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The Crystal Structure of *l*-Cysteic Acid

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The crystal structure of cysteic acid, $C_3H_7NO_5S$, has been determined. The crystal is orthorhombic with a space group of $P2_12_12_1$, and four molecules are in a unit cell with these dimensions: $a=8.35$, $b=10.16$, and $c=7.44$ Å. The molecule is a zwitter ion, $^-O_3SCH_2CH(NH_3^+)COOH$; its dimensions are generally similar to those found in other amino acids and sulfonic acids. The acidic groups occupy the trans positions with respect to the C_α–C_β bond, while the amino group is in a gauche position to the sulfonic group and forms an intramolecular hydrogen bond between them.

The X-ray crystal structure analysis of some α-amino acids and peptides has long been in progress in this Laboratory; the present work on cysteic acid was undertaken as part of this program. This amino acid is, in nature, found normally in sheep's fleece.

Recently, Hirota and Izumi[1)] employed cysteic acid as a resolution reagent in the optical resolution of 2-amino-2′-nitro-6,6′-bitolyl; they obtained an optically highly pure compound. Izumi and others have also studied the asymmetric hydrogenation of methyl acetoacetate into methyl 2-hydroxybutyrate with catalysts modified with 2-amino acids or 2-hydroxy acids.[2)] A characteristic result has been found in the asymmetric hydrogenation with the catalysts modified by cysteic acid.[3)] In connection with the mechanisms of these resolutions and asymmetric reductions, it is worthwhile clarifying the ionic state of cysteic acid in the

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1) K. Hirota and Y. Izumi, private communication.

2) Y. Izumi, *Yuuki Goosei Kagaku Kyookai-shi* (*J. Soc. Org. Synth. Chem., Japan*), **25**, 1013 (1967).

3) Y. Izumi, private communication.

crystal, since two types of zwitter ions are possible for this amino acid.

Experimental

Cysteic acid, $C_3H_7NO_5S$, prepared from cystine by treatment with aqueous bromine was supplied to the authors by Professor Yoshiharu Izumi. Colorless, transparent, and prism-like crystals were obtained by recrystallization from a methanol-water solution. They showed a pronounced cleavage perpendicular to the *b* axis. The lattice constants were obtained by oscillation and Weissenberg photographs taken around the *b* and *c* axes. More accurate values of the unit cell dimensions obtained on a single crystal diffractometer, using Mo$K\alpha$ radiation ($\lambda=0.7107$ Å), are: $a=8.35\pm0.01$, $b=10.16\pm0.01$, $c=7.44\pm0.01$ Å. The crystal belongs to the orthorhombic system; the absence of all $(h00)$, $(0k0)$, and $(00l)$ reflections having odd values of h, k, and l respectively showed the space group to be $P2_12_12_1$. The observed density of the crystal obtained by the flotation method in a mixture of CH_3I and CCl_4 is 1.77 g cm^{-3}, while the calculated value is 1.77 g cm^{-3} (assuming four molecules in a unit cell).

The diffraction was measured on an AFC-model-1 (Automatic Four Circle) diffractometer made by Rigaku Denki Co., Ltd. The intensities in the $0<2\theta$(Mo$K\alpha$) $<55°$ range, which corresponds to the limiting sphere of Cu$K\alpha$ radiation, were collected. Zr-filtered Mo$K\alpha$ radiation was used with the pulse-height analyzer. The diffractometer was operated in an "open-loop" manner by a NEAC-2101 electronic computer. The $\omega/2\theta$-scan method was adopted for measuring the integrated intensities. The background was estimated from the measurements at the starting and end points of the scan. The programs designed by Tatzuo Ueki were used for the goniostat setting and the data processing.

The intensities were corrected only for Lorentz and polarization factors. In this way the integrated intensities of 1044 independent reflections were recorded, of which 121 (11.6%) were observed to be zero.

