Acta Cryst. (1960). **13**, 320

A Neutron Diffraction Study on the Crystal Structure of Sulfamic Acid*

By Ronald L. Sass†

Chemistry Department, Brookhaven National Laboratory, Upton, N.Y., U.S.A.

(*Received* 6 *July* 1959)

A single crystal neutron diffraction investigation of sulfamic acid has been made in which the intensities of 219 reflections in all three prism zones were measured. The structure was refined by Fourier and least-squares techniques. The heavy-atom positions obtained agree quite well with those of Osaki, Tadokoro & Nitta (1955). The hydrogen atom positions found confirm the zwitterion form of the molecule but differ substantially from those postulated from the X-ray work by Osaki *et al.* (1955). The hydrogen bonding system consists of three single N–H · · · O bonds in which the N–H bond makes angles of 7°, 13°, and 14° with the various N · · · O vectors.

Introduction

The crystal structure of sulfamic acid has been studied, using X-ray diffraction techniques, by Kanda & King (1951) and Osaki, Tadokoro & Nitta (1955). Both determinations are in agreement with respect to the general shape and disposition of the molecule in the crystal, but differ by as much as 0·1 Å in some of the atomic positional parameters. The work of Kanda & King is based on a 2*D*-Fourier refinement of the three prism zones, while Nitta and co-workers utilized all reflections available in the copper sphere, refining by successive 3*D*-Fourier syntheses. Both authors state that the molecule exists in the crystal as the zwitterion, $[\overset{+}{N}H_3SO_3^-]$, although no attempt was made to locate the hydrogen atoms directly. The zwitterion structure is also supported by an infra-red study on solid sulfamic acid (Vuagnat & Wagner, 1957). A possible hydrogen bonding system was discussed by Osaki *et al.* (1955), who was led to conclude that the $-NH_3^+$ group must bond to five oxygen atoms, resulting in one single and two bifurcated hydrogen bonds.

The present investigation was initiated in order to locate accurately the hydrogen atoms in the molecule and also to compare the heavy-atom parameters obtained from neutron diffraction with those obtained by the use of X-rays.

Unit cell and space group

The space group of sulfamic acid has been shown to be D_{2h}^{15}–*Pbca*. The unit cell contains eight molecules; all atoms are in eight-fold general positions. The lattice constants are those reported by Osaki *et al.* (1955):

$$a = 8{\cdot}115 \pm 0{\cdot}001,\ b = 8{\cdot}066 \pm 0{\cdot}001,\ c = 9{\cdot}255 \pm 0{\cdot}003\ \text{Å}.$$

Experimental procedure

Crystals of sulfamic acid were grown from an aqueous solution by slow evaporation. For each of the three prism zones, a crystal was cut and ground into a cylinder about 2·5 mm. in diameter and approximately 6 mm. in length, such that the cylinder axis corresponded to the zone axis. The crystals were then dipped several times into liquid nitrogen to reduce extinction and oriented on the neutron spectrometer. Complete neutron diffraction data were collected for the (*hk*0), (*h*0*l*), and (0*kl*) zones out to $\sin\theta/\lambda = 0{\cdot}830$, the neutron wave length being 1·066 Å. Intensities were placed on an absolute scale by calibration with a crystal of potassium bromide. The intensity of the incident monochromatic neutron beam was found to be about $2{\cdot}7 \times 10^5$ neutrons cm.$^{-2}$/sec.$^{-1}$. The intensities of 219 independent reflections were measured. These were corrected for absorption and a set of observed structure factors was obtained in the usual manner. The linear absorption coefficient was found to be 4·55 cm.$^{-1}$.

Treatment of data

Signs were given to the observed (*hk*0) and (*h*0*l*) structure factors based on the parameters of Osaki *et al.* (1955). The resulting Fourier projections showed that the heavy atoms were identified correctly and also indicated the approximate positions of the three hydrogen atoms. The atomic parameters were refined by two more stages of Fourier syntheses. A temperature parameter for each atom was then estimated by trial and error. At this point calculated intensities based on the trial structure were used to make an estimate of the crystal mosaic spread and the secondary extinction effect on the various observed reflections was calculated as outlined by Hamilton (1958). The extinction was rather severe. In the equation $F_o/F_c = \exp(-\alpha F_c^2)$, α was found to be 0·0027. This value leads to a mosaic spread parameter, η, of 11 sec.

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* Research performed under the auspices of the U.S. Atomic Energy Commission.

