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A Study on Electronic Spectra of Organic Compounds with S-Cl Group

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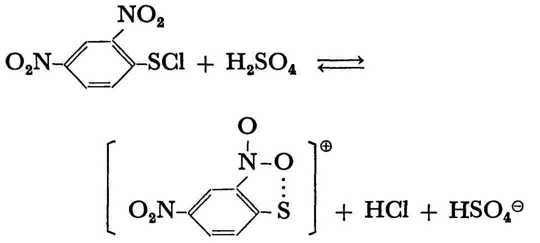
MO calculations were carried out for CH_3SCl, C_6H_5SCl, and related compounds with the S–Cl group by the CNDO/2 or the ASMO-SCF method. The absorption bands in the 300—400 nm region observed were assigned to the $\sigma^*_{S\text{-}Cl} \leftarrow n_S$ transition in view of transition energy and oscillator strength. Such characteristic bands are attributed to the extraordinarily low energy level of the $\sigma^*_{S\text{-}Cl}$ orbital.

Various organic compounds containing the sulfenyl group (S–Cl) are generally known to be highly reactive ones, often with characteristic colors (orange-red) irrespective of whether they are arylsulfenyl or alkanesulfenyl.

The first discussion on the color of such compounds was given by Kharasch *et al.*,1) for *o*-nitrobenzenesulfenyl chloride and its derivatives which have an intensely red color, especially in sulfuric acid. They attributed this to the intramolecular π resonance formed between the sulfenium cation and the nitro group adjoining, as shown below.



The characteristic color, however, is common to *o*-nitrobenzene-sulfenyl chloride and such compounds as benzenesulfenyl chloride and methanesulfenyl chloride which have no nitro group adjacent to the S–Cl group. Studies2,3) concerning the electronic absorption spectra of organic compounds with the S–Cl group were reported without theoretical investigation on the absorption bands of 300—400 nm common to such compounds. It seemed to be of interest to study the characteristic bands which may be closely related to formation of the S–Cl bond.

In the present study, MO calculation by the CNDO/2 4) or ASMO-SCF method5) using the zero-differential overlap approximation were carried out for CH_3SCl, C_6H_5SCl and some related compounds containing the S–Cl bond, in order to investigate the character of the S–Cl bond. For the sake of comparison, electronic absorption spectra of methanesulfenyl and *p*-toluenesulfenyl chlorides were measured in various solvents.

Method of Calculation

Calculations of σ-electron systems such as alkanesulfenyl chlorides were carried out by the CNDO/2 method, developed by Pople *et al.*,4) and the singlet excitation energies and oscillator strengths were calculated using the virtual orbital approximation. The atomic orbitals of sulfur atom were employed up to its 3p orbitals.* For calculations of $SOCl_2$, SO_2Cl_2, and CH_3SO_2Cl we tried to include 3d orbitals of sulfur atom having the same exponent ζ_{3d} as ζ_{3s}.6)

In the case of benzenesulfenyl chloride, the singlet excitation energies and oscillator strengths were calculated by the ASMO-SCF method with the zero-defferential overlap approximation,5) in order to avoid defects of the CNDO/2 method when applied to the π electron systems.** In the present calculation, the configurational interaction is not taken into account, because the transition energies of CH_3SCl and C_6H_5SCl are not changed so remarkably by the consideration of CI.

Table 1. Molecular structures of CH_3SCl, CF_3SCl, and C_6H_5SCl

Compound	Bond distance (Å) C–S	Bond distance (Å) S–Cl	Bond angle (deg.) ∠CSCl
CH_3SCla)	1.815	2.014	100.39
CF_3SCl	1.829		105.4
C_6H_5SCl	1.805		103.2

a) See Ref. 7.