Structure Determination

The coordinates of the sulfur atom were deduced from the Patterson function. The first electron density map was synthesized by the use of the phases estimated from the coordinates of the S atom. Since the z parameters of S is nearly 1/4, the resulting map revealed the pseudo mirror plane on $z=1/4$. However, all the non-hydrogen atoms except for two carboxyl oxygen atoms could be located on the basis of the knowledge of the bond lengths and angles. In the succeeding Fourier map, all the non-hydrogen atoms of a

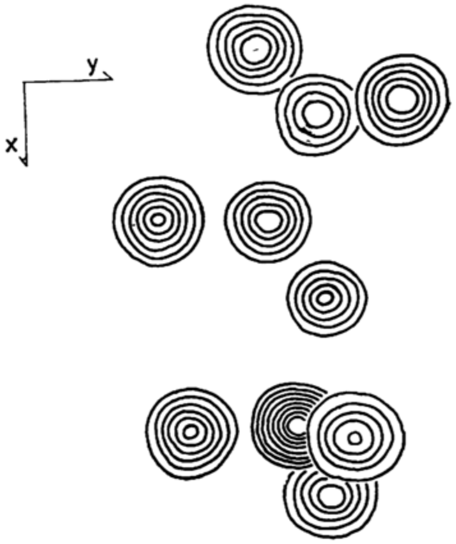

Fig. 1. A composite drawing of the final electron density map. Contour intervals: sulfur, 5 e.Å^{-3} starting at 2 e.Å^{-3}; other atoms 2 e.Å^{-3} starting at 2 e.Å^{-3}.

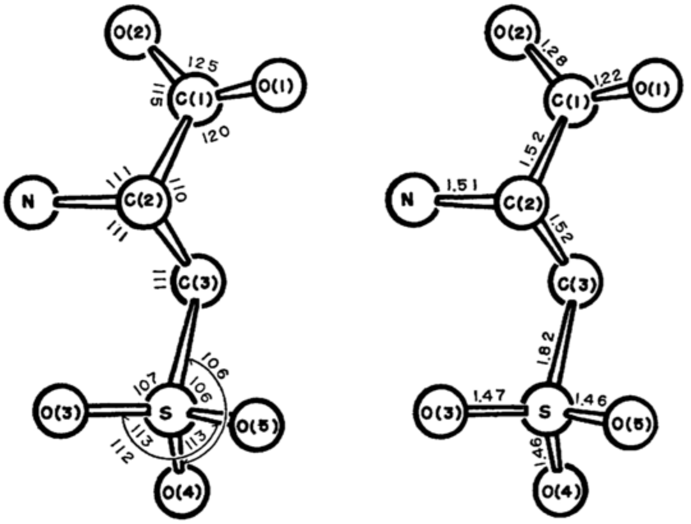

Fig. 2. Bond distances and angles.

Table 1(a). The atomic coordinantes and their standard deviations

	x/a	y/b	z/c	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
S	0.5579	0.3430	0.2640	0.003 Å	0.003 Å	0.003 Å
C(1)	0.0701	0.3756	0.2642	0.014	0.012	0.012
C(2)	0.2324	0.3121	0.2951	0.011	0.012	0.012
C(3)	0.3585	0.3797	0.1801	0.012	0.012	0.012
N	0.2261	0.1660	0.2564	0.010	0.010	0.011
O(1)	0.0474	0.4901	0.3068	0.011	0.009	0.011
O(2)	−0.0360	0.3012	0.1905	0.009	0.010	0.012
O(3)	0.5612	0.2007	0.3019	0.010	0.009	0.012
O(4)	0.6682	0.3819	0.1221	0.009	0.012	0.010
O(5)	0.5765	0.4212	0.4272	0.012	0.012	0.010

Table 1(b). The anisotropic thermal parameters and their standard deviations ($\times 10^4$)
The thermal parameters are of the from

$$T=\exp\left(-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\right)$$

	B_{11}	σ	B_{22}	σ	B_{33}	σ	B_{12}	σ	B_{13}	σ	B_{23}	σ
S	84	3	77	3	117	4	5	6	36	8	−45	7
C(1)	137	18	67	10	87	17	4	25	− 7	38	30	25
C(2)	78	14	68	11	104	19	− 1	21	31	29	13	25
C(3)	92	16	69	11	118	20	−27	23	85	32	71	26
N	121	14	61	9	128	18	−29	21	−25	31	−13	27
O(1)	148	16	70	9	219	23	5	22	39	37	96	25
O(2)	88	12	91	10	316	30	12	20	164	34	83	31
O(3)	108	13	75	9	276	27	5	20	46	38	−88	27
O(4)	84	12	140	14	156	18	48	23	− 5	28	−85	29
O(5)	189	20	134	13	110	16	−49	31	97	36	5	26

Table 1(c). The coordinates of the hydrogen atoms and their isotropic thermal parameters

	Bonded to	x/a	y/b	z/c	B
H(1)	C(3)	0.345	0.462	0.187	3.5 Å^2
H(2)	C(3)	0.379	0.352	0.040	0.7
H(3)	C(2)	0.260	0.322	0.423	2.6
H(4)	O(2)	−0.154	0.335	0.173	1.2
H(5)	O(5)	0.196	0.127	0.355	7.1
H(6)	O(4)	0.212	0.147	0.129	4.5
N(7)	O(3)	0.317	0.161	0.243	5.2

$\sigma<(x)>=0.17$ Å $\sigma<(y)>=0.17$ Å $\sigma<(z)>=0.18$ Å $\sigma<(B)>=4.4$ Å

molecule were clearly defined. The final Fourier map is given in Fig. 1.

