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Infrared Spectra of Bisarylsulfonimide Derivatives

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The infrared (IR) spectra of bisbenzenesulfonimide, bistoluenesulfonimide and benzenetoluenesulfonimide are reported together with the spectra of the corresponding N-deuterated samples. The isotopic shifts of the bands near 3180 cm^{-1} and 1400 cm^{-1} of bisarylsulfonimide derivatives give the evidence of the assignment of these bands to the N–H group. The dichroic properties of these bands in bisbenzenesulfonimide suggest that the molecule has the C_s symmetry. On this ground, the symmetric and antisymmetric S–N–S stretching bands are clearly distinguished from each other in the polarized spectra.

The IR spectrum of bispentadeuterobenzenesulfonimide has been measured. The effects of the N-deuteration and the ring deuteration on the characteristic frequencies are discussed. The IR spectra of the corresponding N-alkyl-bisarylsulfonimide derivatives are also discussed.

Introduction

In the course of study on the infrared spectra of sulfonamide derivatives,[2,3] the assignment of the band near 900 cm^{-1} to the S–N stretching vibration has been confirmed by the comparison with related compounds and by the frequency shifts on N-deuteration. An analogous isotope effect was found for bisarylsulfonimide derivatives containing the S–N–S group.[4] Although this group is expected to give rise to the S–N–S symmetric and antisymmetric stretching vibrations, only one S–N–S stretching band was observed near 860 cm^{-1} for the previously investigated compounds.

In the present work, in order to confirm the absorptions due to the S–N–S symmetric and antisymmetric stretching vibrations in the group of SO_2–N–SO_2, the infrared spectra of bisbenzenesulfonimide have been recorded for ordinary and polarized radiations. The other characteristic bands of bisarylsulfonimide derivatives were also examined.

Experimental

Materials——Bisbenzenesulfonimide (BBSI): Benzenesulfonamide (1.7 g) was completely dissolved into the aqueous solution (10 ml) of sodium hydroxide (0.4 g). The solution was dried up on the water bath and the residue was dried in a desiccator by P_2O_5 under reduced pressure. The dried residue and benzenesulfonyl chloride (2.0 g) was heated at about 220° for three hours. After cooling, the reaction mixture was washed by acetone, and was recrystallized several times from methanol and water. mp 140—141°. *Anal.* Calcd. for $C_{12}H_{11}O_4NS_2$: C, 48.45; H, 3.64; N, 4.71. Found: C, 48.76; H, 3.84; N, 4.60.

Bistoluenesulfonimide (TTSI) was prepared by the similar way with BBSI. mp 173°. *Anal.* Calcd. for $C_{14}H_{15}O_4NS_2$: C, 51.68; H, 4.65; N, 4.30. Found: C, 51.69; H, 4.69; N, 4.08.

Benzenetoluenesulfonimide (BTSI) was prepared by the similar way with BBSI. mp 160—161°. *Anal.* Calcd. for $C_{13}H_{13}O_4NS_2$: C, 50.15; H, 4.21; N, 4.49. Found: C, 50.75; H, 4.29; N, 4.64.

N-alkyl-bisarylsulfonimide derivatives were prepared in the way described above. Experimental data are summarized in Table I.

Bisdeuterobenzenesulfonimide (BBSI-d_{10}) was prepared by a similar way with BBSI. Benzenesulfonyl chloride-d_5 was prepared by a method similar to that described by Uno, *et al.*[5] NaOD was obtained by usual exchange reaction with heavy water.

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[1] Location: *Tsushima, Okayama.*

[2] Yu. Tanaka and Yo. Tanaka, *Chem. Pharm. Bull.* (Tokyo), 13, 399 (1965).

[3] Yu. Tanaka and Yo. Tanaka, *Chem. Pharm. Bull.* (Tokyo), 13, 858 (1965).

[4] Yu. Tanaka, *Chem. Pharm. Bull.* (Tokyo), 18, 824 (1970).

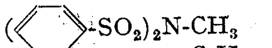
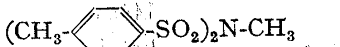
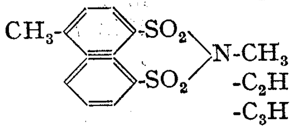
[5] T. Uno, K. Machida, and K. Hanai, *Spectrochim. Acta*, **24A**, 1705 (1968).