The assumed molecular structures of the compounds with the S–Cl group are given in Table 1. Microwave spectral analysis7) was used for methanesulfenyl chloride, while CF_3SCl and C_6H_5SCl were estimated from both calculations and the molecular structures of $(CF_3)_2S_2$8) and $(C_6H_5)_2S_2$,9) respectively. For the molecular structures of all the other compounds, the observed structures were employed.10–13)

Experimental

Methanesulfenyl chloride and *p*-toluenesulfenyl chloride were prepared by the previously reported methods14,15) from dimethyl disulfide in 1,1,2,2-tetrachloroethane and chlorine, and from *p*-thiocresol in carbon tetrachloride and chlorine,

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* Preliminary calculations including those of 3d orbitals of the sulfur atom were carried out to estimate their contribution. The results predict the unacceptable polarization of S($\delta-$)–Cl($\delta+$) and the larger bond energy of E_{S-Cl} than E_{C-S} in contrast with the results obtained by restricting up to the 3p orbitals. These results are unreasonable from experimental aspects and the 3d orbitals for sulfur have thus been excluded from this study.

** For example, the π-MO of ethylene is not calculated as the highest occupied molecular orbital (HOMO) but as the next highest occupied molecular orbital (NHOMO). Furthermore, our preliminary calculation on C_6H_5SCl by the CNDO/2 gave a too large $\pi^* \leftarrow \pi$ excitation energy, *i.e.*, 12.5eV.

respectively. The products were isolated by vacuum distillation, and their electronic absorption spectra in the region 210—700 nm were measured in various solvents.

Results and Discussion

The observed electronic spectra of methanesulfenyl chloride and *p*-toluenesulfenyl chloride are shown in Fig. 1. The most stable conformation of CH_3SCl in its ground state was calculated by means of the CNDO/2 method to optimize the total energy by changing the bond distance R(S–Cl) between sulfur and chlorine atom. The optimized bond length, R=2.064 Å, is in good agreement with the experimental value (2.014 Å) in the gas phase. With this bond length, the transition energies were calculated to be 301.1 nm (the first band) and 203.0 nm (the second band) in the ultraviolet region. The predicted wavelength for the first band seems a little shorter than the observed one (355.0 nm). The calculated wavelengths for both bands, however, are sensitive to the change of the bond distance R(S–Cl) and shift toward the longer wavelengths by a slight elongation of the bond (Table 3).

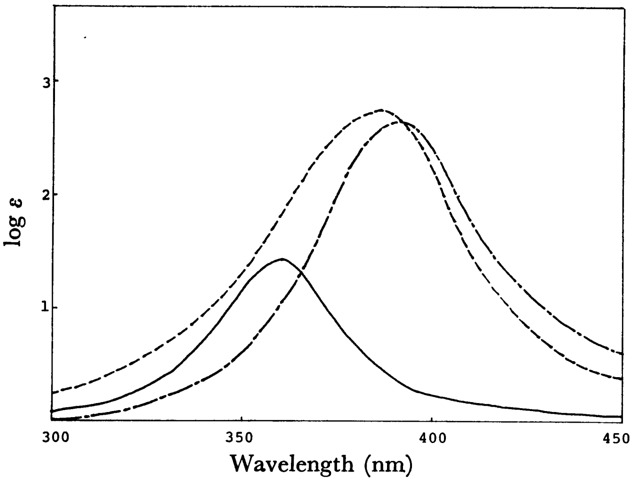

Fig. 1. Electronic absorption spectra of CH_3SCl (——), C_6H_5SCl (------), and *p*-$CH_3C_6H_4SCl$ (-·-·-) in the region of 300—450 nm.