The positional and thermal parameters were refined by block-diagonal least-squares calculations, which minimize $\sum w(|F_o|-|F_c|)^2$. The weighting scheme was: $w=0$ when $F_o=0$ and $w=1$ when $F_o \neq 0$. The scattering factors for all the atoms were taken from "International Tables for X-Ray Crystallography (1959)". After several cycles of the least-squares calculation, the R index reached 15.6%. In the next calculation, all the hydrogen atoms were included. Their coordinates were assigned so that they are consistent with the tetrahedral bond angles and the optimum hydrogen bonding. Then, the maximum shift of the parameters (0.007 Å) became less than a half of the estimated standard deviation. It was, therefore, felt that further refinement would not improve the accuracy of the final parameters. The R index was 14.2% ($R=17.2\%$ with $F_o=0$). The mean value of the e.s.d.'s of the atomic coordinates of C, N, and O was 0.011 Å (0.009—0.014 Å). Difference-Fourier synthesis was carried out to confirm the hydrogen positions, but there still remained a little ambiguity about their positions, for there were many false peaks at other than the hydrogen atom positions. The atomic parameters are listed in Table 1, while the observed and calculated structure factors are listed in Table 2.

The computations were made on a NEAC 2200-model 500 in the computing center of this university. The program for the Patterson function was written by Noritake Yasuoka, and the others, by one of the authors (T. A).

TABLE 2. OBSERVED AND CALCULATED STRUCTURE FACTORS (×5)

