Torsional Vibrations in Some Sulphur–Nitrogen Compounds studied by Inelastic Neutron Scattering, Infrared, and Raman Spectroscopy

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The torsional modes in $H_3N^+SO_3^-$, $Na[O_3SNH_2]$, $SO_2(NH_2)_2$, and $Ag_2[O_2SN_2H_2]$ have been assigned and the barrier heights and effective force constants calculated. The last two parameters increase with decreasing S–N bond length. The maximum splitting of the in- and out-of-phase NH_2 torsions in $SO_2(NH_2)_2$ has been shown to be of the order of 16 cm^{-1}. From the spectroscopic data the salt $Ag_2[O_2SN_2H_2]$ has been shown not to contain an NH_2 group, and this conclusion differs from that in an earlier publication. The SO_2 rocking and wagging modes are also observed because of their associated proton motion.

THERE is very little information available concerning the torsional vibrations in sulphur–nitrogen compounds. We have obtained the inelastic neutron scattering (i.n.s.) spectra of sulphamic acid, sodium sulphamate, and of sulphamide and its disilver salt. For some of these compounds considerable structural and spectroscopic data are available, and using this and our own far-i.r. and Raman data, when necessary, we have been able to assign the torsional modes. There has been some discussion [1] as to whether $Ag_2[O_2SN_2H_2]$ contains a single NH_2 or two NH groups. Because i.n.s. spectroscopy is particularly sensitive to those normal modes involving significant proton motion, one would expect very different i.n.s. spectra from these two configurations. We have been able to show that $Ag_2[O_2SN_2H_2]$ does not contain an NH_2 group.

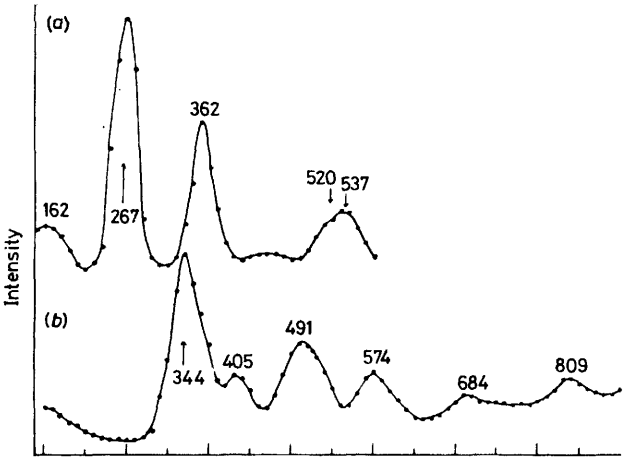

FIGURE 1 Beryllium Filter Detector spectra (*ca.* 90 K) of (*a*) $NH_3^+SO_3^-$ and (*b*) $Na[O_3SNH_2]$

EXPERIMENTAL

Sulphamic acid was obtained from B.D.H. and used without further purification. Sodium sulphamate was prepared by neutralisation of sulphamic acid, and sulphamide [2] and its silver salt [1] were prepared by literature methods.

I.n.s. spectra were obtained using the Beryllium Filter Detector (b.f.d.) [3] and 6 H [4] time-of-flight spectrometers at A.E.R.E. Harwell. The b.f.d. spectra, as presented, are proportional to the amplitude-weighted densities of states and the true transition frequencies were obtained from the band maxima by using the correction factors of Gamlen *et al.*[3] The sample temperatures were *ca.* 90 K for these experiments. Time-of-flight experiments were conducted at ambient temperatures and the data were treated using standard computer programs [5,6] to produce graphs of corrected counts against energy transfer (cm^{-1}) for each of the angles of detection.

The Raman spectra were run on a Cary 82 laser Raman spectrophotometer using a wavelength of 632.8 nm, and the far-i.r. spectra on a Beckman RIIC FS720 spectrophotometer.

