TABLE VI

INTERMOLECULAR DISTANCES[a]

x_i–x_j	Molecule	Distance, A
K(1)–O(1)	B(000)	2.690
K(1)–O(2)	B($\bar{1}$00)	3.230
K(1)–O(2)	E(100)	2.963
K(1)–O(3)	E(110)	2.961
K(1)–O(3)	B($\bar{1}$00)	3.130
K(1)–O(3)	A(000)	3.208
K(2)–O(1)	A(000)	2.027
K(2)–O(1)	D(011)	3.180
K(2)–O(2)	A(000)	2.739
K(2)–O(2)	B($\bar{1}$01)	2.767
K(2)–O(3)	C(001)	2.804
K(2)–O(3)	E(111)	2.719
O(4)–O(4)	D(001)	3.423
O(4)–O(6)	B($\bar{1}$00)	3.442
O(5)–O(6)	D(101)	3.499
O(5)–O(6)	E(111)	3.365
O(6)–O(6)	C(0$\bar{1}$0)	3.189

[a] x_1 is in the molecule A and x_j in the molecule specified after x_j. The molecules are located as follows: A: x, y, z; B: $^1/_2 + x, ^1/_2 - y, ^1/_2 - z$; C: $x, ^1/_2 - y, z$; D: $\bar{x}, \bar{y}, \bar{z}$; E: $-^1/_2 - x, -^1/_2 + y, -^1/_2 + z$.

atoms form a distorted octahedron around the potassium ion K(2). The coordination polyhedron is completed by three other longer contacts, one at 2.927 A and two at 3.180 A. However, in the case of K(1) there is only one oxygen atom less than 2.9 A away from the ion, at 2.690 A. The next nearest oxygen atoms around K(1) are two at 2.961 A and two at 2.963 A. The coordination is completed by five additional oxygen atoms, two at 3.130 A, two at 3.208 A, and one at 3.20 A. The complexity of the coordination polyhedra around the two ions is similar to that found in other potassium salts where the K···O distances range from 2.62 to 3.20 A.

The coordination of oxygen atoms around the two cations cannot be explained on the basis of anion–anion contacts. A survey of the O···O intermolecular distances tabulated in Table VI reveals only one distance (3.189 A) which could represent van der Waals contact. In all other cases the O···O distances are too long. Therefore, the crystal packing must be determined mainly by the cation–anion contacts.

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The Crystal Structure of Hydroxylamine-O-sulfonic Acid

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The crystal structure of hydroxylamine-O-sulfonic acid (H_2NOSO_3H) was determined from Weissenberg and precession single-crystal X-ray diffraction patterns. The diffraction patterns indicated that the crystals were orthorhombic, but satisfactory agreement with the visually observed intensity data was obtained only by assuming that the crystals were monoclinic and twinned on (001) or (100). This assumption led to a structure in which the oxygen atoms are located in a distorted tetrahedral fashion about the sulfur atom at distances of 1.42, 1.46, 1.47, and 1.68 A (average error = ±0.03 A); the oxygen atom involved in the long S–O bond is also bonded to a nitrogen atom at 1.48 A. The structure is compatible with the zwitterion form of the acid found from previous nmr studies of Richards and Yorke.[1] The crystal structure results should be considered corroborative rather than determinative of the zwitterion form.

Introduction

The determination of the structure of hydroxylamine-O-sulfonic acid, H_2NOSO_3H, was begun some 10 years ago at this laboratory in conjunction with a study of some hydroxylaminesulfonic acids and their salts.[2,3] The compounds are generally unstable, but H_2NOSO_3H was stable enough to form crystals. When it became apparent that the structure of H_2NOSO_3H could not be solved without assuming crystal twinning, the computations proved too involved for more than a rough determination of the structure in 1956. Recently there has been some interest in related structures.[4-6] On this basis it seemed worthwhile to undertake a three-dimensional refinement of H_2NOSO_3H using the original intensity data and employing the more elegant computational methods offered by modern computers.