L	FO	FC
H,K=	0	0
2	742	779
4	202	198
6	114	120
8	5	27
10	21	19
H,K=	1	0
1	153	179
2	71	72
3	45	34
4	45	42
5	95	100
6	15	19
7	57	54
8	0	9
9	10	14
10	34	18
H,K=	2	0
0	300	311
1	155	163
2	169	190
3	148	159
4	107	106
5	118	139
6	49	42
7	89	92
8	0	5
9	14	9
10	27	21
H,K=	3	0
1	93	80
2	133	123
3	88	101
4	0	1
5	94	106
6	58	59
7	37	31
8	42	39
9	20	15
10	9	5
H,K=	4	0
0	81	78
1	206	184
2	126	117
3	147	151
4	74	74
5	46	52
6	12	7
7	52	65
8	15	1
9	36	35
H,K=	5	0
1	126	116
2	11	11
3	47	41
4	64	69
5	27	32
6	28	20
7	0	0
8	16	16
9	0	4
H,K=	6	0
0	131	130
1	47	48
2	131	117
3	95	88
4	139	123
5	86	84
6	73	79
7	59	60
8	11	17
H,K=	7	0
1	0	15
2	43	42
3	24	13
4	7	13
5	47	44
6	37	43
7	11	25
8	26	24
H,K=	8	0
0	125	133
1	0	3
2	103	93
3	29	26
4	79	67
5	41	41
6	53	57
7	0	7
H,K=	9	0
1	115	99
2	0	14
3	73	50
4	0	1
5	45	38
6	0	5
H,K=	10	0
0	80	103
1	10	16
2	95	83
3	46	28
4	60	43
5	6	5
H,K=	11	0
1	0	1
2	13	5
3	18	10
H,K=	0	1
1	9	8
2	25	17
3	10	12
4	18	16
5	84	85
6	73	85
7	96	95
8	53	50
9	45	42
10	0	11
H,K=	1	1
0	83	99
1	64	72
2	108	119
3	153	149
4	78	77
5	50	47
6	84	88
7	44	40
8	39	44
9	12	12
10	13	15
H,K=	2	1
0	295	312
1	174	173
2	179	190
3	33	11
4	73	72
5	59	67
6	88	97
7	58	56
8	46	52
9	0	20
10	25	20
H,K=	3	1
0	6	6
1	403	382
2	194	186
3	171	176
4	72	89
5	99	106
6	44	62
7	36	41
8	8	18
9	25	10
10	18	9
H,K=	4	1
0	124	143
1	191	167
2	137	134
3	105	109
4	134	125
5	101	105
6	58	66
7	31	30
8	28	20
9	13	12
H,K=	5	1
0	23	25
1	160	137
2	0	29
3	108	94
4	60	58
5	57	52
6	39	35
7	16	7
8	0	14
9	0	5
H,K=	6	1
0	150	147
1	121	111
2	167	138
3	99	88
4	88	78
5	41	40
6	42	42
7	24	31
8	35	25
H,K=	7	1
0	28	37
1	123	129
2	42	37
3	77	56
4	13	13
5	27	20
6	17	15
7	6	13
8	27	13
H,K=	8	1
0	28	39
1	0	16
2	40	38
3	37	21
4	16	23
5	34	23
6	25	24
7	16	17
H,K=	9	1
0	0	20
1	11	15
2	25	14
3	26	12
4	48	37
5	22	16
6	44	39
H,K=	10	1
0	43	43
1	48	33
2	34	18
3	0	8
4	22	5
5	23	18
H,K=	11	1
0	17	13
1	17	24
2	9	6
3	23	14
H,K=	0	2
0	242	252
1	535	525
2	266	255
3	40	42
4	127	117
5	72	75
6	33	31
7	52	44
8	11	28
9	21	9
10	0	5
H,K=	1	2
0	271	214
1	156	153
2	25	26
3	163	150
4	29	34
5	45	28
6	78	82
7	24	24
8	29	24
9	27	17
10	19	14
H,K=	2	2
0	33	13
1	235	227
2	71	73
3	155	160
4	37	43
5	133	137
6	81	82
7	55	60
8	33	35
9	28	38
10	9	9
H,K=	3	2
0	170	174
1	130	131
2	58	49
3	55	60
4	118	134
5	0	10
6	59	56
7	38	38
8	17	17
9	0	7
H,K=	4	2
0	101	94
1	64	59
2	141	119
3	35	32
4	18	14
5	27	25
6	24	24
7	0	13
8	33	41
9	18	12
H,K=	5	2
0	0	12
1	71	68
2	0	18
3	69	58
4	43	36
5	43	42
6	7	6
7	13	12
8	14	16
9	24	24
H,K=	6	2
0	51	50
1	31	27
2	70	65
3	76	69
4	45	45
5	87	81
6	42	40
7	29	30
8	16	32
H,K=	7	2
0	21	23
1	39	48
2	25	29
3	48	35
4	65	55
5	31	32
6	49	56
7	28	29
8	29	29
H,K=	8	2
0	25	20
1	73	74
2	30	33
3	63	54
4	54	39
5	75	63
6	27	27
7	50	47
H,K=	9	2
0	47	58
1	55	52
2	36	34
3	51	38
4	37	22
5	14	19
6	30	21
H,K=	10	2
0	23	29
1	73	62
2	44	36
3	51	42
4	36	24
5	30	24
H,K=	11	2
0	25	15
1	19	3
2	19	22
H,K=	0	3
1	16	13
2	182	182
3	74	77
4	55	58
5	16	9
6	33	30
7	38	49
8	36	43
9	8	6
10	36	34
H,K=	1	3
0	139	143
1	18	9
2	121	116
3	116	108
4	137	124
5	79	66
6	54	57
7	42	39
8	45	50
9	11	20
10	11	27
H,K=	2	3
0	126	137
1	117	104
2	93	93
3	64	67
4	65	66
5	70	70
6	60	59
7	84	78
8	29	30
9	33	35
10	30	27
H,K=	3	3
0	125	125
1	151	123
2	127	120
3	140	140
4	54	62
5	46	54
6	36	31
7	15	26
8	16	11
9	17	16
H,K=	4	3
