〔Chem. Pharm. Bull. 18(4) 824—827 (1970)〕

UDC 547.541.02 : 543.422.4

The Infrared Absorption Spectra of Organic Sulfur Compounds. VI.[1]
The Studies of the Compounds including S-N-S Linkage

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(Received September 12, 1969)

This report is a continuation of the previous paper dealing with the characteristic infrared absorption bands of the $-SO_2N-R_2$[3,4] $-SONR_2$,[5] $-SNR_2$[1] groups of organic sulfur compounds and deals with the infrared spectra of bis-benzenesulfenimide derivatives including S-N-S linkage and their N-deuterated compounds.

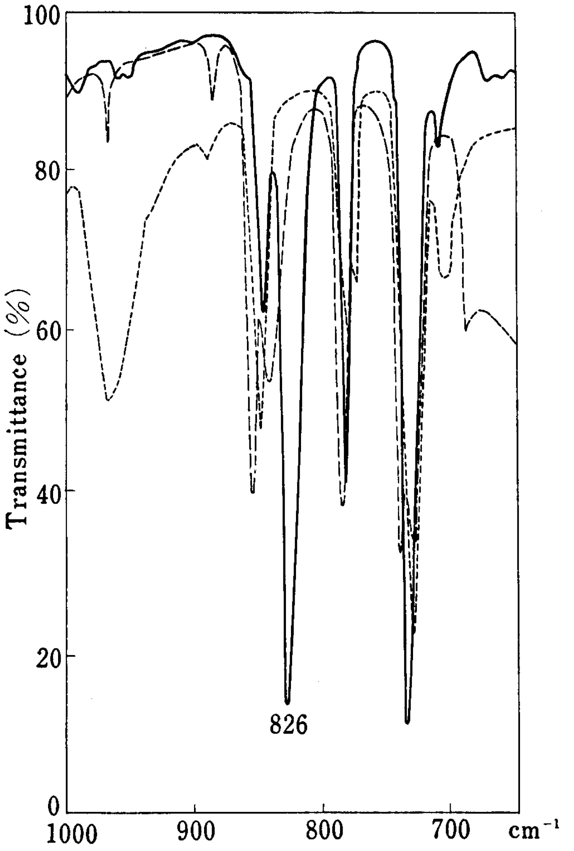

Fig. 1. Infrared Spectra of *o*-Nitrobenzenesulfenamide Derivatives

——— : N-methyl-bis-*o*-nitrobenzenesulfenimide
— — — : N-methyl-*o*-nitrobenzenesulfenamide
·········· : N,N-dimethyl-*o*-nitrobenzenesulfenamide

Fig. 1 shows the infrared spectra of N-methyl-bis-*o*-nitrobenzenesulfenimide, N-methyl-*o*-nitrobenzenesulfenamide and N,N-dimethyl-*o*-nitrobenzenesulfenamide. The three bands at 850, 785 and 730 cm^{-1} are observed commonly among the three compounds. The bands at 850 cm^{-1} are assigned to the C-N stretching vibration.[6] and the 785 cm^{-1} bands are the characteristic bands in aromatic nitro-compounds.[7] The bands at 730 cm^{-1} are the characteristic bands of *o*-disubstituted derivatives.[8] It should be noted that N-methyl-bis-*o*-nitrobenzenesulfenimide shows a strong band at 826 cm^{-1}, which may be ascribed to the S–N–S linkage but the assignment to the S–N–S stretching vibration has no sure evidence. Therefore, the infrared spectrum of bis-benzenesulfenimide was measured to make sure that the band is due to the S–N–S stretching vibration.