RESULTS AND DISCUSSION

Sulphamic Acid and Sodium Sulphamate.—Sulphamic acid is a zwitterion. Its i.n.s. spectra are shown in Figures 1(*a*) and 2(*a*). Detailed i.r. (>250 cm^{-1}) [7] and Raman [8] studies have been published and the low-frequency data (0—900 cm^{-1}) together with our far-i.r. and i.n.s. (0—550 cm^{-1}) results are given in Table 1. The i.n.s. bands at 362, 520, and 537 cm^{-1} can be assigned by direct comparison with the results from optical spectra. The most intense i.n.s. band occurs at 267 (77 K) and 245 cm^{-1} (295 K). In view of their intensities we assign these bands to the NH_3 torsion at the two temperatures. We have also observed a weak i.r. band at 268 cm^{-1} (77 K) but this was absent at room temperature. From the N–H stretching frequencies and the neutron-diffraction data [9,10] it has been shown that extensive hydrogen bonding occurs in $H_3N^+SO_3^-$. Each hydrogen forms one

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[1] E. Nachbaur, A. Popitsch, and P. Burkert, *Monatsh.*, 1974, **105**, 822.

[2] M. Ferneyhough, Research Assignment, Durham, 1964.

[3] P. H. Gamlen, N. F. Hall, and A. D. Taylor, A.E.R.E. Harwell, unpublished report RRL 74/793, 1974.

[4] L. J. Bunce, D. H. C. Harris, and G. C. Stirling, A.E.R.E. Harwell, report R6246, 1970.

[5] A. H. Baston, A.E.R.E. Harwell, report M2570, 1972.

[6] R. E. Ghosh, A.E.R.E. Harwell, unpublished report RRL 74/552, 1974.

[7] A. M. Vaugnant and E. L. Wagner, *J. Chem. Phys.*, 1957, **26**, 77.

[8] N. Krishnamurthy, *Proc. Indian Acad. Sci.*, 1965, **A61**, 146.

[9] R. L. Sass, *Acta Cryst.*, 1960, **13**, 320.

[10] J. W. Bats, P. Coppens, and T. F. Koetzle, *Acta Cryst.*, 1977, **B33**, 37.

hydrogen bond (Table 2) and the shift in frequency of the torsion with temperature is explained by the effect of the contraction of the lattice on the hydrogen bonds.

TABLE 1

I.n.s., Raman, and i.r. data (cm^{-1}) for sulphamic acid

	I.n.s.[a]				
I.r.[a,b]	b.f.d.[b]	6 H	I.r.[c]	Raman[c]	Assignment[c]
				50	
				68	
				80	
91					
103.5		105			
				110	
114					
126				125	
142				140	
				155	
175br	162	162		170	NH · · · O
				240	NH · · · O
268	267	245			Torsion[a]
	362	360	352	357 378	SO_3^- rock
	520 537		526 540	535 550	SO_3^- def.
			682	678	S–N str.
			695	697	
				862	

[a] This work. [b] Liquid-nitrogen temperature. [c] Ref. 8.

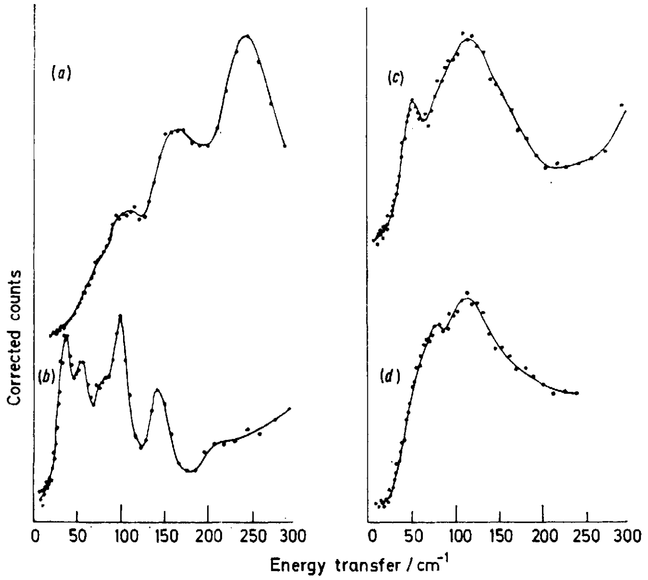

FIGURE 2 Time-of-flight spectra (295 K) of (*a*) $H_3N^+SO_3^-$, (*b*) $Ag_2[O_2SN_2H_2]$, (*c*) $SO_2(NH_2)_2$, and (*d*) $Na[O_3SNH_2]$

In the most general case of a molecule containing two rotors and with non-zero internal and external fields there should be two torsions.[11,12] These modes have been assigned in the hydrazinium salts;[11] however, in this case the external fields and moments of inertia of the two rotors are identical. For sulphamic acid the moments of inertia of the two rotors are very different and so probably are the external fields. In this case we would also expect two modes with one being more associated with the SO_3 group (lower frequency, low intensity in the i.n.s. spectrum) and the other mainly associated with the NH_3 group (higher frequency, greater intensity in the i.n.s. spectrum). If the internal field were zero then there would be two independent rotors so that only the NH_3 torsion would be seen in the i.n.s. experiments. Although we do not know the magnitude of the internal field in sulphamic acid, and we have no way of assigning the lower-frequency i.n.s. bands, the band at 267 cm^{-1}, in view of its intensity, must be mainly associated with the NH_3 torsion.