† Present address: Department of Chemistry, The Rice Institute, Houston, Texas, U.S.A.

Further parameter refinement was carried out by means of a least-squares treatment of the data using an IBM 704 program by Sayre, modified by Vand. This program refines all positional parameters and individual isotropic temperature factors simultaneously. The interatomic cross-terms in the normal equation matrix are not calculated and all reflections are weighted equally. The nuclear scattering amplitudes used were N, 0·94; S, 0·32; O, 0·58; H, $-0·378$; all in cm. $\times 10^{-12}$. The three zones were refined independently. The general procedure was to refine only positional parameters for a number of cycles and then to refine both positional and thermal parameters until convergence was obtained. Approximately ten cycles of refinement were required for each zone. A final set of positional parameters was obtained from the average of each pair of least-squares values obtained from the three zones. In only two cases was the difference between the two estimates greater than the calculated standard deviation of the parameter. These were the y parameters of N and H_1. These atoms, however, lie almost directly above equivalent atoms in the [001] projection. Thus for these two atoms the y parameters from the [100] zone were considered to be the best value. The values of the parameters and their standard deviations are compared with those obtained by X-ray methods in Table 1. Standard deviations were calculated assuming only one zone of data was used to determine the parameters. However, considering the least-squares method used, this value is probably more realistic than the smaller value calculated on the basis of two independent estimates of each parameter. The various heavy-atom parameters agree with those of Osaki *et al.* (1955) to within their quoted standard deviation, but in some cases vary with those of Kanda & King (1951) by more than 0·1 Å.

Table 1. *Sulfamic acid positional parameters*

		Kanda & King	Nitta *et al.*	This work	Standard deviation
S	x	0·170	0·1668	0·1636	0·0022
	y	0·095	0·0940	0·0945	0·0026
	z	0·170	0·1719	0·1715	0·0024
O_1	x	0·055	0·0601	0·0606	0·0011
	y	$-0·045$	$-0·0486$	$-0·0477$	0·0014
	z	0·175	0·1767	0·1776	0·0014
O_2	x	0·305	0·3057	0·3036	0·0012
	y	0·080	0·0750	0·0746	0·0015
	z	0·060	0·0757	0·0752	0·0014
O_3	x	0·200	0·2025	0·2025	0·0012
	y	0·190	0·1758	0·1755	0·0015
	z	0·305	0·3055	0·3065	0·0015
N	x	0·055	0·0436	0·0406	0·0006
	y	0·255	0·2377	0·2411	0·0009
	z	0·095	0·0790	0·0803	0·0009
H_1	x	—	—	0·0947	0·0029
	y	—	—	0·3556	0·0035
	z	—	—	0·0651	0·0032
H_2	x	—	—	$-0·0725$	0·0019
	y	—	—	0·2443	0·0025
	z	—	—	0·1303	0·0027
H_3	x	—	—	0·0126	0·0027
	y	—	—	0·1978	0·0028
	z	—	—	$-0·0202$	0·0024

Table 2. *Temperature parameters from least squares*

Atom	B_{hk0}	B_{h0l}	B_{0kl}	$B_{\text{aver.}}$	σ_B
S	1·91	2·03	1·71	1·88	0·24
O_1	1·90	2·09	1·88	1·96	0·14
O_2	2·07	2·26	2·05	2·13	0·15
O_3	2·20	2·28	1·91	2·13	0·15
N	1·83	1·94	1·43	1·73	0·06
H_1	3·29	3·81	4·70	3·93	0·41
H_2	2·73	3·00	3·62	3·12	0·30
H_3	3·46	3·21	3·77	3·48	0·38