Experimental Details

Hydroxylamine-O-sulfonic acid was prepared by the method of Sommer, Schulz, and Nassau.[7] The powdery product was recrystallized from water under reduced pressure at 0°. Single crystals were sealed in glass capillaries and examined by X-ray diffraction. The crystal constants are $a = 6.395 \pm 0.017$ A, $b = 10.707 \pm 0.010$ A, $c = 5.050 \pm 0.007$ A, and $\beta = 90.0 \pm 0.2°$. The X-ray density for four molecules per unit cell is 2.17 g/cm^3 which is in excellent agreement with the experimental value of 2.17 g/cm.[3]

Intensity data were taken including $0kl$ through $3kl$ and $hk0$ Weissenberg films and $h0l$ precession films. The relative intensities were estimated visually using a calibrated strip. Lorentz

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(1) R. E. Richards and R. W. Yorke, *J. Chem. Soc.*, 2821 (1959).
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(3) R. F. Belt and N. C. Baenziger, *J. Am. Chem. Soc.*, **79**, 316 (1957).
(4) D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).
(5) D. W. J. Cruickshank and D. W. Jones, *Acta Cryst.*, **16**, 877 (1963).
(6) C. Pascard-Billy, *ibid.*, **18**, 829 (1965).

(7) F. Sommer, O. Schulz and M. Nassau, *Z. Anorg. Allgem. Chem.*, **147**, 142 (1925).

Table I

Atom Parameters

	Two-dimensional refinement (1956)			Three-dimensional refinement (1965)			
Atom	x	y	z	x	y	z	B, A^2
S	0.766	0.091	0.700	0.769 (2)[a]	0.0892 (8)	0.693 (2)	0.95 (19)
O(1)	0.710	0.980	0.800	0.700 (4)	0.967 (2)	0.796 (5)	0.6 (4)
O(2)	0.939	0.143	0.810	0.951 (3)	0.138 (2)	0.816 (5)	0.6 (4)
O(3)	0.581	0.195	0.710	0.596 (4)	0.191 (2)	0.816 (6)	1.0 (4)
O(4)	0.766	0.096	0.400	0.749 (5)	0.102 (2)	0.406 (6)	1.2 (5)
N	0.383	0.163	0.800	0.378 (5)	0.165 (2)	0.728 (7)	1.1 (6)
H(1)[b]	. . .	. . .	. . .	0.324	0.090	0.858	1.0
H(2)[b]	. . .	. . .	. . .	0.376	0.118	0.544	1.0
H(3)[b]	. . .	. . .	. . .	0.270	0.236	0.764	1.0

[a] Standard deviations in last significant digit are given in parentheses. [b] Estimated position.

Table II

Comparison of Bond Lengths and Angles with Other Structures[a]

Compound	S–O, A	O–S–O, deg	S–OR, A	N–O, A	NH··O, A	Ref
H_3NOSO_3	1.47 (3)	115 (5)	1.68 (3)	1.48 (4)	2.83 (2)	This work
	1.42 (2)	114 (1)			3.04 (2)	This work
	1.46 (3)	118 (2)			2.77 (3)	This work
$C_2H_5OSO_3K$	1.464 (4)	113	1.603 (7)	. . .	. . .	*c*, *d*
$K_2(O(SO_3)_2)$	1.437 (4)	114	1.645 (5)	. . .	. . .	*e*
NH_3SO_3	1.439 (10)[b]	115	. . .	. . .	. . .	*f*
$K(NH_2SO_3)$	1.42	111	. . .	. . .	. . .	*g*
	1.45 (3)	112	. . .	. . .	. . .	*g*
$NH_4SO_3 \cdot N_2O_2$	1.464 (12)	114	. . .	. . .	. . .	*g*
	1.434 (12)	112	. . .	. . .	. . .	*g*
$K(OHNHSO_3)$	1.463 (9)	112 (1)	. . .	1.51 (2)	2.86 (3)	*h*
	1.464 (11)	112 (1)	. . .	. . .	2.90 (3)	*h*
	1.478 (13)	115 (1)	. . .	. . .	. . .	*h*
$K_2(NH(SO_3)_2)$	1.453 (5)[l]	112	. . .	. . .	. . .	*i*
		113				*i*
		114				*i*
H_2SO_4	1.426 (15)	119 (1)	1.535 (15)	. . .	. . .	*j*
NH_2OH	. . .	. . .	. . .	1.470 (3)	. . .	*k*
NH_3OHCl	. . .	. . .	. . .	1.450 (4)	. . .	*k*
NH··O or N··HO	. . .	. . .	. . .	. . .	2.73–3.22 Av 2.88	*k*