Since the S–N bond length[9] (1.764 Å) in $H_3N^+SO_3^-$ is very close to that predicted for a single bond (1.74 Å),[13] the external field resulting from the hydrogen bonds possibly explains, at least in part, the increase in frequency of the NH_3 torsion relative to that found in the amines of Pd, Pt, Co, and Ni (150—200 cm^{-1}).[14] With a barrier multiplicity of three we can use Herschbach's tables[15] of the solutions of the Mathieu equation to calculate the barrier to the torsion. The calculated values (Table 2) are 11.3 (953) at 77 K and 9.7 kJ mol^{-1} (811 cm^{-1}) at 295 K.

TABLE 2

Summary of the barrier heights, effective force constants, and structural data for the sulphur–nitrogen compounds

Compound	Barrier height (cm^{-1}) ($n = 3$)	Effective force constant (cm^{-1})	S–N Bond length (Å)	Hydrogen bonds, H · · · O (Å)
$H_3N^+SO_3^-$	953	3 595 (77 K) 3 027 (295 K)	1.764	1.918 1.938 2.004
$Na[O_3SNH_2]$	1 083	3 978	1.66 *	2.15 * 2.15
$SO_2(NH_2)_2$	1 574	5 874	1.60	
$Ag_2[O_2SN_2H_2]$	2 839	10 704	?	

* Data for potassium salt.

Some i.r. and Raman data and assignments are available for the sulphamates of Na,[16] Ca,[16] and K.[17] The high values (3 301 and 3 281 cm^{-1}) for the NH_2 stretching modes in the sodium salt indicate that there is no appreciable hydrogen bonding in the crystal. The i.n.s. spectra of $Na[O_3SNH_2]$ are shown in Figures 1(*b*) and 2(*d*), and Table 3 summarises the i.r., Raman, and i.n.s. data (200—900 cm^{-1}). Because the $[O_3SNH_2]^-$ ion has C_s symmetry,[18] all the normal modes are formally both i.r. and Raman active. The only i.n.s. band which does not have an i.r. or Raman counterpart is the most intense feature in the spectrum, at 344 cm^{-1}. We assign

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[11] C. J. Ludman, C. I. Ratcliffe, and T. C. Waddington, *J.C.S. Faraday II*, 1976, 1741.

[12] C. J. Ludman, C. I. Ratcliffe, and T. C. Waddington, *J.C.S. Faraday II*, 1975, 1759.

[13] V. Shomaker and D. P. Stevenson, *J. Amer. Chem. Soc.*, 1941, **63**, 37.

[14] J. Howard, Ph.D. Thesis, University of Durham, 1976.

[15] D. R. Herschbach, 'Tables for the Internal Rotation Problem,' Harvard University; described in *J. Chem. Phys.*, 1957, **27**, 975.

[16] R. S. Katiyar and R. S. Krishnan, *Indian J. Pure Appl. Phys.*, 1968, **6**, 686.

[17] R. S. Katiyar, *Proc. Indian Acad. Sci.*, 1965, **A62**, 169.

[18] G. W. Cox, *Acta Cryst.*, 1967, **23**, 578.

this to the NH_2 torsion. A Raman band at 305 cm^{-1} in the spectrum of $K[O_3SNH_2]$ has been assigned to the NH_2 torsion;[17] however, no reasons were given and an incorrect structure for the ion was assumed, *i.e.* the protons were assumed to be on a plane of symmetry. No band is found in this region of the optical spectra of $Na[O_3SNH_2]$.

TABLE 3

Summary of i.n.s., i.r., and Raman data (cm^{-1}) for $Na[O_3SNH_2]$

I.n.s.	I.r.[a]	Raman[a]	Assignment[a]
		204	Lattice modes
		221	
		244	
		259	
344			Torsion[b]
		374	sym SO_3 rock
405	402	392	asym SO_3 rock
	433		
	480		
491	498	495	sym SO_3 def.
	518		
574	565	564	sym SO_3 def.
	596	580	asym SO_3 def.
	615		H_2O rock
684	685		
	730		H_2O wag
809	800	796	sym S–N str.