N-Deuterated Compounds: All the corresponding N-deuterated compounds were prepared by the usual exchange reaction with heavy water.

Measurements of the Spectra——The infrared spectra were recorded on a JASCO DS-403G Spectrophotometer (4000—350 cm^{-1}). The spectra of the ordinary samples were recorded for KBr disks, Nujol or hexachlorobutadiene (H.C.B.) mulls and those of N-deuterated samples were recorded for Nujol or H.C.B. mulls.

For the measurement of infrared dichroism, the oriented sample of BBSI was obtained from the melt between two potassium bromide plates by crystal growth along the direction of an applied temperature gradient.

TABLE I. Analytical Data of N-Alkyl-bis-arylsulfonimide Derivatives

Compounds	mp (°C)	Formula	Analysis (%) Calcd. C	H	N	Found C	H	N
 $(\text{-}SO_2)_2N\text{-}CH_3$	111—112	$C_{13}H_{13}O_4NS_2$	50.15	4.21	4.49	49.93	4.42	4.84
$\text{-}C_2H_5$	84—85	$C_{14}H_{15}O_4NS_2$	51.68	4.65	4.30	51.60	4.54	4.25
$\text{-}C_3H_7(n)$	74—75	$C_{15}H_{17}O_4NS_2$	53.08	5.05	4.13	53.25	5.09	3.87
$\text{-}C_4H_9(n)$	83	$C_{16}H_{19}O_4NS_2$	54.37	5.42	3.96	54.09	5.20	3.69
 $(CH_3\text{-}\;\text{-}SO_2)_2N\text{-}CH_3$	111	$C_{15}H_{17}O_4NS_2$	53.08	5.05	4.13	52.02	4.61	4.47
$\text{-}C_2H_5$	114—115	$C_{16}H_{19}O_4NS_2$	54.37	5.42	3.96	54.24	5.30	3.87
$\text{-}C_3H_7(n)$	79—80	$C_{17}H_{21}O_4NS_2$	55.56	5.76	3.81	55.78	6.09	4.01
$\text{-}C_4H_9(n)$	87—88	$C_{18}H_{23}O_4NS_2$	56.67	6.08	3.67	56.81	5.96	3.55
 $CH_3\text{-}\;\text{-}SO_2,\;\text{-}SO_2\;N\text{-}CH_3$	92—93	$C_{14}H_{15}O_4NS_2$	51.68	4.65	4.30	52.02	4.61	4.47
$\text{-}C_2H_5$	76—78	$C_{15}H_{17}O_4NS_2$	53.08	5.50	4.13	53.25	5.37	4.40
$\text{-}C_3H_7(n)$	77—78	$C_{16}H_{19}O_4NS_2$	54.37	5.42	3.96	54.82	5.36	3.58
$\text{-}C_4H_9(n)$	68	$C_{17}H_{21}O_4NS_2$	55.56	5.76	3.81	55.78	6.09	4.01

Results and Discussion

The infrared spectra of BBSI and N-deuterated BBSI are shown in Fig. 1 and the observed frequencies of BBSI are listed in Table II. Benzenesulfonamide (BSA) shows a medium band at 901 cm^{-1} due to the S–N stretching vibration,[3,5] while BBSI shows a very strong band at 875 cm^{-1}. In other respects, the infrared spectra between 1200 cm^{-1} and 650 cm^{-1} of BBSI and BSA are very similar to each other. The 875 cm^{-1} band of BBSI can be assigned to the S–N–S stretching vibration by the comparison with that of BSA and by the shift to the 785 cm^{-1} on N-deuteration. The observed shifts are quite characteristic of the N–S–N frequencies.[6] In addition, the band at 1380 cm^{-1} and 3165 cm^{-1} of BBSI were assigned to the δNH and νNH mode from the shifts to the 1070 cm^{-1} and 2145 cm^{-1} respectively.[7,8]

The nitrogen atom of BBSI is expected to be pyramidal from analogy with the X-ray crystallographic data for various sulfonamide derivatives.[9–11] Accordingly, if the molecular symmetry of BBSI is that of the point group C_s with the planar skeleton C–S–N–S–C, (Fig. 2), the νNH mode should belong to the a$'$ species and the δNH mode to the a$''$ species.[7] The infrared spectra of the oriented sample recorded for the polarized incident radiations are shown in Fig. 3. The band at 3165 cm^{-1} attains the maximum intensity when the electric vector of the incident radiation is parallel to the direction of crystal growth (a$'$ species). On the other hand, the band at 1380 cm^{-1} becomes strong for the incident radiation polarised per-

