.[10] The result undoubtedly supports the consideration that the S–N bond is of semipolar nature.



The stretching vibrations of the N–S(IV) and the N–S(VI) bonds can be calculated simply by the following equation[11] using the values 1.63 and 1.58 Å, and the values 878 and 971 cm^{-1} are obtained.

$$\nu = \frac{1}{2\pi c}\left(\frac{f}{M_n \cdot M_s / M_n + M_s}\right)^{1/2}, \quad f = \frac{1.86 \times 10^5}{(r - 0.88)^3}$$

where

ν: the stretching frequency (cm^{-1})
c: the velocity of light (cm/sec)
f: the force constant of bond (dyn/cm)
r: the bond length (Å)
M_n and M_s: the mass of N atom and S atom respectively (g)

N-p-Tolylsulfonylsulfilimine has only one very intense band around 930—980 cm^{-1} whose intensity is stronger than those of the SO_2 bands and the S–N stretching vibration of chloramine T (see Fig. 1). Thus, both bands due to both N–S(IV) and N–S(VI) stretching are considered to apper at the same or nearly the same position and would overlap each other.

UV Spectra of N-p-Tolylsulfonylsulfilimines. UV spectra of several N-p-tolylsulfonylsulfilimines are shown in Table 3. All the sulfilimines except those having p-amino or p-methoxyphenyl group give UV spectra having the maximum absorption bands (λ_{max}) at around 228 mμ with intensities (log ε_{max}) between 4.06 and 4.35.

There is practically no shift of λ_{max} when R_1 and R_2 change from dialkyl to alkylpheny or diphenyl. This suggests that the maximum absorption bands at around 228 mμ are the ^1L_a bands due to the phenyl ring of p-tolylsulfonyl group connected to sulfilimine group, since λ_{max} and log ε_{max} between S,S-dialkyl-N-p-tolylsulfonylsulfilimine and p-tolylsulfonamide having the ^1L_a band at 225 mμ are very similar.

If the S(IV)–N bond of N-p-tolylsulfonylsulfilimine has a normal double bond character, the resonance interaction between the S=N bond and the adjacent phenyl ring shown below, would lead the λ_{max} to a red-shift.

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[7] S–N bond of sulfoximine is considered to be of double bond character from the following evidence. i) S–N bond length obtained from X-ray analysis is appropriate for S=N double bond distance. 1.56 Å for methionine sulfoximine; B. W. Christensen and A. Kjaer, *Chem. Commun.*, **1969**, 169. 1.53 Å for methyl-p-nitrophenyl sulfoximine; A. Shimada, K. Hirotsu and K. Iwama, unpublished work. ii) The substituent effect of pK_a of arylmethylsulfoximine does not obey σ^+ value but σ value; S. Oae, K. Tsujihara and N. Furukawa, *Chem. Ind.* (London), **1968**, 1569.

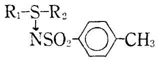
[8] L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen Co. Ltd. Londn (1968), p. 220.

[9] H. P. Klug, *Acta Crystallogr.*, **24**, 792 (1968).

[10] K. N. Trueblood and S. W. Mayer, *ibid.*, **9**, 628 (1956).

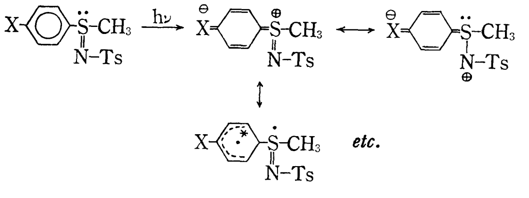
[11] R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934).