[a] From ref. 16. [b] This work.

The hydrogen bonding in $Na[O_3SNH_2]$ is weaker than in $K[O_3SNH_2]$ and from the neutron-diffraction data[18] (Table 2) it is known that the O ··· H distances are greater in the potassium salt than in sulphamic acid. This implies that the external barrier to the NH_2 torsion in $Na[O_3SNH_2]$ should be lower than in $H_3N^+SO_3^-$. However, due to the availability of the lone pair for π bonding, the S–N bond length is shorter {1.66 Å for $K[O_3SNH_2]$}[18] than in $H_3N^+SO_3^-$ (1.764 Å)[9,10] and this will increase the internal barrier. The shorter S–N bond length in $Na[O_3SNH_2]$ is reflected in the relatively high frequency of the S–N stretching vibration (Table 3). If we consider the barrier in $Na[O_3SNH_2]$ to be largely internal then its multiplicity is three, and with the moment of inertia of NH_2 taken as two-thirds that of NH_3 we obtain a barrier height of 12.9 kJ mol^{-1} (1 083 cm^{-1}) using Herschbach's tables.[15] The barrier height in $Na[O_3SNH_2]$ is therefore greater than in $H_3N^+SO_3^-$, although their origins are different.

Sulphamide and its Disilver Salt $Ag_2[O_2SN_2H_2]$.—Nearly complete vibrational assignments for $SO_2(NH_2)_2$ have been given by Herrick and Wagner[19] and Uno *et al.*[20] Their results are in reasonable agreement. The isolated molecule has, at least approximately, C_{2v}, symmetry and so we would expect nine skeletal vibrations ($4A_1 + A_2 + 2B_1 + 2B_2$) all of which are i.r. and Raman active except the A_2 mode which is i.r. inactive. The site symmetry[21] of the molecule is C_2 and in this case all the normal modes are formally *both* i.r. and Raman active.

The i.n.s. spectra of sulphamide are shown in Figures 2(*c*) and 3(*a*) and the available i.n.s., i.r., and Raman data and assignments are summarised in Table 4. The assignment[19,20] of the NH_2 torsion at 420 (i.r.) and 422 (Raman) cm^{-1} appears to be in reasonable agreement with the i.n.s. data (423 cm^{-1}). We would also expect the NH_2 torsion in sulphamide to be of higher frequency than in $Na[O_3SNH_2]$ because of the shorter S–N distance and the consequent increase in double bond character (Table 2; S=N is predicted[21] at 1.54 Å).

TABLE 4

Spectroscopic data (cm^{-1}) and assignments for $SO_2(NH_2)_2$ and $Ag_2[O_2SN_2H_2]$

$SO_2(NH_2)_2$						$Ag_2[O_2SN_2H_2]$		
Gaussians fitted to i.n.s. spectrum								
f.w.h.h.	Peak position	i.n.s.	I.r.[a]	Raman[b]	Assignment	i.n.s.	I.r.[c]	Assignment[c]
				322				
34	328	328						
				335				
34	370	380	358	363	NSN bend		300	
						ca. 350		
44	418	423	420	422	NH_2 torsion		475	
			440[d]		SO_2 rock		487	
			450[d]		SO_2 twist			
			502		SO_2 wag	513	512	
			532	528	SO_2 bend			
		540		537			582	
				546				
			562	574		609	611	
							622	
		746	730		NH_2 wag	798	780	NH torsion[b]
			904		(N–S) sym str.		838	(N–S) sym str.
			931		(N–S) asym str.			
							875	(N–S) asym str.

[a] Ref. 20. [b] This work. [c] Ref. 1. [d] Estimated from data for $SO_2(ND_2)_2$.

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[19] I. W. Herrick and E. L. Wagner, *Spectrochim. Acta*, 1965, **21**, 1569.

[20] T. Uno, K. Machida, and K. Hanai, *Spectrochim. Acta*, 1966, **22**, 2065.

[21] K. N. Trueblood and S. W. Mayer, *Acta Cryst.*, 1956, **9**, 628.