0	76	84
1	36	34
2	42	42
3	124	125
4	55	59
5	106	117
6	10	35
7	72	76
8	0	19
9	42	45
H,K=	5	3
0	117	136
1	41	34
2	166	149
3	14	18
4	104	106
5	19	25
6	42	42
7	17	16
8	27	22
9	18	14
H,K=	6	3
0	51	58
1	51	45
2	55	47
3	48	45
4	29	22
5	56	47
6	13	10
7	35	28
8	0	16
H,K=	7	3
0	81	111
1	16	13
2	90	76
3	25	18
4	26	20
5	5	8
6	19	9
7	0	12
8	0	2
H,K=	8	3
0	26	15
1	13	11
2	14	11
3	17	4
4	17	6
5	31	25
6	0	10
7	42	33
H,K=	9	3
0	0	6
1	15	15
2	17	21
3	16	20
4	23	16
5	47	34
6	0	5
H,K=	10	3
0	26	23
1	29	38
2	6	10
3	0	19
4	0	3
H,K=	11	3
0	0	14
1	15	4
2	15	11
H,K=	0	4
0	315	307
1	49	46
2	139	117
3	136	126
4	63	65
5	43	34
6	91	93
7	28	24
8	49	51
9	19	12
10	33	22
H,K=	1	4
0	105	102
1	230	219
2	58	51
3	70	61
4	98	89
5	34	31
6	69	64
7	28	21
8	59	51
9	19	6
H,K=	2	4
0	71	67
1	93	89
2	29	36
3	116	111
4	72	77
5	43	60
6	56	51
7	65	64
8	0	22
9	24	40
H,K=	3	4
0	0	11
1	51	58
2	67	66
3	90	83
4	32	36
5	53	54
6	0	39
7	0	7
8	10	21
9	24	19
H,K=	4	4
0	73	76
1	66	56
2	46	44
3	17	9
4	37	42
5	18	25
6	24	23
7	21	23
8	17	18
9	22	33
H,K=	5	4
0	0	5
1	36	41
2	57	52
3	26	30
4	22	14
5	28	23
6	22	20
7	0	8
8	20	22
H,K=	6	4
0	12	16
1	21	25
2	52	43
3	54	51
4	77	73
5	18	13
6	43	46
7	0	21
8	32	25
H,K=	7	4
0	22	19
1	12	4
2	61	43
3	30	24
4	56	47
5	38	33
6	48	44
7	39	19
H,K=	8	4
0	32	37
1	25	25
2	41	32
3	56	45
4	37	33
5	43	37
6	35	38
H,K=	9	4
0	10	17
1	46	58
2	31	29
3	39	34
4	31	31
5	23	23
H,K=	10	4
0	17	32
1	29	34
2	29	30
3	42	31
4	23	21
H,K=	11	4
0	13	6
1	15	21
H,K=	0	5
1	82	75
2	20	14
3	7	3
4	44	35
5	80	70
6	5	19
7	60	48
8	18	10
9	54	46
H,K=	1	5
0	84	70
1	61	48
2	32	29
3	32	21
4	76	74
5	24	16
6	39	26
7	31	28
8	21	22
9	0	11
H,K=	2	5
0	87	94
1	63	61
2	164	150
3	40	36
4	91	89
5	19	26
6	72	70
7	33	30
8	58	53
9	27	29
H,K=	3	5
0	9	14
1	130	143
2	74	66
3	128	138
4	37	45
5	54	62
6	23	18
7	40	45
8	23	27
9	34	27
H,K=	4	5
0	53	62
1	38	44
2	117	123
3	32	30
4	106	110
5	0	19
6	57	55
7	21	33
8	32	40
9	34	24
H,K=	5	5
0	23	23
1	65	67
2	0	10
3	80	80
4	12	12
5	38	32
6	38	37
7	12	9
8	41	45
H,K=	6	5
0	69	98
1	22	28
2	107	104
3	30	27
4	76	75
5	29	24
6	47	42
7	24	19
8	18	22
H,K=	7	5
0	0	6
1	76	77
2	24	20
3	57	54
4	33	31
5	33	28
6	18	14
7	19	17
H,K=	8	5
0	0	2
1	0	3
2	0	16
3	0	17
4	23	19
5	36	28
6	11	21
H,K=	9	5
0	12	19
1	15	10
2	10	5
3	18	16
4	22	27
5	0	7
H,K=	10	5
0	14	20
1	20	15
2	24	16
3	30	6
H,K=	0	6
0	265	255
1	108	97
2	298	267
3	47	40
4	171	157
5	24	24
6	67	57
7	14	28
8	35	37
9	35	15
H,K=	1	6
0	189	182
1	34	28
2	120	107
3	129	118
4	0	10
5	90	92
6	35	34
7	57	58
8	20	17
9	32	32
H,K=	2	6
0	62	70
1	33	40
2	85	85
3	71	85
4	58	53
5	73	68
6	37	42
7	27	20
8	0	20
9	6	21
H,K=	3	6
0	7	1
1	69	61
2	42	41
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2	36	39
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H,K=	7	7
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4	15	11
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H,K=	8	7
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H,K=	9	7
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H,K=	6	8
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H,K=	4	9
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H,K=	4	11
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H,K=	3	13
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H,K=	4	13
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Discussion