In Fig. 2, the infrared spectrum of bisbenzenesulfenimide is compared with that of the diphenyldisulfide. The former is quite similar to the latter, but has three additional bands

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[1] Part V: Yu. Tanaka and Yo. Tanaka, *Yakugaku Zasshi*, **89**, 837 (1969).
[2] Location: *Oe-motomachi*, *Kumamoto.*
[3] Yu. Tanaka and Yo. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **13**, 399 (1965).
[4] Yu. Tanaka and Yo. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **13**, 858 (1965).
[5] Yu. Tanaka, T. Sugimura and Yo. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **13**. 1384 (1965).
[6] R.N. Haszeldin, *J. Chem. Soc.*, **1953**, 2525.
[7] N.B. Colthup, L.H. Daly and S.E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, 1964, p. 285.
[8] *a*) L.J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., Metheuen Co., Ltd., London, 1958, p. 65; *b*) J.C. Evans, *Sepct. Acta*, **16**, 428 (1960).

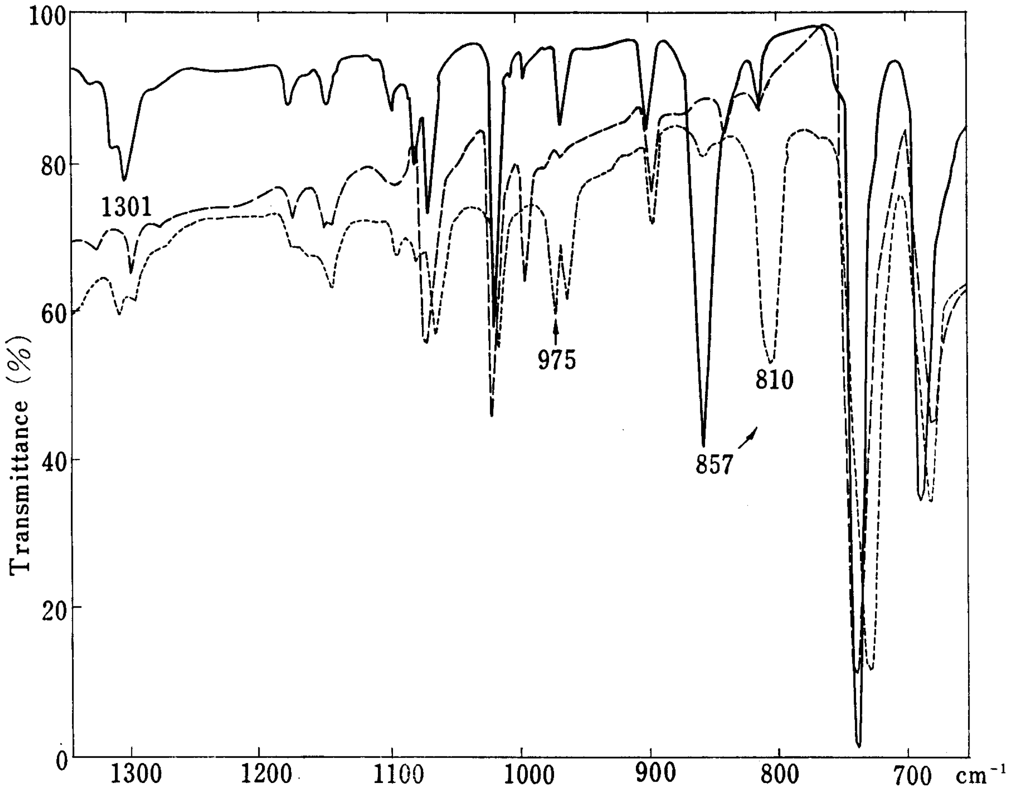


Fig. 2. Infrared Spectra of Bis-benzenesulfenimide (Solid Line), Its Deuterated Compound (Dotted Line) and Diphenyldisulfide (Broken Line)

at 3275, 1301 and 857 cm^{-1}. As well known, the band at 3275 cm^{-1} is assigned to the NH stretching vibration by the shift to 2445 cm^{-1} on N-deuteration. The band at 1301 cm^{-1} can be assigned to the NH deformation vibration. On N-deuteration, this band disappears