Table 3. UV spectra of N-p-tosylsulfilimine



R_1	R_2	λ_{max}	log ε_{max}	Solvent
CH_3	CH_3	227	4.10	CH_3OH
$(CH_3)_2CH$	$(CH_3)_2CH$	230	4.13	CH_3OH
$CH_3(CH_2)_3$	$CH_3(CH_2)_3$	230	4.06	CH_3OH
$-(CH_2)_4-$		228	4.07	CH_3OH
$-(CH_2)_5-$		228	4.07	CH_3OH
CH_3	C_6H_5	226	4.26	CH_3OH
CH_3	p-$CH_3C_6H_4$	230	4.32	CH_3OH
CH_3	p-$CH_3OC_6H_4$	239	4.30	CH_3OH
		234 267	4.19 4.02	75%-H_2SO_4
CH_3	p-$NH_2C_6H_4$	222 275	4.17 4.27	CH_3OH
		228	4.24	75%-H_2SO_4
CH_3	p-$NO_2C_6H_4$	230 255*	4.21 (3.96)	CH_3OH
CH_3CH_2	C_6H_5	226	4.27	CH_3OH
$(CH_3)_2CH$	C_6H_5	228	4.28	CH_3OH
$(CH_3)_3C$	C_6H_5	227	4.28	CH_3OH
$C_6H_5CH_2$	C_6H_5	229	4.38	CH_3OH
$C_6H_5CH_2$	$C_6H_5CH_2$	227	4.35	CH_3OH
$C_6H_5(CH_2)_2$	C_6H_5	226	4.30	CH_3OH
C_6H_5	C_6H_5	229	4.39	CH_3OH
C_6H_5	p-$CH_3C_6H_4$	230	4.37	CH_3OH
C_6H_5	p-ClC_6H_4	232	4.46	CH_3OH
C_6H_5	p-$NO_2C_6H_4$	227	4.37	CH_3OH
		257*	(4.12)	CH_3OH
p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	242	4.37	CH_3OH
p-$CH_3C_6H_4SO_2NH_2$		225	4.07	CH_3OH

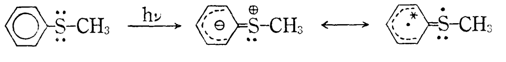
* shoulder



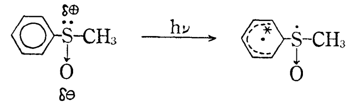
(Ts: p-$CH_3C_6H_4SO_2$–)

Fig. 2

Lack of such a red-shift suggests that the S(IV)–N bond in sulfilimine cannot be of the usual double bond character. This resonance interaction between the lone pair electrons on the S atom with phenyl ring is well known in sulfides.[12]

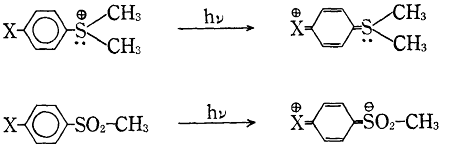


Even in the case of sulfoxides having both a lone electron pair and a somewhat positive charge on the S atom, this resonance interaction is observed.[12] In this case, however, the resonance interaction is not as large as in the case of sulfide, since the positive charge on the sulfoxide sulfur atom increases the energy required to excite an electron on the lone pair.



As the positive charge on the S atom becomes larger, this resonance interaction of the lone electron pair with phenyl ring would become difficult, and when the S atom bears a discrete positive charge such as in sulfonium salts, this type of resonance interaction is no longer observed.[12]

In this case, resonance involving the donation of electrons from an occupied orbital in phenyl ring into a vacant $d\pi$ orbital of the S atom would be observed. This type of interaction is known to occur in sulfones attached to a phenyl ring and occasionally in sulfoxides having a pheny ring substituted with an electron-releasing group such as amino or methoxyl group.[12]



In the case of N-p-tolylsulfonylsulfilimine the lone electron pair would be bound somewhat tightly on the S atom and not readily excited to the energy level of d orbitals, because the λ_{max} and log ε_{max} of p-nitrophenyl or p-ammoniumphenyl-methylsulfilimine (σ_p of p-NO_2 and p-$NH_3^{\oplus}$ are 0.778 and 0.60 respectively) scarcely alter when solvent changes from methanol or dilute sulfuric acid to 75% sulfuric acid in which sulfilimine is protonated with sulfuric acid and bears a discrete positive change on the S atom (see Table 4).

This observation indicates that the S atom of N-p-tolylsulfonylsulfilimine would bear a considerable positive charge which makes the lone electron pair tightly bound on the S atom.

UV spectra of S-aryl-S-methyl-N-p-tolylsulfonylsulfilimine in various solvents are shown in Table 4. The maximum band of S-methyl-S-p-methoxyphenylsulfilimine (σ_p^+ of p-CH_3O is -0.778) at 239 mμ is shifted to 232 mμ with a shoulder at 242 mμ when solvent changes from methanol to water.

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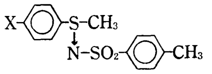
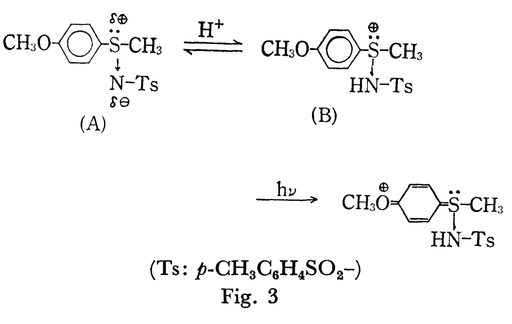
[12] C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York (1962); H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," J. Wiley and Sons, Inc., New York, (1962), p. 474.