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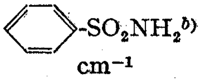
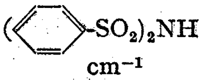
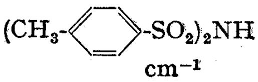
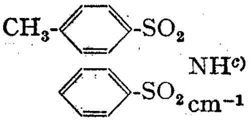
6) T. Uno, K. Machida, and K. Hanai, *Spectrochim. Acta*, **22**, 2065 (1966).
7) G. Dellepin and G. Zerbi, *J. Chem. Phys.*, **48**, 3573 (1968).
8) L.J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen & Co., Ltd. London, 1958, p. 207.
9) H.P. Klug, *Acta Cryst.*, **B24**, 792 (1968).
10) T. Jordan, H.W. Smith, L.L. Lohr, Jr., and W.N. Lipscom, *J. Am. Chem. Soc.*, **85**, 846 (1963).
11) E. Shefter and P. Sackman, *J. Pharm. Sci.*, **60**, 282 (1971).

Table II. The Characteristic Frequencies of Bisarylsulfonimide Derivatives

Assignment[a]	 $C_6H_5-SO_2NH_2$[b] cm^{-1}	 $(C_6H_5-SO_2)_2NH$ cm^{-1}	 $(CH_3-C_6H_4-SO_2)_2NH$ cm^{-1}	 $CH_3-C_6H_4-SO_2$ $C_6H_5-SO_2$ NH[c] cm^{-1}
$\nu asNH_2$	3530 s			
νsNH_2	3365 s			
νNH		3160	3170	3190
νCH	3970 sh	3060 sh	3060 sh	3060 sh
νCH_3			2920 w	2890 w
			2875 sh	2875 vw
			2826 vw	2910 w
				2880 w
νCC	1582 sh	1587 w	1595 m	1597 w
αNH_2	1555 m			
$\beta CH+\nu CC$	1483 w	1480 m	1488 w	1493 w
βCH_3			1455 vw	1482 w
			1450 sh	
			1445 w	
$\beta CH+\nu CC$	1450 s	1445 s		1448 m
αNH		1380 s	1383 m	1395 s
αCH_3			1378 m	1377 m
$\nu asSO_2$	1334 vs	1365 s	1360 vs	1365 vs
		1335 s		1355 s
βCH	1310 s	1307 w	1308 w	1312 w
νCC	1289 sh	1297 w	1295 m	1295 w
βCH	1182 s	1185 w	1190 w	
νsSO_2	1158 s	1165 s	1170 sh	1168 vs
		1160 vs	1165 vs	1162 vs
$\alpha CCC+\nu CX$	1090 s	1080 s	1080 m	1092 sh
				1080
$\beta CH+\nu CC$	1071 m	1068 m		1072 sh
	1024 w	1025 m	1018 w	1015 m
γCH_3			1030 w	1038 w
Ring breath	997 m	998 w		996 w
γCH	980 sh	975 w	970 w	975 w
	928 sh			
νSN	903 s	875 vs	858 s	865 s
				848 s
γCH	850 w	844 w	848 sh	830 sh
			808 s	830 sh
γCH	754 vs	758 vs		765 m
$\alpha CCC+\gamma CX$		725 vs	720 m	720 m
			703 sh	703 m
ϕCCC	687 s	683 s	678 sh	680 s
αCCC	593 m	617		
αSO_2	536 m	583 s		
βSO_2		543 s		

a) ν: stretching, α and β: inplane deformation, γ and ϕ: out-of-plane deformation
b) T. Uno, K. Machida, and K. Hanai, *Spectrochim. Acta*, **24A**, 1705 (1968)
c) measured for the unpolarized radiation

pendicularly to the crystal growth direction (a′ or a″ species). The 855 cm^{-1} band shows parallel dichroism, whence it should be assigned to an a′ mode. We have assigned it to the S–N–S symmetric stretching vibration. On the other hand, the band at 873 cm^{-1} shows the perpendicular dichroism and can be assigned to the S–N–S antisymmetric stretching vibration. These two bands at 855 cm^{-1} and at 873 cm^{-1} were observed as a single absorption band at 875 cm^{-1} on the measurement for the unpolarized radiation. The corresponding