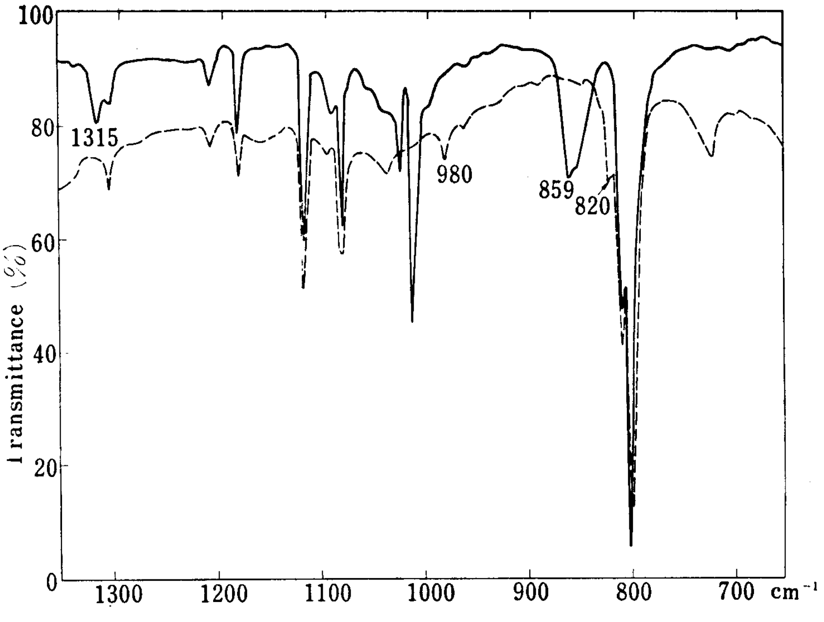


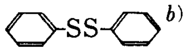
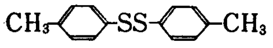
Fig. 3. Infrared Spectra of Bis-toluenesulfenimide (Solid Line) and Its Deuterated Compound (Broken Line)

and a new band due certainly to the ND deformation vibration appears at 975 cm^{-1}.[9,10] It has been reported that the S–N band shifts to lower wave number region by the N-deuteration.[1,3–5] The S–N–S stretching band must show a similar isotopic shift to lower wave number region. In fact, the band at 855 cm^{-1} shifted to 810 cm^{-1} on N-deuteration.

The infrared spectrum of bistoluenesulfenimide is compared with that of its deuterated compound, in Fig. 3. This is agreeable with the results of the investigation of bisbenzenesulfenimide.

For diphenyldisulfide, the fundamental frequencies arising from the benzene ring and benzene-S linkage have been assigned by Green.[11] Whiffen[12] has described the vibration mode of monosubstituted benzenes. From analogy with the data of these authors, the corres-

Table I. Vibrational Frequencies and Assignment for Bisbenzenesulfenimide, Bistoluenesulfenimide and Ditoluenedisulfide

Assignment[a]	 [b]			
ν (NH)	—	3275s	3270s	—
ν (CH_3)	3072w	3060w	3060w	—
	3059w	3030w	—	—
ν (CC)	1575s	1578m	1575m	1593w
ν (CC)	1564m	1573sh	1567w	1568w
ν (CC) δ (CH)	1475s	1477m	1488s	1487s
ν (CC) δ (CH)	1436s	1440m	1449w	1447w
ν (CC)	1326w	1330w	—	—
δ (CH)	—	1310w	1303w	1305m
δ (NH)	—	1301w	1315w	—
δ (CH)	1275w	1275w	—	—
δ (CH)	1177m	1177w	1205w	1205w
δ (CH)	1153m	1147w	1180w	1179m
δ (CCC) ν (CX)	1073s	1080w	1088w	1096w
	—	1070m	1080m	1075m
δ (CH)	1067sh	—	—	—
γ (CH_3)	—	—	1035w	1037w
δ (CH) ν (CC)	1022s	1018m	1023w	—
	1013sh	—	1010m	1012m
ring breath	997m	994w	995w	—
γ (CH)	983w	969m	—	—
γ (CH)	967w	900m	—	—
γ (CH)	903m	—	—	—
	900m	—	—	—
	894w	—	—	—
ν (SN)	—	857s	859s	—
γ (CH)	845sh	835sh, w	—	832w
	843m	815w	808m	—
γ (CH)	—	—	801s	798s
γ (CH)	741vs	740s	—	—
	736vs	736vs	—	—
δ (CCC) ν (CX)	692sh	703sh	—	—
γ (CC)	688vs	689s	—	—