TABLE 4. UV SPECTRA OF ARYLMETHYLSULFILIMINES



X	Solvent	λ_{max}	log ε_{max}	σ_p (σ_p^+)
H	CH_3OH	226	4.26	0
	H_2O	226	4.26	
	75%-H_2SO_4	230	4.27	
CH_3	CH_3OH	230	4.32	−0.170(−0.311)
Cl	CH_3OH	231	4.37	0.227(0.114)
NO_2	CH_3OH	230	4.21	0.778(0.790)
		255 (shoulder)	(3.96)	
	75%-H_2SO_4	235	4.23	
		254 (shoulder)	(4.07)	
OCH_3	CH_3OH	239	4.30	−0.268(−0.778)
	H_2O	232	4.25	
		242 (shoulder)		
	75%-H_2SO_4	234	4.19	
		267	4.02	
NH_2	CH_3OH	222	4.17	−0.66 (−1.3)
		275	4.27	
NH_3^+	2%-H_2SO_4	226	4.21	+0.60
	75%-H_2SO_4	228	4.24	

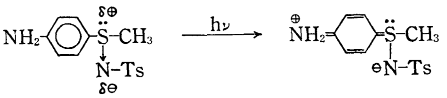
The increase of the concentration of sulfuric acid gives a bathochromic shift to the shoulder at 242 mμ while in 75% sulfuric acid the sulfilimine gives two isolated bands at 234 and 267 mμ. This observation obviously indicates that there is some resonance interaction between *p*-methoxyphenyl ring and the somewhat positively charged S atom, while the resonanse interaction becomes stronger when the sulfilimine group is protonated with sulfuric acid and bears a discrete positive change on the S atom as shown in Fig. 3.



(Ts: p-$CH_3C_6H_4SO_2$-)
Fig. 3

This type of resonance interaction can be more clearly observed in the case of *S*-*p*-aminophenyl-*S*-methylsulfilimine (σ_p^+ of p-NH_2 is −1.3): namely, in methanol solution in addition to 222 mμ band due to *p*-tolylsulfonyl group 275 mμ band appears and completely disappears when solvent is changed to 2% sulfuric acid in which amino group is completely protonated.

This clearly indicates that *p*-aminophenyl ring interacts with the S atom bearing somewhat positive charge as shown below.



(Ts: p-$CH_3C_6H_4SO_2$-)

The fact that the resonance interaction involving the donation of electrons from an occupied orbital of the phenyl ring into a vacant *dπ* orbital of the S atom occurs obviously in the case of sulfilimines having an electron releasing substituent such as amino or methoxyl group, indicates that the S atom of sulfilimine possesses an appreciable positive charge.

The resonance interaction which involves the donation of electrons from the lone electron pair of the S atom into an unoccupied orbital of the benzene ring would not occur, since the UV spectra of *p*-ammoniumphenyl- and *p*-nitrophenylmethylsulfilimine are not altered when sulfilimine group protonated and bears a discrete positive charge on the S atom.

This suggests that the S(IV)–N bond is not a discrete double bond, and there is at least some positive charge on the S atom to bind the lone pair electrons tightly on the atom. From these results the S(IV)–N bond in *N*-*p*-tolylsulfonylsulfilimine is considered to be a semipolar rather than a double bond. The negative charge on the N atom is considered to be delocalized over the SO_2 and the sulfilimine groups. *p*-Methoxyphenylmethylsulfilimine gave two isolated bands at 234 and 267 mμ in aqueous sulfuric acid. The latter band has been considered to be due to the resonance interaction between *p*-methoxyphenyl ring and the S atom having a discrete positive charge as shown in Fig. 3.

It is of interest that this observation can be used to determine the basicity of N atom of the sulfilimine group. The basicity of sulfilimine is shown in the following equation.

$$\mathrm{p}K_a=H_0+\log\frac{C_{\mathrm{B}}{}^+}{C_{\mathrm{A}}}$$

where

H_0: the acidity function

C_{A} and $C_{\mathrm{B}}{}^+$: the concentrations of sulfilimine and protonated sulfilimine respectively.

When the decrease of 242 mμ band or the increase of 267 mμ band is measured, the pK_a value can be obtained from the H_0 when the sulfilimino group is half protonated. The value of pK_a of *S,S-p*-methoxyphenylmethyl-*N-p*-tolylsulfonylsulfilimine thus obtained is -1.78 and this value is considerably larger than that of *p*-tolylsulfonamide (p$K_a=-3.30$).[13] This fact indicates that the electron density on the N atom is increased in the form of a coordination of the lone electron pair of the S atom to the N atom.