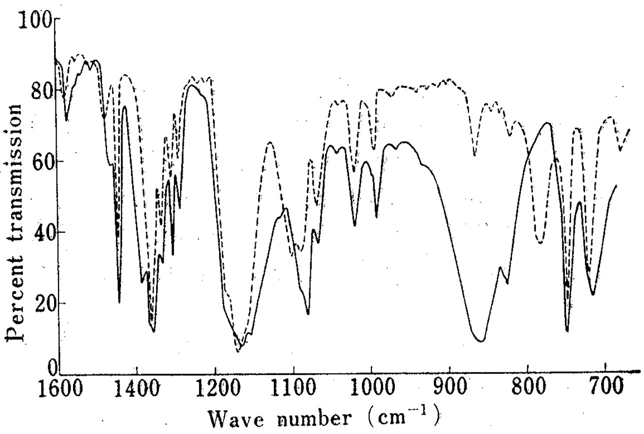


Fig. 1(a). Infrared Spectta of Bisbenzenesulfonimide (——) and Its N-Deuterated Compound (------) (1600 cm^{-1} —700 cm^{-1})

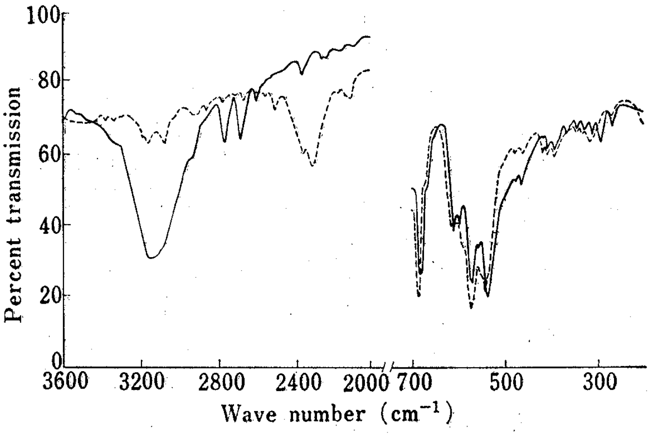


Fig. 1(b). Infrared Spectra of Bisbenzenesulfonimide (——) and Its N-Deuterated Compound (------) (3600 cm^{-1} —2000 cm^{-1} and 700 cm^{-1} —200 cm^{-1})

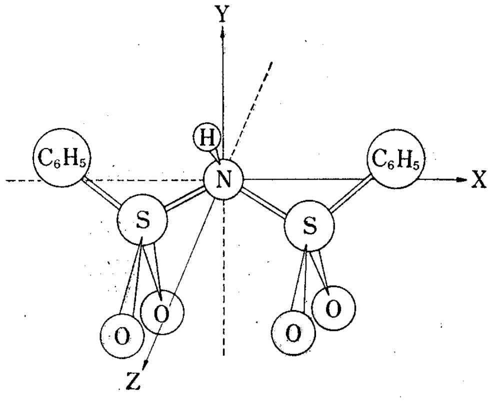


Fig. 2. Molecular Structure of Bisbenzenesulfonimide

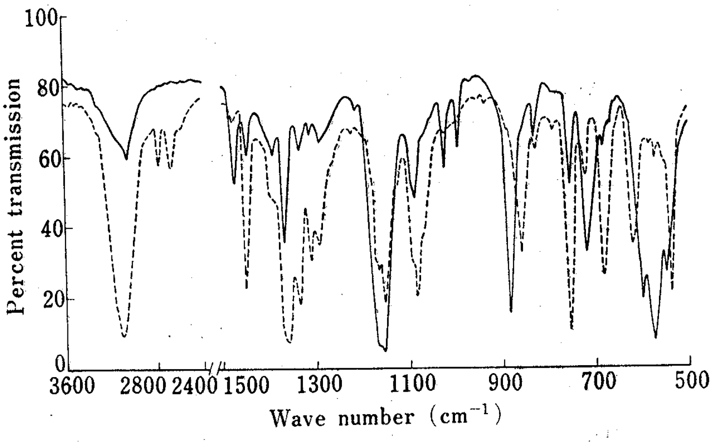


Fig. 3. Polarized Infrared Spectra of Bisbenzenesulfonimide

------: electric vector parallel to direction of crystal growth (a′)
——: electric vector perpendicular to direction of crystal growth (a″)

S–N–S stretching absorption bands in the polarized spectra of deuterated BBSI were identified at 777 cm^{-1} and 770 cm^{-1} from analogy with BBSI.