TABLE 2. OBSERVED ELECTRONIC TRANSITIONS OF COMPOUNDS WITH THE S–Cl GROUP

Compound	Solvent	λ_{max}(nm)	ε_{max}	Reference
CH_3SCl	(Gas phase)	355.0	24.5	3
		205.0	671	
	Cyclohexane	360.0	27.2	This work
		275.6	542	
	CCl_4	361.0	29.7	This work
		276.3	503	
CF_3SCl	(Gas phase)	333.0	25	2
		214.0	235	
CCl_3SCl	Light petroleum	322.0	10.0	2
	CCl_4	324.0	12.0	
p-$CH_3C_6H_4SCl$	Cyclohexane	391.2	424	This work
		243.0	10240	
	Ethyl ether	391.0	254	This work
		241.0	9325	
	Methylene chloride	391.5	451	This work
C_6H_5SCl	CCl_4	386	589	This work

TABLE 3. DEPENDENCE OF THE SINGLET EXCITATION ENERGIES OF CH_3SCl ON THE BOND DISTANCE R(S–Cl)

R(S–Cl) (Å)	$\sigma^*_{S\text{-}Cl}\leftarrow n_S$		$\sigma^*_{S\text{-}Cl}\leftarrow n_{Cl}$	
	Transition energy (nm)	Oscillator strength	Transition energy (nm)	Oscillator strength
2.014	288.1	3.77×10^{-5}	196.9	8.07×10^{-3}
2.064	301.1	4.36×10^{-5}	203.0	3.21×10^{-3}
2.114	316.0	4.15×10^{-5}	206.7	2.90×10^{-2}
2.314	379.4	3.93×10^{-5}	239.2	5.21×10^{-2}

From the calculated results, the first band is assigned to the excitation of the lone pair electron on the sulfur atom to the lowest unoccupied orbital (LUMO), which is mainly localized in the anti-bonding MO of the S–Cl bond (σ^*_{S-Cl}). The band is thus closely related to the presence of the S–Cl bond. In fact, atom to the lowest unoccupied orbital (LUMO), which is mainly localized in the anti-bonding MO of the S–Cl

TABLE 4. OBSERVED AND CALCULATED EXCITATION ENERGIES OF COMPOUNDS WITH THE S–Cl BOND

Compound	Solvent	Observed		Calculated		Assignment
		λ_{max} (nm)	ε_{max}	Excitation energy (nm)	Oscillator strength	
SCl_2	*n*-hexane[a]	263	520	286.4[b]	4.56×10^{-5}	$\sigma^*_{S\text{-}Cl}\leftarrow n_S$
		246	417	250.2	4.18×10^{-5}	$\sigma^{*\prime}_{S\text{-}Cl}\leftarrow n_S$
$SOCl_2$	*n*-hexane	253†	2240	205.2[b]	2.15×10^{-4}	$\sigma^*_{S\text{-}Cl}\leftarrow n_S$
				201.1[c]	2.81×10^{-4}	
SO_2Cl_2	cyclohexane	<210[d]		218.2[b]	3.74×10^{-2}	
				196.9[c]	3.92×10^{-2}	
CH_3SO_2Cl	ethyl ether	<210[d]		221.0[b]	4.51×10^{-2}	
				197.4[c]	5.03×10^{-2}	

† Absorption shoulder.

a) H. P. Koch, *J. Chem. Soc.*, **1949**, 394, C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press Company (1962). b) Calculated by the CNDO/2 method excluding the 3d orbitals of sulfur atom. c) Calculated by the CNDO/2 method including the 3d orbitals of sulfur atom. d) No absorption band exists in the region 210—700 nm.

bond ($\sigma^*_{\text{S-Cl}}$). The band is thus closely related to the presence of the S–Cl bond. In fact, CH_3SH and $(CH_3)_2S$ have no absorption band above 300 nm.[16] Other possibilities of excitation of either the lone pair electron on chlorine atom or the σ-electron of the S–Cl bond might be considered. The former is assigned to the second band, but the latter is hardly acceptable since the excitation energy of the $\sigma^*\leftarrow\sigma$ transition is much larger than that of the $\sigma^*\leftarrow n$ transition (*e.g.*, for $(CH_3)_2S$ $\Delta E^*_{\sigma\text{-}\sigma}=6.2$ eV $\Delta E^*_{\sigma\text{-}n}=5.2$ eV). This may be supported by the fact that methanesulfonyl chloride (CH_3SO_2Cl) without lone pairs on the sulfur atom has no absorption band in the ultraviolet and visible regions (Table 4). Moreover, the molar extinction coefficient of the $\sigma^*\leftarrow\sigma$ transition is, in general, of the order of 10^2—10^3 as $\varepsilon_{\max}$ whereas the observed one is less by one order, implying that the assignment ($\sigma^*\leftarrow\sigma$) is not reasonable for the first band.