NMR Chemical Shifts of *N-p*-Tolylsulfonylsulfilimines. The chemical shifts of sulfilimines are measured from TMS internal standard as a reference peak in $\mathrm{CDCl_3}$.

N-p-Tolylsulfonylsulfilimine has an asymmetric center which may give the chemical shift difference between the protons of an adjacent methyl or methylene group, and the AB-type NMR spectrum due to magnetically non-equivalent protons is expected to be observed.

Actually benzyl protons of *S*-benzyl-*S*-phenyl-*N-p*-tolylsulfonylsulfilimine appear as double doublet ($J_{\mathrm{AB}}=13$ Hz). The chemical shifts of methyl protons attached to the S(IV) atom of *S*-methyl-*S-p*-tolylsulfilimine, sulfoxide and sulfone are 2.81, 2.69, 3.04 ppm respectively. This indicates that the sulfilimino group is somewhat more electron-withdrawing than the sulfoxide group but less than the sulfone group, while a substantial positive charge is centered on the S(IV) atom of *N-p*-tolylsulfonylsulfilimine.

From these IR, UV, NMR spectroscopic studies together with X-ray crystallographic data, *N-p*-tolylsulfonylsulfilimine is considered to be represented better by the ylide structure in which the charges on the S atom and the N atom are considerably delocalized with strong $d\pi$ conjugation into S(IV)–N–S(VI) bondings. Therefore the S–N bond of sulfilimino group is considered to be essentially semipolar.

Experimental

Preparation of Sulfilimines. All the *N-p*-tolylsulfonylsulfilimines were prepared from the reaction of corresponding sulfides and chloramine T by the same procedure described previously.[14] The melting points of sulfilimines are listed in Table 1.

Measurement of the Basicity of *S*-Methyl-*S-p*-methoxyphenyl-*N-p*-tolylsulfonylsulfilimine. UV spectra of *S*-methyl-*S-p*-methoxyphenyl-*N-p*-tolylsulfonylsulfilimine were taken in sulfuric acid of several concentrations (from 0% to 75%). Increase of the concentration of sulfuric acid gave a bathochromic shift for the shoulder at 242 mμ. In 75% sulfuric acid the sulfilimine gave two isolated bands at 234 and 267 mμ, but above 75% the pattern of the spectrum no longer altered. The height of the spectrum at the suitable wavelength, for instance 266 mμ was used for calculation of the concentration in the equation

$$\mathrm{p}K_a=H_0+n\log\frac{C_{\mathrm{B}}{}^{\oplus}}{C_{\mathrm{A}}}=H_0+n\log\frac{h-h_0}{h_{75}-h}$$

where

H_0: acidity function

n: constant (1.0 for Hammet base)

h, h_0 and h_{75}; height of spectrum at 266 mμ

h; at an arbitrary concentration of sulfuric acid

h_0; at 0% sulfuric acid (no protonation)

h_{75}; at 75% sulfuric acid (completely protonated)

The pK_a value was obtained from the H_0 when the sulfilimine group is half protonated ($\log(h-h_0/h_{75}-h)=0$), see Fig. 4.

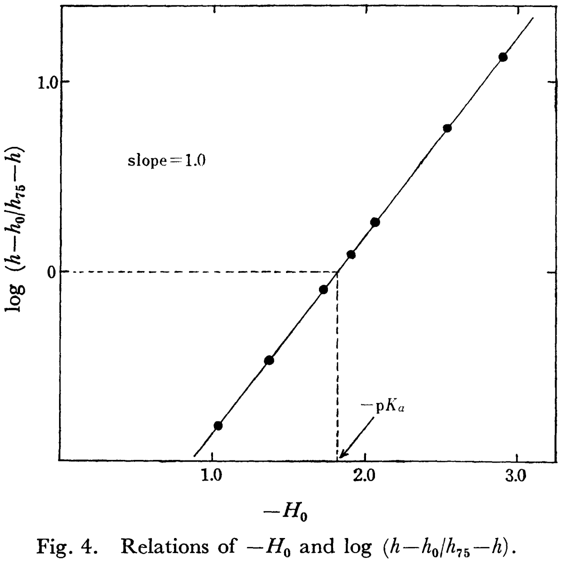


Fig. 4. Relations of $-H_0$ and log $(h-h_0/h_{75}-h)$.

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