A broad band centred at 540 cm^{-1} in the i.n.s. spectrum of $SO_2(NH_2)_2$ [Figure 3(*a*)] can be seen to be due to several unresolved vibrational bands (Table 4). We are therefore left with a very intense i.n.s. band at 328 cm^{-1} [Figure 3(*a*)]. Because there are no reasonable grounds on which to doubt the majority of the assignments from optical spectra, there are only two possible assignments for this band: (*i*) the i.n.s. bands at 328 and 423 cm^{-1} are the in- and out-of-phase NH_2 torsions; (*ii*) the band at 328 cm^{-1} is the O_2–S–N_2 twisting mode which has been tentatively assigned by Herrick and Wagner [19] at 486 cm^{-1}. (Uno *et al.*[20] did not assign this mode nor did they observe a band at 486 cm^{-1}. We were also unable to detect an i.r. band close to this frequency.)

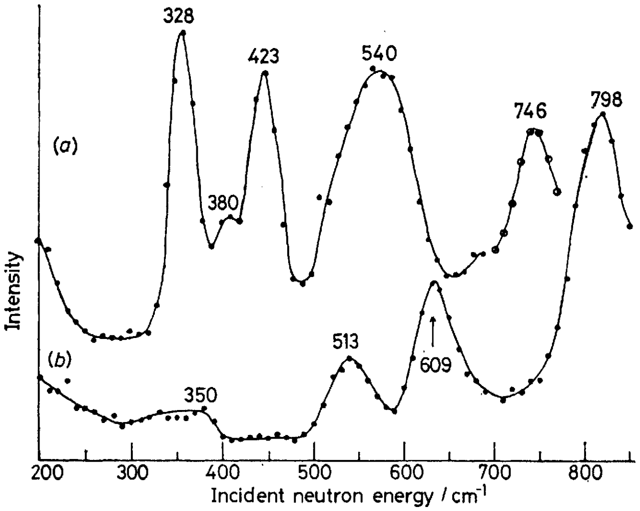
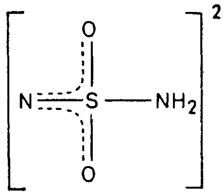


FIGURE 3 Beryllium Filter Detector spectra (*ca.* 90 K) of (*a*) $SO_2(NH_2)_2$ and (*b*) $Ag_2[O_2SN_2H_2]$

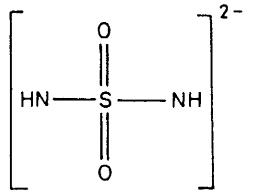
The fundamentals associated with hydrogen-atom motions should be split because of the in- and out-of-phase motions of the two NH_2 groups. Herrick and Wagner [19] observed some indication of splittings, particularly at low temperatures, although the resolution of the spectrum was not good enough to allow separate assignments. If the bands at 328 and 423 cm^{-1} were the in- and out-of-phase torsions then this would indicate very significant interaction between the two groups. The n.m.r. work of Pedersen [22] however indicates that the interaction between the two NH_2 groups is certainly less than that found for urea, and the i.n.s. spectrum of urea does not show any splitting of the NH_2 torsional band.[23] Furthermore, we would expect the splitting of the NH_2 torsional modes in $SO_2(NH_2)_2$ to be less than that for the methyl groups in, for example, Pr^iX [X = Cl (35), Br (16), or I (9 cm^{-1})] [24] because the C–C bond (*ca.* 1.54 Å) [25] is shorter than the S–N bond. The assignment of the band at 328 cm^{-1} to the O_2–S–N_2 twisting mode (A_2) seems to be more reasonable and the intensity in the i.n.s. spectrum is compatible with the large mean-square vibrational amplitude calculated by Copinath and Rao [26] for the O · · · N distance (0.064 88 Å^2) compared with that found for the S–N distance (0.044 00 Å^2). The corresponding mode occurs at 392 cm^{-1} in crystalline $SO_2(OH)_2$.[27] We have also observed two poorly resolved bands at 322 and 335 cm^{-1} in the Raman spectrum of $Na[O_3SNH_2]$. The existence of two modes is possibly due to factor-group splitting. The full width at half-height (f.w.h.h.) of the neutron band at 328 cm^{-1} is 34 cm^{-1}, however, which indicates it is a single mode and not two unresolved bands.