a) ν: stretching, δ: deformation (inplane), γ: deformation (out of plane)
b) J.H.S. Green *Spectrochim. Acta*, **24A**, 1627 (1968)

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9) D. Hadzi and M. Skrbljak, *J. Chem. Soc.*, **1957**, 843.
10) A. Hass and N. Sheppard, *J. Chem. Soc.*, **1965**, 6613.
11) J.H. Green, *Spectrochim. Acta*, **24A**, 1627 (1968).
12) D.H. Whiffen, *J. Chem. Soc.*, **1956**, 1350.

ponding frequencies of bisbenzenesulfenimide have been given streightforward assignments. The assignment of the infrared absorption of *p*-toluenesulfonamide by Rademacher, *et al.*[13] was also referred to. The infrared absorption frequencies of bisbenzenesulfenimide, bistoluenesulfenimide, and ditoluenedisulfide are listed in Table I together with the frequencies of reference molecules. There are good agreements of the corresponding frequencies among these three compounds.

The S–N–S group is expected to give rise to the S–N–S symmetric stretching vibration and the asymmetric stretching vibration. However, only one S–N–S stretching band was observed for the presently investigated compounds. More investigation is nescesary on this problem.

Experimental

***o*-Nitrobenzenesulfenamide Derivatives**——These were prepared by the method described by Zincke.[14]

Bisbenzenesulfenimide——Chloroform solution of thiophenol (1 mole) was added dropwise to supersaturated chloroform solution of chlorine (50 ml) with stirring at −10°. After the stirring for one hour, nitrogen gas was bubbled through the solution for one hour in order to remove the remaining chlorine. A chloroform solution of benzenesulfenyl chloride was saturated with dry ammonia gas in tightly closed bottle for twelve hours at room temperature. Remaining ammonia gas and chloroform were removed under a reduced pressure and the residue was extracted with ether. Removal of the solvent gave the crude product, which was recrystallized from a mixture of water and ethanol. Repeated recrystallization from water gave colourless crystal, mp 115—116° (decomp.). Bistoluenesulfenimide was prepared by similar way with bisbenzenesulfenimide.

Diphenyldisulfide and bis-*p*-methylbenzenesulfide were obtained as the by-products on the way to prepare the main products. N-deuterated compounds were made by the usual exchange reaction with the heavy water and ethanol-d.

Measurements of the Spectra——The infrared spectra were recorded on a Koken DS-301 infrared spectrophotometer equipped with sodium chloride prism between 4000 and 650 cm^{-1}. The spectra of all samples were measured in the form of solid dispersed in Nujol or in hexachlorobutadien mulls and in KBr disks.

Acknowledgement The author is pleased to acknowledge the considerable assistance of Dr. Toyozo Uno in Kyoto University. The author also would like to express her appreciation to Dr. Katsunosuke Machida in Kyoto University. Thanks are due to Mrs. Kuniko Shiraki of Kumamoto University for elemental analysis and due to Miss Mihoko Sato of Kumamoto University for measurement of infrared spectra.

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13) P. Rademacher, W. Wiegrabe and W. Luttke, *Chem. Ber.*, **100**, 1213 (1967).

14) Th. Zincke, *Ann.*, 391, 57 (1912).