The second band is assigned from the present calculation to be the excitation of the lone pair electron (n′) of chlorine atom to the $\sigma^*_{\text{S-Cl}}$ orbital ($\sigma^*\leftarrow n'$). The wavelength, however, is considerably longer than that of the usual alkyl chloride, *e.g.*, CH_3Cl (154–161 nm);[17] in addition the wavelength of the first band is greater than that of usual alkyl sulfides. The main reason for such large shifts toward the longer wavelength of these two bands in comparison with those of the related compounds, $(CH_3)_2S$ and CH_3Cl, may be attributed to the extraordinarily low orbital level of $\sigma^*_{\text{S-Cl}}$ in CH_3SCl. Moreover, it is seen from the increase of the S–Cl bond length that the energy level of $\sigma^*_{\text{S-Cl}}$ is greatly lowered in comparison with that of the lone pairs of sulfur and chlorine atoms (Fig. 2). Such a tendency may be connected with the color of the sulfenyl compounds. Furthermore the ratio between the calculated oscillator strengths of the two bands is in good agreement with that between the observed $\varepsilon_{\max}$'s. Thus, it may be concluded that the first band is assigned to the σ* (S–Cl)←n(S) transition and the second one to the σ* (S–Cl)←n′ (Cl).

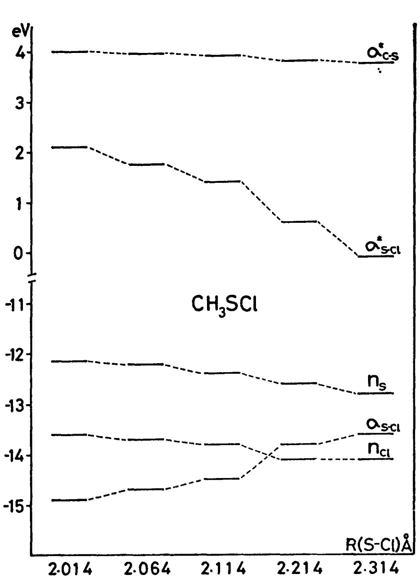

Fig. 2. The relation between the bond distance *R*(S–Cl) and the molecular orbital levels in CH_3SCl.

As a related compound, sulfur dichloride (SCl_2) was also studied. The results are given in Table 4. The observed absorption bands at 263 and 246 nm which have almost the same intensities as and shorter wavelengths than the $\sigma^*_{\text{S-Cl}}\leftarrow n_S$ transition of CH_3SCl were predicted to be due to the excitations of $\sigma^*_{\text{S-Cl}}\leftarrow n_S$ and $\sigma^{*\prime}_{\text{S-Cl}}\leftarrow n_S$, respectively. These assignments may be reasonable since the two σ* orbitals of the S–Cl bond are nearly degenerate and therefore the calculated oscillator strengths for the transitions give almost the same values. For $SOCl_2$, where one oxygen atom combines with the lone pair electron of sulfur atom, its absorption band further shifts toward a shorter wavelength in comparison with that of SCl_2. This may be attributed to the stabilization of the S–Cl bond by the formation of S–O bond. The $\sigma_{\text{S-Cl}}$ orbital level of $SOCl_2$ is lower than that of SCl_2 by *ca.* 1.2 eV and the corresponding σ* orbital becomes higher accordingly. Furthermore, the absorption bands of SO_2Cl_2 and CH_3SO_2Cl, which have a sulfur atom combining with two oxygen atoms and hence no lone pair electrons, have not yet been found in the ultraviolet region. From these experimental and theoretical investigations it is demonstrated that compounds with the S–Cl group have, in general, weak absorption bands in the 350—400 nm region due to the transition between the lone pair orbital of sulfur (n_S) with small ionization potential and the low-energy anti-bonding orbital, $\sigma^*_{\text{S-Cl}}$.