We have fitted three gaussian curves to the 250—470 cm^{-1} region of the i.n.s. spectrum of $SO_2(NH_2)_2$ and the band centres and f.w.h.h. are shown in Table 4. The torsional band is significantly broader than the other two and we have fitted this band with two identical gaussians (f.w.h.h. 34 cm^{-1}) and the band maxima occur at 410 and 426 cm^{-1}. This indicates that the maximum splitting of the in- and out-of-phase torsions is 16 cm^{-1}. Only a single broad i.r. band is found in this region; however, the torsions have different symmetries and probably different i.r. intensities. Because of the lack of uniqueness in curve-fitting procedures this analysis must be regarded as tentative.

If we now consider the disilver salt of sulphamide there are at least two possible molecular structures for the $[O_2SN_2H_2]^{2-}$ ion [(A) and (B)]. In fact, of course, very much more complicated arrangements could exist in the solid state, *e.g.* $3Ag^+[NH_2SO_2N{\rightarrow}Ag{\leftarrow}NSO_2NH_2]^{3-}$ or chains involving $3Ag^+[NHSO_2NH{\rightarrow}Ag{\leftarrow}NHSO_2\text{-}NH{\rightarrow}]^{3-}$, and this might in fact explain the low water solubility of the material. The structures shown will, however, serve to illustrate our main arguments.



(A)



(B)

Very little information concerning the molecular structure can be gained from a knowledge of the number of skeletal modes observed in the i.r. and Raman spectra because in each case there is a total of nine possible modes and even for the most symmetrical conformation, *i.e.* $[SO_2(NH)_2]^{2-}$, eight of these are both i.r. and Raman active and the ninth is Raman active only. It has been concluded from i.r., broadline ^1H n.m.r., and chemical (alkylation) evidence that structure (A) is the correct one.[1] It must be acknowledged, however, that the

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[22] B. Pedersen, *Acta Chem. Scand.*, 1968, **22**, 1813.

[23] R. E. Ghosh, Ph.D. Thesis, University of Oxford, 1972.

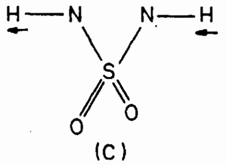
[24] 'Vibrational Spectra and Structure,' vol. 1, ed. J. R. Durig, Marcel Dekker, New York, 1972, p. 115.

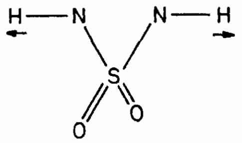
[25] A. F. Wells, 'Structural Inorganic Chemistry,' Clarendon Press, Oxford, 1962.

[26] C. R. Copinath and K. S. Raghavendra Rao, *Current Sci.*, 1975, **44**, 107.

[27] P. A. Giguère and R. Savoi, *Canad. J. Chem.*, 1960, **38**, 2467; *J. Amer. Chem. Soc.*, 1963, **85**, 287.

chemical evidence is *at most* a rather indecisive indication of the structure because of the tendency of sulphur compounds to ionise in solution and because of the rapidity of proton transfer. Also, as far as the i.r. evidence [1] is concerned, the bands at 3 187 and 3 150 cm^{-1}, which were assigned to the in- and out-of-phase stretching modes of the NH_2 group, could equally well be the in- and out-of-phase stretches of two different NH groups, (C) and (D). Corresponding bands have been assigned for the O–H stretches in crystalline $SO_2(OH)_2$,[27] where in fact the difference in frequency between the in- and out-of-phase stretches is very much greater (520 cm^{-1}) than for the disilver salt (37 cm^{-1}) of sulphamide. The NH stretches in the silver salt are of significantly lower frequency than those found [16] for $Na[O_3SNH_2]$ (3 240 and 3 322 cm^{-1}) or $SO_2(NH_2)_2$ [20] (3 320 and 3 210 cm^{-1}). The differences in frequency between the N–H stretching modes are 110 cm^{-1} for $SO_2(NH_2)_2$, 82 cm^{-1} for $Na[O_3SNH_2]$, and 37 cm^{-1} for $Ag_2[O_2SN_2H_2]$. The splitting is therefore smaller in the case of the silver salt than for the two compounds which contain NH_2 groups. There are in fact four stretching modes involving the hydrogen motion in the two NH_2 groups of $SO_2(NH_2)_2$, but as we stated earlier very little splitting, as a result of the in- and out-of-phase motion of the NH_2 groups, was observed. Furthermore, in the 1 500—1 600 cm^{-1} region, where the NH_2 bending mode should occur, there is only a very weak band in the published i.r. spectrum of $Ag_2[O_2SN_2H_2]$.[1]


(C)


(D)

The strongest evidence that there is in fact an NH_2 group present came from a comparison of the ^1H n.m.r. spectra [1] of $Ag_2[O_2SN_2H_2]$ and $Li[NHSO_2NH_2]$. Even in this case, however, the maximum in the n.m.r. spectrum of $Ag_2[O_2SN_2H_2]$ is intermediate between those of $Li[NHSO_2NH_2]$ and the broadening of the N–H band could be due to hydrogen bonding.