Four bands due to the SO$_2$ stretching vibrations are expected for BBSI. As a matter of fact, the antisymmetric stretching bands at 1360 cm^{-1} and 1330 cm^{-1}, and the symmetric stretching bands at 1155 cm^{-1} and 1148 cm^{-1} were recognized. The band due to a mixed mode of the C–S stretching and ring skeletal vibrations⁵⁾ of BBSI is observed at 1083 cm^{-1}.

Undeuterated TTSI shows a strong band at 858 cm^{-1}, which shifts to 773 cm^{-1} on deuteration. This band is resolved into a perpendicular component at 865 cm^{-1} and a parallel component at 835 cm^{-1} on the dichroic mea-

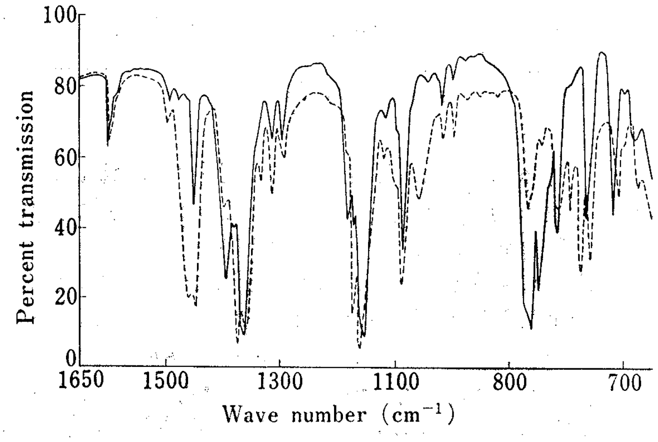


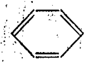
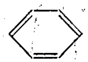
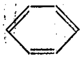
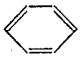
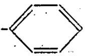
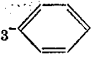
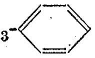
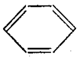
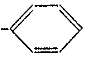
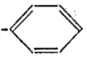
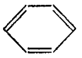
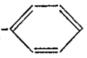
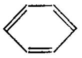
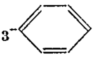
Fig. 4. Infrared Spectra of Benzenetoluenesulfonimide (——) and Its N-Deuterated Compound (------)

surement. Evidently, the high- and the low-frequency components arise from the S–N–S antisymmetric and symmetric stretching vibrations, respectively.

In case of asymmetrically substituted benzenetoluenesulfonimide (BTSI), two bands assignable to the S–N stretching vibrations appear at 865 and 848 cm^{-1} in the unpolarized infrared spectrum (Fig. 4). These bands shift to 795 and 778 cm^{-1} on N-deuteration. The absorption frequencies of BTSI and TTSI are listed in Table II together with the frequencies of reference compounds. In assigning the frequencies of TTSI and BTSI, the data on TSA and N-methyl-TSA by Radmacher, *et al.*, [12] have been a valuable guide and Goldstein's report on N-alkylarylsulfonamides have been referred, too.[13]

The infrared spectra of twelve kinds of N-alkyl-bisarylsulfonimide derivatives were measured and the existence of characteristic infrared frequencies of the molecules which have the SO_2–NR–SO_2 groups were confirmed. The observed frequencies and assignments are summarized in Table III.

TABLE III. The Characteristic Frequencies of N-Alkyl-bisarylsulfonimide Derivatives