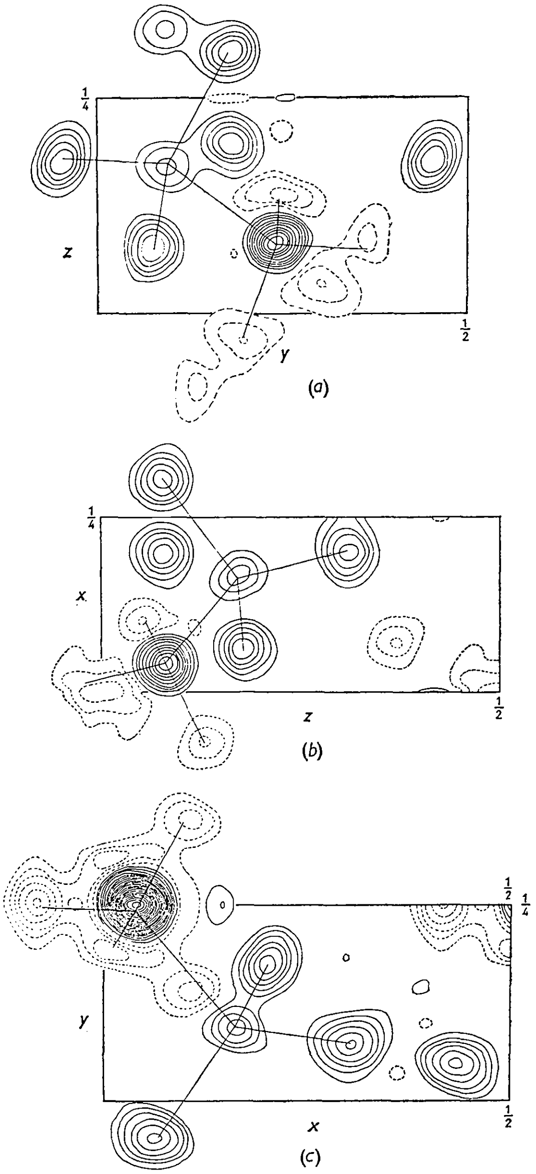

Fig. 1. (*a*) Scattering density function $\varrho(yz)$. (*b*) Scattering density function $\varrho(xz)$. (*c*) Scattering density function $\varrho(xy)$