[a] Standard deviations in last significant digit are given in parentheses. [b] Mean value. [c] J. A. J. Jarvis, *Acta Cryst.*, **6**, 327 (1953). [d] M. R. Truter, *ibid.*, **11**, 680 (1958). [e] H. Lynton and M. R. Truter, *J. Chem. Soc.*, 5112 (1960). [f] R. L. Sass, *Acta Cryst.*, **13**, 320 (1960). [g] G. A. Jeffrey and H. P. Stadler, *J. Chem. Soc.*, 1467 (1951). [h] R. F. Belt and N. C. Baenziger, *J. Am. Chem. Soc.*, **79**, 316 (1957). [i] D. W. J. Cruickshank and D. W. Jones, *Acta Cryst.*, **16**, 877 (1963). [j] C. Pascard-Billy, *ibid.*, **18**, 827 (1965). [k] "International Tables for Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, pp 270–273. [l] Mean, corrected for rotation.

and polarization corrections were applied but no absorption correction was made. The diffraction symmetry appeared to be orthorhombic, showing three mutually pendicular mirror planes. The systematic absences were for $h0l$ when $h + l$ is odd and $0k0$ when k is odd.

Structure Determination

Patterson functions were calculated for projections on (001), (100), and (010). Sulfur positions were located immediately. Because of the orthorhombic diffraction symmetry, the structure was first sought in the orthorhombic space groups Pmnm and $Pmn2_1$, where the systematic absences are $(h0l)$ for $h + l$ odd, and $P2_12_12_1$, where the absences are $(h00)$ for h odd, $(0k0)$ for k odd, and $(00l)$ for l odd. No satisfactory structure could be found with Pmnm and $Pmn2_1$, but a structure which gave R values of 0.18 for $(hk0)$ data and 0.21 for $(0kl)$ data was found for $P2_12_12_1$. The $(h0l)$ data could not be fit, however.

The absences are characteristic of only $P2_1/n$. The apparent orthorhombic symmetry could result if the single crystal used were twinned on (001) or (100) such that (hkl) and $(hk\bar{l})$ reflections from twins of equal volumes were superimposed. (The assumption of equal volumes of twins is demanded by the mirror planes in intensity data which led to the original choice of an orthorhombic cell. There was no evidence on the diffraction films of the existence of disorder in the crystals.) The crystal used in obtaining the intensity data had decomposed long before the twinning possibility arose, but similar crystals of hydroxylamine-O-sulfonic acid examined with a polarizing microscope indicated that multiple crystals were not uncommon.[8] Twinning of structures with monoclinic symmetry to produce orthorhombic diffraction patterns has been reported previously.[9] Furthermore, the plane groups

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(8) Sommer, Schulz, and Nassau[7] state that the crystals of hydroxylamine-O-sulfonic acid appear to be striated or striplike under crossed Nicols, indicating that multiple twinning occurred in their preparation also. Unfortunately, their statement was discovered only after we had completed the X-ray studies and had been forced to make the assumption of twinning to explain the X-ray data.

(9) J. D. Dunitz, *Acta Cryst.*, **17**, 1299 (1964).

for projection of $P2_12_12_1$ on (001) and (100) are identical with similar projections in $P2_1/n$.

On the assumption that the diffraction data were from a twinned crystal, the atom parameters for $P2_1/n$ as obtained from the two-dimensional Fourier refinement of the two groups of data (*hk*0) ($R = 0.18$) and (0*kl*) ($R = 0.21$) are listed in Table I. Further refinement at the time was not feasible. The configuration seemed reasonable: the central sulfur atom was surrounded by four oxygen atoms in a roughly tetrahedral arrangement with O(3) also bonded to nitrogen. The S–O(1) and S–O(2) bonds were shorte than the other sulfur–oxygen bonds and also shorter than sulfur–oxygen bonds in other sulfonates (Table II). The N–O(3) bond was shorter than the corresponding bond in hydroxylamine. Two nitrogen–hydrogen–oxygen hydrogen bonds were proposed based on N–O distances, but the probable location of the third hydrogen was uncertain.