Table 5. Singlet excitation energies of CF_3SCl and C_6H_5SCl

Compound	Excitation energy (nm)	Oscillator strength	Assignment
CF_3SCl[a)]	290.0	4.68×10^{-6}	$\sigma^*_{\text{S-Cl}}\leftarrow n_S$
	194.0	2.40×10^{-2}	$\sigma^*_{\text{S-Cl}}\leftarrow n_{Cl}$
C_6H_5SCl[b)]	372.2	5.40×10^{-3}	$\sigma^*_{\text{S-Cl}}\leftarrow n_S$

a) Calculation carried out with *R*(S–Cl) of 2.060 Å by the CNDO/2 method. b) Calculation carried out with *R*(S–Cl) of 2.070 Å by the ASMO-SCF method.

For further investigation of alkanesulfenyl chloride, CF_3SCl was studied by the same method as mentioned above and the optimized molecular structure was obtained to give a potential energy minimum at 2.060 Å of *R*(S–Cl). The singlet excitation energies for the optimized structure are given in Table 5. The first and second absorption bands are attributed to the excitations of $\sigma^*_{\text{S-Cl}}\leftarrow n_S$ and $\sigma^*_{\text{S-Cl}}\leftarrow n_{Cl}'$, respectively, in a manner similar to the case of CH_3SCl. These calculated results are also in fair agreement with the observed values (Table 2) not only in the wavelengths but also the intensities. The first and second absorption bands of CF_3SCl, however, shift toward shorter and longer wavelength, respectively, in comparison with those of CH_3SCl. This is also realized from a comparison of the energy levels of CH_3SCl and CF_3SCl shown in Fig. 3; in particular, the n_S orbital of CF_3SCl is largely stabilized in comparison with the $\sigma^*_{\text{S-Cl}}$ orbital.

In order to clarify such a trend, we compared the bond energy E_{AB} of CF_3SCl with that of CH_3SCl

TABLE 6. BOND ENERGIES E_{AB} (a.u.) IN CH_3SCl AND CF_3SCl CALCULATED BY THE CNDO/2 METHOD

Compound	R(S–Cl) (Å)	C–S	S–Cl
CH_3SCl	2.064	−0.612	−0.476
CF_3SCl	2.060	−0.588	−0.484

(Table 6).*** CF_3SCl has a larger S–Cl bond energy and a smaller C–S bond energy than those in CH_3SCl. This might be due to the inductive effect of fluorine atom which attracts electron on carbon atom. As a consequence, the C–S bond is weakened but the S–Cl bond undergoes no such remarkable inductive effect. From these results, it may be expected that CF_3SCl has two reactive bonds, C–S and S–Cl, which may lead to interesting chemical reactions. The shifts observed in the absorption bands of CF_3SCl in comparison with those of CH_3SCl seem to be consistent with the change of bond energies of S–Cl and C–S bonds.

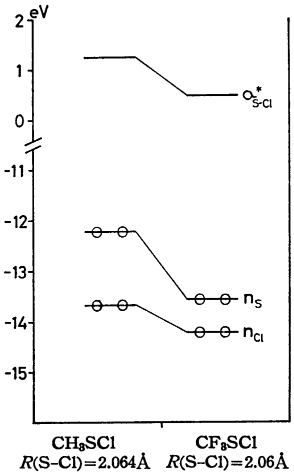

Fig. 3. The molecular orbital levels in CH_3SCl and CF_3SCl.

In the case of the arylsulfenyl chlorides, *o*-nitrobenzenesulfenyl chloride and its derivatives studied previously,[1] there may be interaction between the *ortho*-substituted nitro group and the sulfur atom to give rise to the sulfenium cation. These molecules are therefore not suitable for an investigation of the cause of the reddish color which many arylsulfenyl chlorides bear. Accordingly, benzenesulfenyl chloride which can not have such an interaction was taken as the simplest arylsulfenyl chloride.