Table 3. *Observed and calculated structure factors*

*hk*0	F_o	F_c
200	3·92	−4·38
400	4·11	4·78
600	3·91	4·15
800	9·46	−9·86
10,0,0	2·04	−2·93
12,0,0	5·57	−5·27
210	3·95	−4·54
410	2·54	−2·25
610	7·23	−6·99
810	3·86	−3·56
10,1,0	1·32	−1·22
12,1,0	0·93	0·51
020	3·30	3·41
220	0·39	0·18
420	3·06	−3·46
620	2·08	−1·97
820	1·20	−1·18
10,2,0	2·38	1·90
12,2,0	3·69	3·83
230	8·83	9·18
430	7·56	8·14
630	10·31	10·98
830	< 0·44	−0·14
10,3,0	< 0·45	−0·06
12,3,0	< 0·44	0·06
040	3·60	3·08
240	7·41	7·89
440	2·59	2·00
640	2·85	−2·59
840	0·22	−0·59
10,4,0	3·64	−3·28
12,4,0	3·75	−2·68
250	1·01	−1·01
450	8·03	−8·41
650	1·66	1·26
850	3·95	−3·98
10,5,0	1·73	−2·14
060	8·46	−8·61
260	4·87	−4·78
460	1·28	−1·27
660	2·25	−2·24
860	2·25	1·95
10,6,0	2·72	2·76
270	5·02	5·12
470	9·78	9·62
670	4·02	3·59
870	5·11	5·10
10,7,0	0·63	−0·32
080	2·67	−2·59
280	5·70	6·15
480	2·42	2·46
680	2·31	1·72
880	2·90	3·00
10,8,0	3·49	−3·07
290	0·70	−0·73
490	1·93	−2·35
690	3·92	−4·21
890	1·73	−2·08
10,9,0	0·80	−1·69
0,10,0	4·17	−4·41
2,10,0	5·50	−5·23
4,10,0	4·02	−3·66
6,10,0	0·94	0·54
8,10,0	1·73	1·82
2,11,0	0·53	0·51
4,11,0	2·42	3·21
6,11,0	2·68	2·14
8,11,0	2·52	2·06
0,12,0	4·17	4·35
2,12,0	0·92	−0·46
4,12,0	1·14	1·83
6,12,0	2·53	2·27
2,13,0	4·15	−3·37
4,13,0	1·06	−1·11
*h*0*l*		
002	5·76	−5·63
004	4·96	−5·29
006	2·59	−2·86
008	14·19	−14·19
0,0,10	4·66	4·33
0,0,12	7·19	7·39
0,0,14	0·67	0·63
102	5·47	−5·47
104	5·32	−4·47
106	2·78	2·26
108	1·17	0·32
1,0,10	3·55	3·57
1,0,12	2·47	1·81
1,0,14	2·68	−2·17
202	0·27	−0·46
204	2·69	−2·67
206	4·38	−3·92
208	1·21	−1·38
2,0,10	0·52	−0·15
2,0,12	3·30	3·16
2,0,14	0·45	0·57
302	8·07	−8·13
304	5·15	5·92
306	1·45	−0·13
308	0·45	0·33
3,0,10	2·68	2·77
3,0,12	1·45	−2·14
3,0,14	0·45	−0·10
402	1·22	0·87
404	2·72	−2·93
406	5·13	−5·10
408	3·79	−3·72
4,0,10	0·45	0·38
4,0,12	0·92	0·88
502	7·07	−7·37
504	3·48	−3·31
506	2·03	−0·50
508	1·26	1·76
5,0,10	3·12	2·94
5,0,12	0·89	0·27
602	0·53	0·11
604	3·48	−3·10
606	2·17	−2·04
608	1·37	−1·13
6,0,10	1·14	−0·88
6,0,12	< 0·39	−0·05
702	8·14	−8·19
704	5·42	−6·34
706	2·78	−2·44
708	1·53	1·25
7,0,10	3·69	5·03
7,0,12	0·46	1·16
802	< 0·45	−0·31
804	0·25	0·10
806	0·75	−0·20
808	6·60	6·08
8,0,10	1·68	−1·51
8,0,12	2·48	−2·70
902	1·49	−1·38
904	0·73	−0·28
906	1·90	−2·62
908	1·22	0·73
9,0,10	1·22	0·94
10,0,2	1·54	−1·64
10,0,4	1·34	0·62
10,0,6	< 0·45	0·01
10,0,8	0·68	0·88
10,0,10	0·41	0·58
11,0,2	1·57	1·70
11,0,4	4·82	−5·79
11,0,6	0·45	0·45
11,0,8	1·78	1·54
12,0,2	2·08	−1·77
12 0,4	0·83	0·88
12,0,6	3·08	2·50
13,0,2	0·86	0·84
13,0,4	0·44	0·88
0*kl*		
021	5·58	−6·48
041	5·17	5·23
061	2·49	1·91
081	3·44	3·13
0,10,1	2·31	2·63
0,12,1	0·30	−0·93
022	0·79	−0·52
042	3·97	4·18
062	6·96	−7·18
082	4·71	4·83
0,10,2	0·74	−1·68
0,12,2	2·20	1·96
023	5·03	−5·68
043	2·68	−3·36
063	2·24	−2·29
083	2·80	3·39
0,10,3	1·85	−1·38
0,12,3	4·33	3·53
024	< 0·33	0·03
044	1·49	−1·47
064	3·47	3·32
084	0·89	0·41
0,10,4	1·39	0·45
0,12,4	1·55	−0·79
025	3·04	−4·10
045	1·93	−1·49
065	4·32	−4·35
085	< 0·36	0·06
0,10,5	0·24	−0·80
0,12,5	3·43	2·72
026	7·46	7·85
046	7·03	−7·31
066	6·91	7·23
086	4·21	−4·09
0,10,6	1·25	2·05
0 12,6	3·54	−3·30
027	2·42	−1·63
047	5·40	5·05
067	2·30	2·59
087	1·33	1·15
0,10,7	2·73	2·37
0,12 7	2·49	−2·72
028	3·05	2·39
048	3·28	−3·47
068	4·49	4·33
088	2·34	2·05
0,10,8	2·28	2·18
029	4·40	4·46
049	1·77	−2·29
069	0·34	0·60
089	2·03	−2·18
0,10,9	0·76	−0·93
0,2,10	3·63	−3·51
0,4,10	2·16	2·05
0,6,10	< 0·45	0·02
0,8,10	< 0·24	0·10
0,10,10	1·44	−1·68
0,2,11	0·38	1·02
0,4,11	3·68	3·21
0,6,11	1·26	−0·84
0,8,11	3·23	−2·84
0,2,12	1·88	−1·32
0,4,12	3·68	3·85
0,6,12	7·19	−6·76
0,8,12	1·98	2·00
0,2,13	0·29	−0·01
0,4,13	0·70	1·35

The temperature factors obtained from the three sets of least squares are given in Table 2. There is probably no significant difference in the B values of the heavy atoms. The apparent differences in the B values of a particular hydrogen atom could very easily be due to the different degrees of hydrogen–nitrogen overlap in the three projections. It is quite apparent from the Fourier diagrams shown in Figs. 1(*a*), (*b*), (*c*) that diffraction effects from the nitrogen atom, a very efficient neutron scatterer, considerably affect the shape of the nearest hydrogen peaks. Since correlation coefficients among the various atomic parameters were not obtained in the least-squares calculation it seems unwise to attempt any detailed discussion of the different thermal vibration parameters.