Refinement of the Structure.—Since only two zones of data were used in the original work, it was expected that use of three-dimensional data would clarify some features of the structure. A full-matrix least-squares program was employed to refine 328 independent reflections on an IBM 7044 computer. (See Table III.) The quantity minimized was $\Sigma w(F_o^2 - F_c^2)^2$ where, because of the twinning, $F_c^2 = F_{hkl}^2 + F_{hk\bar{l}}^2$. The weight, *w*, was proportional to F_o^2 for smaller intensities and proportional to $1/F_o^2$ for larger intensities. Only isotropic temperature factors were used because too few data were available to refine reliably six atoms with nine parameters each.

Because F^2 was used exclusively in these calculations, the conventional discrepancy factor, $R = \Sigma||F_o| - |F_c||/\Sigma F_o$, was never calculated but rather a discrepancy factor based on F^2 was found: $R_2 = \Sigma w|F_o^2 - F_c^2|/\Sigma wF_o^2$. It is expected that R_2 will be approximately twice as large as R. At the beginning of the refinement R_2 was 0.36. After several cycles of least squares $R_2 = 0.22$, and at this time equivalent reflections were averaged and interatomic distances calculated. When it was found that three of the sulfur–oxygen bond distances were approximately equal, a zwitterion structure was proposed and three hydrogen atoms were placed in nearly tetrahedral positions about nitrogen. This had little effect on the general agreement of calculated and observed intensities. A final R_2 of 0.20 was obtained; the conventional R value for (0*kl*) is 0.14 and that for (*hk*0) is 0.11.

Discussion of the Structure

The final atom parameters and the assumed hydrogen positions are shown in Table I. The assumption of a twinned crystal leads to a satisfactory structure for hydroxylamine-O-sulfonic acid. The zwitterion structure seems reasonable and the bond lengths and angles (Table IV) compare well with those found in related structures. Three sulfur–oxygen bonds are not significantly different from each other in length and fall within the range observed for SO_3 groups in other molecules (Table II). It appears that the SO_3 group frequently exhibits an O–S–O bond angle greater than the ideal tetrahedral value, and the present structure is consistent in this respect. Actually, the S, O(1), O(2), and O(4) atoms are distorted from the tetrahedral