		$Aryl_1\text{-}SO_2\text{-}\underset{R}{N}\text{-}SO_2\text{-}Aryl_2$ (cm^{-1})				
$Aryl_1$	$Aryl_2$	R	$\nu_{as}SO_2$	ν_sSO_2	$\alpha CCC+\nu CX$	$\nu S+N$
		CH_3	1323 s	1170 s	1085 m 1095 sh	830 s
		C_2H_5	1378 s	1166 s 1158 s	1083 m	878 s
		n-C_3H_7	1375 s 1370 s	1161 s 1168 s	1083 m 1093 m	820 s
		n-C_4H_9	1374 s	1175 s	1087 m 1093 sh	852 s 845 s
CH_3- 	CH_3- 	CH_3	1378 s 1354 s	1165 s 1173 sh	1085 m 1093 sh	830 s
CH_3- 	CH_3- 	C_2H_5	1374 s 1355 s	1166 s 1157 sh	1086 m 1093 sh	868 s
CH_3- 	CH_3- 	n-C_3H_7	1372 s	1170 s 1160 s	1084 m 1093 sh	823 s
CH_3- 	CH_3- 	n-C_4H_9	1372 s 1356 s	1165 s	1085 m 1093 sh	852 s
	CH_3- 	CH_3	1373 s 1355 s	1165 s 1172 s	1085 m 1093 sh	820 s
	CH_3- 	C_2H_5	1372 s 1352 s	1175 s 1166 s	1085 m 1093 sh	874 s
	CH_3- 	n-C_3H_7	1368 s 1352 m	1162 s	1085 m 1093 sh	825 s
	CH_3- 	n-C_4H_9	1374 s 1357 m	1165 s 1175 s	1085 m 1093 sh	852 s 845 s

s: strong, m: medium, sh: shoulder

It is seen from Table II and III that the $\nu_{as}SO_2$ bands of bisarylsulfonimide derivatives are observed at higher wave number region (about +30 cm^{-1}) than those of corresponding arylsulfonamide derivatives.[12–15]

The νC–N mode has been identified in a study of N-methylmethanesulfonamides (1076—1062 cm^{-1}),[16] and in N-methyl-*p*-toluenesulfonamide (1062 cm^{-1}),[14] and it has been established

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[12] P. Radmacher, W. Wiegrabe, and W. Lutthe, *Chem. Ber.*, **100**, 1213 (1967).

[13] M. Goldstein, M.A. Russell, and H.A. Willis, *Spectrochim. Acta*, **25A**, 1295 (1969).

[14] D. Hadzi and M. Skrbijak, *J. Chem. Soc.*, **1957**, 847.

[15] E.A. Robinson, *Can. J. Chem.*, 39, 247 (1961).

[16] M.J. Buttler and D.C. McKean, *Spectrochim. Acta*, 21, 465 (1965).

by Goldstein[13] that N-alkyl-arylsulfonamide show C–N stretching bands at 1074—1083 cm^{-1}. In the present work, a medium band at 1060±2 cm^{-1} observed for bisarylsulfonimides is assigned to the C–N stretching vibration.

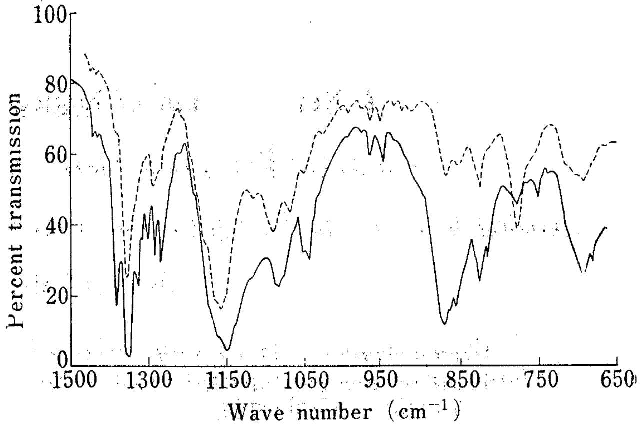

Fig. 5. Infrared Spectra of Bisbenzenesulfonimide-d_{10} (——) and its N-Deuterated Compound (------)

A particularly noticeable feature in all the spectra of the bisarylsulfonimides is a medium band at 1080±1 cm^{-1} having a shoulder at 1093 cm^{-1}. These bands can satisfactorily be assigned to a mixed mode of the C–S stretching and ring skeletal vibrations.[5] The shift of the characteristic band near 1090 cm^{-1} of benzenesulfonyl compounds on the ring deuteration has given an evidence of the assignment of this band to a mixed mode of the αCCC and νC-X. Figure 5 shows the infrared spectra of bisdeuterobenzenesulfonimide and its N-deuterated compound. The 1080 cm^{-1} band of BBSI shifts to 1053 cm^{-1} on ring deuteration in this work. The effect of ring deuteration on $\nu_{as}SO_2$, ν_sSO_2 and benzene ring frequencies of BBSI are quite similar to the case of benzene- and deuterobenzene-sulfonamide.[5]

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