The values of observed structure factors and those calculated from the final least-squares parameters are shown in Table 3. The reliability indices of the three zones of data, neglecting unobserved reflections, are $R_{hk0} = 0{\cdot}09$, $R_{h0l} = 0{\cdot}13$, $R_{0kl} = 0{\cdot}11$.

Discussion

The sulfamic acid molecule

All three hydrogen atoms were found to be chemically bonded to the nitrogen atom, thus confirming the zwitterion configuration of sulfamic acid. The heavy atom positions result in a molecular symmetry of C_{3v}. The hydrogen atoms are staggered with respect to the sulfur bonded oxygen atoms, but distort somewhat from trigonal symmetry.

Table 4. *Sulfamic acid intramolecular bond distances and angles*

Bond	Distance (Å)	Standard deviation (Å)	Bonds	Angle (°)
S–N	1·764	0·020	N–S–O_1	103·2
			N–S–O_2	102·9
S–O_1	1·421	0·021	N–S–O_3	103·5
S–O_2	1·452	0·022	O_1–S–O_2	113·4
			O_2–S–O_3	114·7
S–O_3	1·445	0·022	O_1–S–O_3	117·3
N–H_1	1·032	0·026	S–N–H_1	115·1
			S–N–H_2	107·9
N–H_2	1·028	0·020	S–N–H_3	111·0
N–H_3	1·013	0·022	H_1–N–H_2	114·7
			H_2–N–H_3	103·0
			H_1–N–H_3	105·2

Interatomic distances and bond angles calculated from the parameters listed in Table 2 are given in Table 4. The comparable values agree quite well with those of Osaki *et al.* (1955). The average S–O distance of 1·439 Å agrees with the nearly constant value of 1·44 Å reported in various oxides, oxyacids, and acid salts of sulfur (Jeffrey & Stadler, 1951). The S–N distance of 1·76 Å is not significantly longer than the value of 1·75 Å given by Osaki *et al.* (1955). In nearly every reported structure determination of molecules containing an S–N bond, the length of this bond has been considerably shorter than the predicted single-bond value of 1·74 Å (Pauling, 1940; Schomaker & Stevenson, 1941). In all of these molecules the nitrogen atom has available p-electrons which can π-bond with sulfur d-orbitals, giving the bond considerable double bond character. However, since sulfamic acid exists in the crystalline state as the zwitterion, the nitrogen atom has no electrons available for π-bonding and the S–N bond is essentially a single bond. The only other reported S–N chemical bond of comparable length, namely 1·791 Å reported in the dinitrososulfite ion (Jeffrey & Stadler, 1951), can also be interpreted to be a single σ-bond. The environment of the sulfur atom in sulfamic acid and the dinitrososulfite ion is essentially the same. It is interesting to note, however, that whereas the nitrogen atom in sulfamic acid is bonding to four other atoms essentially tetrahedrally, the nitrogen atom in the dinitrososulfite ion is bonded to only three atoms in a nearly sp^2 type configuration, the fourth orbital being used to give considerably double bond character to both the N–O and N–N chemical bonds.

Molecular environment

A point of interest in this investigation was to determine if sulfamic acid is present in the crystalline state as the zwitterion and if so if the $-NH_3$ group utilizes all of the available neighboring oxygen atoms in a system of hydrogen bonds. Fig. 2 views a sulfamic acid molecule projected down the sulfur–nitrogen bond axis. The nearest oxygen neighbors are also indicated. The various observed intra-molecular contact distances and important angles are listed in Table 5. There are six oxygen atoms closer than three Ångströms to the nitrogen atom. Of these, five are arranged in space such that the S–N $\cdots$ O angle is favorable for hydrogen bonding, namely from about 100° to 112°. As pointed out in the introduction, Osaki *et al.* (1955) suggested that the sulfamic acid molecule is in an eclipsed configuration. If the molecule does assume this form in the crystal, the hydrogen bonding system would contain one single and two bifurcated hydrogen bonds. A staggered configuration of the molecule would also result in a bonding system which would contain a bifurcated hydrogen bond. Thus if the molecule exhibits either of these two expected configurations, one should observe such a bifurcated bond. The structure is actually a distorted staggered configuration. The distortion is sufficiently great such that all three hydrogen atoms form essentially single hydrogen bonds, indicated by dashed lines in Fig. 2. These hydrogen bonds are not strictly linear. The N–H bond axes are bent with respect to the nitrogen–oxygen vector by angles of 7°, 13°, and 14°, respectively, for the N–$H_1 \cdots O_2(7)$, N–$H_2 \cdots O_3(3)$, and N–$H_3 \cdots O_1(2)$ contacts.