TABLE III

h	k	l	F^2 obs.	F^2 calc.
0	0	2	17752	16480
0	0	4	281	85
0	0	6	70	306
0	1	1	800	654
0	1	2	756	640
0	1	3	149	9
0	1	4	141	63
0	1	5	88*	0
0	1	6	44*	113
0	2	0	1090	838
0	2	1	11873	13528
0	2	2	97	68
0	2	3	3287	3081
0	2	4	141	1
0	2	5	88*	128
0	2	6	44*	4
0	3	1	26*	2
0	3	2	299	359
0	3	3	141	80
0	3	4	2663	2580
0	3	5	79*	2
0	3	6	387	791
0	4	0	7373	7795
0	4	1	2109	1695
0	4	2	562	550
0	4	3	114	9
0	4	4	88*	26
0	4	5	79*	38
0	4	6	26*	33
0	5	1	2671	2197
0	5	2	1353	1259
0	5	3	2531	2307
0	5	4	677	999
0	5	5	457	659
0	6	0	264	296
0	6	1	765	659
0	6	2	70*	25
0	6	3	404	514
0	6	4	88*	87
0	6	5	62*	2
0	7	1	272	259
0	7	2	79*	0
0	7	3	712	769
0	7	4	598	398
0	7	5	193	364
0	8	0	228	105
0	8	1	712	753
0	8	2	264	216
0	8	3	571	552
0	8	4	70*	36
0	8	5	26*	58
0	9	1	114	194
0	9	2	88*	89
0	9	3	141	107
0	9	4	316	396
0	10	0	554	702
2	3	2	1541	1097
2	4	2	110	103
2	5	2	118*	49
2	6	2	1180	800
2	7	2	157*	20
2	8	2	165*	338
2	9	2	165*	182
2	10	2	142*	238
2	11	2	111*	56
2	12	2	102	216
2	1	3	1447	1148
2	2	3	684	606
2	3	3	1447	1173
2	4	3	881	563
2	5	3	1581	1429
2	6	3	479	332
2	7	3	283	241
2	8	3	865	1120
2	9	3	134*	145
2	10	3	228	434
2	11	3	409	444
2	1	4	1738	1609
2	2	4	165*	9
2	3	4	2241	2549
2	4	4	165*	73
2	5	4	165*	69
2	6	4	157*	12
2	7	4	275	345
2	8	4	142	256
2	9	4	385	222
2	1	5	283	209
2	2	5	142*	76
2	3	5	236	311
2	4	5	126*	161
2	5	5	236	488
2	6	5	87*	6
2	7	5	102	132
2	8	5	24*	141
2	1	6	181	350
2	2	6	55*	57
2	3	6	228	789
3	0	1	846	694
3	0	3	2156	2466
3	1	0	607	811
3	2	0	1677	1520
3	3	0	192	159
3	4	0	3354	2726
3	5	0	703	608
3	6	0	1150	961
3	7	0	639	507
3	8	0	2236	2374
3	9	0	240	137
3	10	0	559	762
0	10	1	1028	1262
0	10	2	88*	30
0	10	3	220	317
0	10	4	35*	55
0	11	1	132	362
0	11	2	70*	69
0	11	3	448	970
0	12	0	439	326
0	12	1	62*	0
0	12	2	228	167
1	0	1	9464	7135
1	0	3	2969	2549
1	0	5	174	263
1	1	0	109	73
1	2	0	7571	8046
1	3	0	174	102
1	4	0	1273	1235
1	5	0	2448	2021
1	6	0	1577	1571
1	7	0	131	239
1	8	0	4558	5280
1	9	0	131	158
1	10	0	642	674
1	11	0	98	177
1	12	0	207	278
1	13	0	44	89
1	1	1	500	651
1	2	1	2883	2429
1	3	1	5286	4029
1	4	1	163	192
1	5	1	402	326
1	6	1	751	712
1	7	1	936	940
1	8	1	326	297
1	9	1	315	587
1	10	1	348	406
1	11	1	98*	35
1	12	1	131	61
1	13	1	109	242
1	1	2	272	202
1	2	2	457	458
1	3	2	315	167
1	4	2	141	140
1	5	2	1697	1309
1	6	2	577	490
1	7	2	370	384
1	8	2	1218	1697
1	9	2	228	108
1	10	2	272	478
1	11	2	131	288
1	1	3	152	134
1	2	3	990	849
1	3	3	2958	2710
1	4	3	707	586
1	5	3	925	1012
1	6	3	870	835
3	11	0	208	285
3	12	0	112	128
3	1	1	1262	1833
3	2	1	1725	1773
3	3	1	2252	1650
3	4	1	176	16
3	5	1	1214	1257
3	6	1	1198	839
3	7	1	351	172
3	8	1	303*	103
3	9	1	447	188
3	10	1	271*	55
3	11	1	208*	108
3	12	1	607	611
3	1	2	607	557
3	2	2	272	267
3	3	2	814	761
3	4	2	623	375
3	5	2	719	370
3	6	2	383	248
3	7	2	415	329
3	8	2	623	589
3	9	2	351	105
3	10	2	399	510
3	11	2	351	295
3	12	2	48*	3
3	1	3	2140	2205
3	2	3	463	484
3	3	3	1884	1512
3	4	3	527	380
3	5	3	415	257
3	6	3	415	358
3	7	3	415	47
3	8	3	272*	3
3	9	3	399	338
3	10	3	144*	125
3	11	3	64*	49
3	1	4	1230	1507
3	2	4	303*	177
3	3	4	878	1057
3	4	4	303*	67
3	5	4	1054	849
3	6	4	256*	175
3	7	4	224*	252
3	8	4	160*	225
3	9	4	96*	105
3	1	5	240*	664
3	2	5	240*	176
3	3	5	367	449
3	4	5	192*	12
3	5	5	160*	7
3	6	5	112*	210
3	7	5	64*	6
1	7	3	631	535
1	8	3	207	287
1	9	3	261	308
1	10	3	250	575
1	1	4	674	373
1	2	4	141	226
1	3	4	109	38
1	4	4	109*	8
1	5	4	2545	2642
1	6	4	109*	167
1	7	4	664	690
1	8	4	185	287
1	9	4	326	366
1	1	5	109*	27
1	2	5	109*	13
1	3	5	424	749
1	4	5	87*	208
1	5	5	348	652
1	6	5	65*	29
1	7	5	87	53
1	8	5	33*	117
1	1	6	109	88
1	2	6	44*	175
1	3	6	33*	31
1	4	6	33*	0
2	0	2	1187	1530
2	0	4	425	636
2	0	6	111	258
2	1	0	684	726
2	2	0	5041	5273
2	3	0	2006	2422
2	4	0	503	325
2	5	0	87	52
2	6	0	4592	4302
2	7	0	126*	7
2	8	0	149*	58
2	9	0	259	397
2	10	0	889	1105
2	11	0	134*	77
2	12	0	315	546
2	13	0	47	41
2	1	1	1887	1657
2	2	1	102	74
2	3	1	1879	1498
2	4	1	1518	984
2	5	1	2532	2180
2	6	1	173	88
2	7	1	212	297
2	8	1	1958	2004
2	9	1	165*	167
2	10	1	527	971
2	11	1	307	194
2	12	1	87*	38
2	13	1	228	333
2	1	2	1298	818
2	2	2	1699	1200
2	0	0	10630	8739
4	0	0	1981	1852
6	0	0	2484	224[illegible]
8	0	0	219	191
3	0	5	346	505
4	0	2	346	675
4	0	4	233	781
4	0	6	117	335
5	0	1	1808	2098
5	0	3	875	1284
5	0	5	204	368
6	0	2	377	456
6	0	4	148	91
7	0	1	148	99
7	0	3	148	513
8	0	2	233	567
4	1	0	242	170
4	2	0	2374	1882
4	3	0	294	230
4	4	0	887	910
4	5	0	1058	974
4	6	0	2776	3006
4	7	0	37*	111
4	8	0	37*	139
4	9	0	335	391
4	10	0	361	488
4	11	0	41	91
5	1	0	410	159
5	2	0	5344	4293
5	3	0	1282	1268
5	4	0	417	332
5	5	0	123	104
5	6	0	410	527
5	7	0	257	211
5	8	0	503	448
5	9	0	22*	0
5	10	0	123	103
6	1	0	399	382
6	2	0	38*	2
6	3	0	932	919
6	4	0	730	737
6	5	0	220	150
6	6	0	313	456
6	7	0	71	60
6	8	0	104	43
6	9	0	60	6
7	1	0	276	186
7	2	0	309	367
7	3	0	97	183
7	4	0	566	500
7	5	0	611	660
7	6	0	15*	71
7	7	0	7*	21