For the calculations, the molecular structure was determined by using the CNDO/2 method; two conformations of the chlorine atom (Fig. 4, A and B) were compared. Conformation A, where the chlorine atom is on the same plane as the benzene ring, is more stable than B, where it is out of plane. The stabilization of A may be attributed to the π-conjugation effect between the lone pair electrons on the sulfur atom and the π-electrons on the benzene ring; there is no such conjugation effect in B since the lone pair orbital is perpendicular to the π-orbitals.

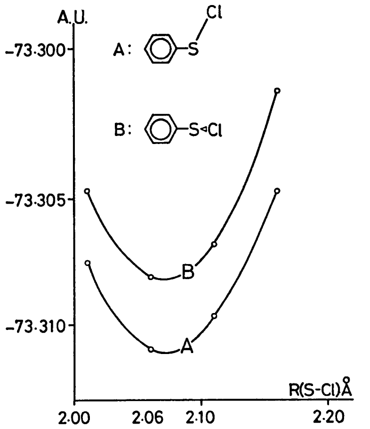

Fig. 4. Dependence of the total energies of benzenesulfenyl chloride on the parameter R(S–Cl).

Using the resulting bond distance R(S–Cl)=2.070 Å *i.e.*, the optimized bond distance of conformation A, the singlet excitation energies and oscillator strengths were calculated by the ASMO-SCF method (Table 5). It is seen that the calculated location of the absorption band of the longest wavelength (372.2 nm) is in accord with the observed one (386 nm), and that it is also due to the excitation of $\sigma^*_{S\text{-}Cl} \leftarrow n_S$ is accord with the assignment for the alkanesulfenyl chlorides.

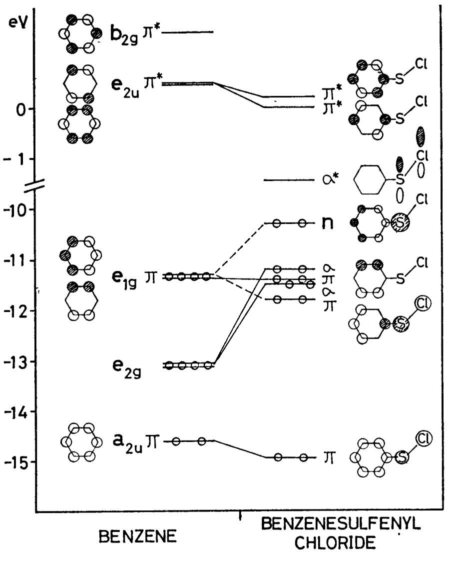

Fig. 5. The relation between the molecular orbital levels of benzene and benzenesulfenyl chloride.

In molecules having π and lone pair electrons such as carbonyl compounds, the absorption bands of the longest wavelength are generally known to be π*←n transitions.[18] However, the energy level of the $\sigma^*_{S\text{-}Cl}$ orbital is lower than that of the π* orbital in this molecule, which may lead the σ*←n transition to be the lowest energy excitation (Fig. 5). Furthermore, the σ*←n transition in C_6H_5SCl is smaller than that of the alkane sulfenyl chlorides. This may be attributed to

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*** In the CNDO/2 approximation, the total energy E_T can be expressed by the following equation, $E_T=\sum_A E_A+\sum_{A<B} E_{AB}$, where E_A and E_{AB} denote the monatomic and diatomic terms, respectively.