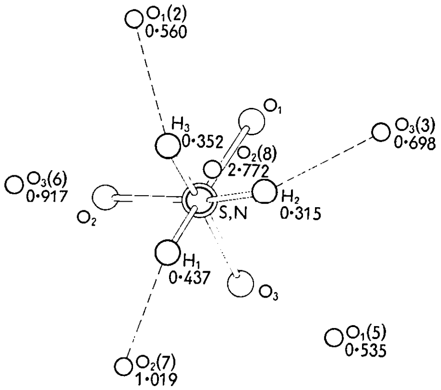

Fig. 2. Sulfamic acid molecule projected down the S–N bond axis. The nearest neighbors are shown together with their distance in Ångströms above the nitrogen atom.

It is interesting to note that, although intramolecular bonds in which a bonded hydrogen atom is electrostatically attracted to two other atoms have

Table 5. *Sulfamic acid hydrogen bonding system*

Atoms	Distance	Atoms	Angle
$N-O_1(2)$	2·967 Å	$S-N\cdots O_1(2)$	100·9°
$N-O_1(5)$	2·931	$S-N\cdots O_1(5)$	100·5
$N-O_2(7)$	2·973	$S-N\cdots O_2(7)$	111·9
$N-O_2(8)$	2·824	$S-N\cdots O_2(8)$	169·2
$N-O_3(3)$	2·984	$S-N\cdots O_3(3)$	103·5
$N-O_3(6)$	2·932	$S-N\cdots O_3(6)$	108·3
$H_1-O_2(7)$	1·953	$N-H_1\cdots O_2(7)$	169·3
$H_2-O_3(3)$	1·997	$N-H_2\cdots O_3(3)$	160·2
$H_3-O_1(2)$	1·985	$N-H_3\cdots O_1(2)$	159·0
$H_1-O_3(6)$	2·560	$N-H_1\cdots O_3(6)$	100·6
$H_2-O_1(5)$	2·445	$N-H_2\cdots O_1(5)$	108·0
$H_3-O_3(6)$	2·447	$N-H_3\cdots O_3(6)$	109·5

been predicted, no actual example has ever been proven to exist. In the first X-ray structure determination of glycine, Albrecht & Corey (1939) postulated a bifurcated hydrogen bond from the $-NH_3^+$ group. In a very extensive refinement of new X-ray data from glycine (Marsh, 1958), the hydrogen atoms were directly located and the hydrogen bonding scheme of Albrecht & Corey was essentially substantiated. One of the hydrogen atoms on the NH_3^+ group was located between two neighboring oxygen atoms at distances of 1·29 and 1·44 Å, thus forming two rather weak hydrogen bonds. In a recent neutron diffraction investigation of glycine, Burns & Levy (1958) placed this hydrogen atom at a distance of 2·10 and 2·44 Å respectively from these neighboring oxygen atoms, thus indicating one strong and one substantially weaker hydrogen bond. Other structures reported to contain bifurcated hydrogen bonds are also disputed. Iodic acid was claimed to contain such a bond (Rogers & Helmholz, 1941). An alternate interpretation consistent with the X-ray data was given by Wells (1949) in which no bifurcated bond was necessary to explain the molecular packing. In a recent structure determination of nitramide (Beevers & Trotman-Dickenson, 1957), assuming the molecule contains an H–N–H bond angle of 120°, both hydrogen atoms are equivalent and are located between neighboring oxygen atoms at a distance of 2·1 and 2·4 Å. This assumption would then lead to a bifurcated hydrogen bond, the 2·4 Å bond being again rather weak. In this investigation of sulfamic acid it was found that the structure expected in an isolated $O_3^-S-NH_3^+$ molecule, namely the staggered configuration, is actually distorted somewhat to prevent the formation of such a bond. This fact indicates that a single hydrogen bond is stable with respect to a bifurcated hydrogen bond by at least the amount of energy required to cause this distortion. This energy requirement also indicates that a bifurcated hydrogen bond would probably be observed very rarely and only under quite stringent packing conditions.

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