The i.n.s. spectra of the disilver salt are shown in Figures 2(*b*) and 3(*b*). They are obviously very different from that of sulphamide or $Na[O_3SNH_2]$. There are no intense bands in the 200—480 cm^{-1} region where the NH_2 torsions were located in the other sulphur compounds. The most intense feature occurs at 798 cm^{-1}. The S–N stretches are of higher frequency than this and in any case from our i.n.s. data for $Na[O_3SNH_2]$ we know that these are relatively weak in the i.n.s. spectra. By comparison with our results for $Na[O_3SNH_2]$ and $SO_2(NH_2)_2$, it appears that the band at 798 cm^{-1} is of far too high frequency to be assigned to an NH_2 torsion. It is more likely to be the NH torsion (alternatively described as a wag) if we accept structure (B). If we consider only the change in moment of inertia on going from NH_2 to NH then the torsional mode should increase in frequency by a factor of $2^{\frac{1}{2}}$ if the force field remains unchanged. Thus from our results for $SO_2(NH_2)_2$ and $Na[O_3SNH_2]$ we predict the NH torsion to occur between 486 and 598 cm^{-1}. This does not agree very well with the observed value for the disilver salt (790 cm^{-1}); however, this calculation does assume that the force field remains unchanged and therefore a change in the S–N distance or the presence of the Ag^+ could easily lead to an increase in the NH torsional frequency.

In practice, of course, we would expect both an in- and out-of-phase NH torsion; however, our data for $SO_2(NH_2)_2$ lead us to expect that these would be unresolved. Figure 2 shows that the low-frequency i.n.s. spectra (0—250 cm^{-1}) of the two compounds known to contain NH_2 groups are very similar, while the spectrum of the silver salt is far more complex.

If our assignment of the molecular structure to type (B) is correct then the skeletal modes should be rather similar to those of $SO_2(NH_2)_2$ and particularly $SO_2(OH)_2$. This in fact leads to some difficulty because for $SO_2(NH_2)_2$ we observed an intense band at 328 cm^{-1}, which we assigned to the O_2–S–N_2 twist [occurring at 392 cm^{-1} in $SO_2(OH)_2$],[27] and this mode should also occur in the spectrum of $[SO_2(NH)_2]^{2-}$. The mode at 798 cm^{-1} is by far the most intense band in the i.n.s. spectrum, however. One fairly obvious possible explanation for this is that, as a result of the introduction of the Ag^+ ions, the amplitude of vibration of the oxygen atoms is greater than the nitrogens (and hence the hydrogen atoms) in this mode. This would then lead to a reduction of its intensity in the i.n.s. spectrum. This argument, of course, implies some degree of covalent bonding of the silver atoms to the nitrogens. From previous work on silver amidosulphates and amidoselenates, it is thought that the amidosulphates are more salt-like than the selenates.[28] This is deduced mainly from the existence of ν(AgN) bands in the selenates and their absence in the sulphur compounds.

Barrier Heights and Effective Force Constants.—For $H_3N^+SO_3^-$ and $Na[O_3SNH_2]$ the barrier multiplicity is known to be three, while for $SO_2(NH_2)_2$ and $Ag_2[O_2SN_2H_2]$ the barrier multiplicity is unknown. For comparison we have assumed a value of 3 and the barrier heights have been calculated (Table 2). We can also calculate effective force constants, $n^2V_0/2$, for the torsions by making the harmonic-oscillator approximation and in this case the barrier multiplicities are not required. These values are also given in Table 2. It can be seen that the barrier heights and effective force constants do increase as the S–N bond length decreases, and that for the disilver salt these values are much greater than for the other compounds.

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[28] R. Paetzold, K. Dostal, and A. Ruzicka, *Z. anorg. Chem.*, 1966, **348**, 1.