Table IV

Bond Lengths and Angles

Bond lengths, A		Bond angles, deg	
S–O(1)	1.47 ± 0.03	O(1)–S–O(2)	115 ± 5
S–O(2)	1.42 ± 0.02	O(1)–S–O(3)	104 ± 2
S–O(3)	1.68 ± 0.03	O(1)–S–O(4)	114 ± 1
S–O(4)	1.46 ± 0.03	O(2)–S–O(3)	98 ± 4
N–O(3)	1.48 ± 0.04	O(2)–S–O(4)	118 ± 2
		O(3)–S–O–(4)	104 ± 2
O(1)–O(2)	2.43 ± 0.03	S–O(3)–N	113 ± 8
O(1)–O(3)	2.49 ± 0.03		
O(1)–O(4)	2.46 ± 0.02	H(1)–N–O(3)	105
O(2)–O(3)	2.35 ± 0.04	H(2)–N–O(3)	112
O(2)–O(4)	2.47 ± 0.02	H(3)–N–O(3)	115
O(3)–O(4)	2.48 ± 0.02	H(1)–N–H(2)	100
		H(1)–N–H(3)	103
N–O(1)	2.97 ± 0.04	H(2)–N–H(3)	119
N–O(1)′	2.83 ± 0.02		
N–O(1)″	3.04 ± 0.02	N–H(1)–O(1)′	147
N–O(2)′	2.78 ± 0.04	N–H(2)–O–(1)″	167
N–O(2)″	3.00 ± 0.02	N–H(3)–O(3)′	110
N–O(3)′	3.16 ± 0.03	N–H(3)–O(4)′	142
N–O(4)′	2.78 ± 0.03		