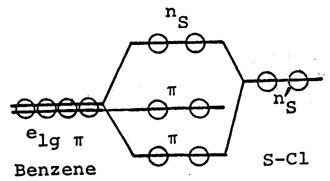

Fig. 6. Energy level of benzenesulfenyl chloride.

the participation of the lone pair orbital in the π-conjugation as follows; the n_S orbital in C_6H_5SCl is constructed from the interaction between the n_S' orbital (lone pair orbital on the sulfur atom) and degenerate π orbitals (e_{1g}) of benzene, and hence the lone pair orbital as shown in Fig. 6. This result suggests that the $\sigma^* \leftarrow n$ transition in C_6H_5SCl gives a smaller excitation energy than that of alkanesulfenyl chlorides which can not have such interactions. Moreover, there is no absorption band in the region above 300 nm in $C_6H_5SC_6H_5$.[19] The calculated oscillator strength (of the order of 10^{-3}) is larger than that of CH_3SCl (of the order of 10^{-5}), and such a tendency is also found in the observed values of ε_{max} (Table 2). Thus, as in the case of the alkanesulfenyl chlorides, the observed absorption band at the longest wavelength in C_6H_5SCl is assigned to be the transition of $\sigma^*_{S\text{-}Cl} \leftarrow n$.

Conclusion

The characteristic absorption band in the ultraviolet region of organic compounds with the S–Cl group, commonly appearing at 300—400 nm, was assigned to the excitation of the lone pair electron of sulfur atom to the $\sigma^*_{S\text{-}Cl}$ orbital; the present calculation reveals that such a band at a fairly long wavelength which induces an intensely red color may be mainly due to the extraordinarily low energy level of the $\sigma^*_{S\text{-}Cl}$ orbital and the small ionization potential of 3p electron of the sulfur atom. From the present theoretical study, the high reactivity of S–Cl bond is attributed to the weakness of this bond, probably caused by the large electron repulsion between 3p electrons of sulfur and chlorine atoms.

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References

1) N. Kharasch, C. M. Buess, and W. King, *J. Amer. Chem. Soc.*, **75**, 6035 (1953), and the references cited therein.

2) R. N. Naszeldine and J. M. Kidd, *J. Chem. Soc.*, **1953**, 3219.

3) J. M. White, *Spectrosc. Lett.*, **2**, 301 (1969).

4) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill (1970).

5) T. Yonezawa, H. Konishi, and H. Kato, This Bulletin, **42**, 933 (1969).

6) D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).

7) A. Guarnieri, *Z. Naturforsch.*, **25a**, 18 (1970).

8) H. J. M. Bowen, *Trans. Faraday Soc.*, **50**, 452 (1954).

9) A. Senning, "Sulfur in Organic and Inorganic Chemistry," Vol. 3, pp. 99—112, Marcel Dekker, Inc. (1972).

10) For sulfur dichloride, Y. Morino, T. Ito, and J. Nakamura, *J. Phys. Soc. Japan*, **17**, Supple. B-2, 37 (1962).

11) For thionyl chloride, I. Hargittai, *Magy. Kem. Foly.*, **74** 596 (1968); *Acta Chim.*, (Budapest), **59**, 351 (1969).

12) For sulfuryl chloride, M. Hargittai, *ibid.*, **60**, 231 (1969).

13) For methanesulfonyl chloride, M. Hargittai and I. Hargittai, *J. Chem. Phys.*, **59**, 3251 (1973).

14) H. Brintzinger, K. Phannsteil, H. Koddebusch, and K. E. Kling, *Chem. Ber.*, **83**, 87 (1950).

15) H. Lecher, *ibid.*, **58**, 409 (1925).

16) O. H. Wheeler and L. A. Kaplan, "Organic Spectral Data," Vol. 3, p. 1, Interscience (1966); C. C. Price and S. Oae, "Sulfur Bonding," p. 171, Ronald Press Company, New York (1962).

17) M. J. Kamlet, "Organic Spectral Data," Vol. 1, Interscience (1960).

18) H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press Inc., New York (1967).

19) N. A. Valyashko and F. F. Cheshko, *Sbornik Statei Obshchei Khim.*, **1**, 584 (1953); L. Horner and H. Nickel, *Ann. Chem.*, **597**, 20 (1955).