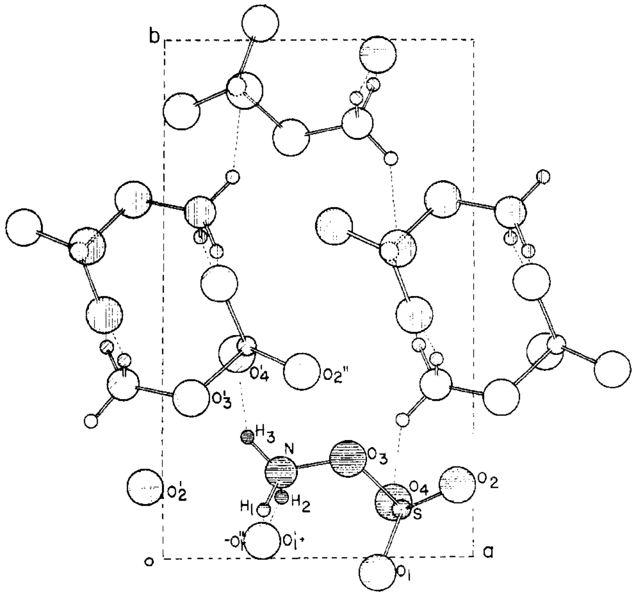

Figure 1.—A projection of the structure of hydroxylamine-O-sulfonic acid onto (001). The H atom positions were not determined from the X-ray data, but a plausible arrangement of H atoms leading to a hydrogen-bonding network is shown.

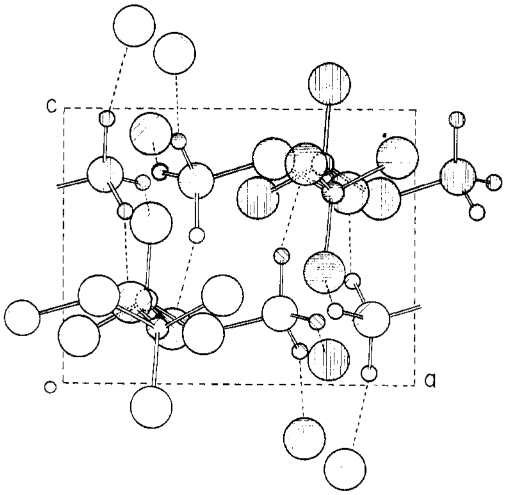

Figure 2.—A projection of the structure of hydroxylamine-O-sulfonic acid onto (010).

arrangement (ideal bond angle sum = 328°) toward planarity (ideal bond angle sum = 360°), since the bond angle sum is 345°. The S–ONH_3 bond is quite long, longer than the S–OC_2H_5 bond in $O_3SOC_2H_5$ which one might expect to be a similar kind of bond. The error in the S–ONH_3 bond length is too large, however, to permit comment on the value in terms of bonding theory. The length of the N–O bond is in good agreement with values found for NH_2OH, NH_3OHCl, and KSO_3NHOH (Table II).

The hydrogen atom positions were not determined from the X-ray data but were artificially placed about the nitrogen atom in an approximately tetrahedral configuration so as to provide reasonable H bonds to the surrounding oxygen atoms. The positions chosen give rise to the possibility of hydrogen bonding which would hold the structure together in three dimensions. The hydrogen atom arrangement was fixed, although, in the zwitterion structure proposed from nmr studies,[1] rotation was indicated. Figures 1 and 2 show the proposed hydrogen-bonding network.

The acid, though somewhat unstable, is not in the class of its salts, which detonate. It may be that the additional hydrogen bonding possible with the zwitterion structure of the acid yields a different arrangement from that of the metallic salts, an arrangement where the rapid decomposition in the solid state is less likely.