The bond distances and angles given in Fig. 2 are generally in good agreement with those previously reported for α-amino acids and sulfonic acids. The estimated standard deviations of the bond distances and angles are: 0.01 Å for S–O and S–C, 0.02 Å for other bonds, and 1.0° for the angles. In the molecule O(4)–S–C(3)–C(2)–C(1) possesses a trans-zigzag conformation, and N and S have a gauche form around the C(2)–C(3) methylene linkage (see Fig. 3).

The asymmetry about the C(1)–C(2) bond in the carboxyl group (C(2)–C(1)–O(1), 120°; C(2)–C(1)–O(2), 115°) is in good agreement with the foregoing findings. The two C–O distances, 1.22 and 1.28 Å, are significantly different from each other. The longer one is that of the oxygen atom with a hydrogen atom. The carboxyl group and C(2) are coplanar, and the equation for the best plane is;

$$0.2922X - 0.2990Y - 0.9061Z + 0.7324 = 0,$$

where X, Y, and Z are in the Å unit. The deviations of the individual atoms from the plane are:

O(1), 0.002; O(2), 0.001
C(1), −0.004; C(2), 0.001 Å.

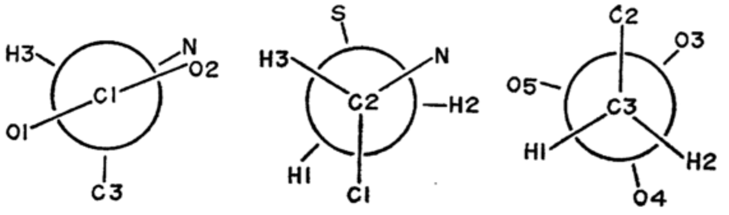
The N atom also lies nearly on the plane, its deviation from the plane being −0.20 Å. The projection along the C(1)–C(2) bond is shown in Fig. 3.

The bond distances and angles of the sulfonic group are compared with those of other related compounds[4,5] in Table 3. The shape and size of the sulfonic group are substantially the same as in other compounds. The three S–O bonds seem to be nearly equivalent to each other, showing that there is no hydrogen atom bonded to this group.

Around the amino group there are four close N–O contacts (I, II, III, and V in Fig. 4) available for hydrogen-bond formations. Considering the configuration around N, the I, II, and III contacts are favorable for hydrogen bonds (see Table 4); of these, the I contact is an intramolecular hydrogen bond. Such a bond has also been found in taurine.[4] If V is assumed to be a hydrogen bond, an unfavorable conformation occurs around N. The three hydrogen atoms, H(7), H(6), and H(5), as refined by least-squares calculation, lie nearly on I, II, and III. These three are, therefore, favorable for hydrogen bonds. The cleavage perpendicular to the *b* axis can be well interpreted by taking V not to be a hydrogen bond. The fourth hydrogen bond (IV in Fig. 4) was found between O(2) of the carboxyl group and O(4) of the sulfonic group.

In the sulfonic group, each oxygen atom forms an NH–O hydrogen bond. In addition, O(4) accepts the OH–O hydrogen bond from the carboxyl group.

In view of the configurations of the carboxyl



(a) (b) (c)

Fig. 3

(a) A view down the C(1)-C(2) bond.
(b) A view down the C(2)-C(3) bond.
(c) A view down the C(3)-S bond.

TABLE 3. COMPARISON OF THE DIMENSIONS OF THE SULFONIC GROUPS

	Taurine[4] $NH_3^+CH_2CH_2SO_3^-$	Potassium α-hydroxy-[5] benzylsulfonate $C_6H_5CH(OH)SO_3^-K^+$	Cysteic acid $^-O_3SCH_2CH(NH_3^+)COOH$
∠OSO	110.9°—113.7°	111°—114°	112°—113°
∠CSO	105.8°—106.9°	106°—108°	106°—107°
S-C	1.78_0 Å	1.83 Å	1.82 Å
S-O	1.44_8—1.46_5 Å	1.42—1.45 Å	1.46—1.47

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4) Y. Okaya, *Acta Cryst.*, **21**, 726 (1966).

5) T. Kuroda T. Ashida, Y. Sasada and M. Kakudo, This Bulletin, **40**, 1377 (1967).

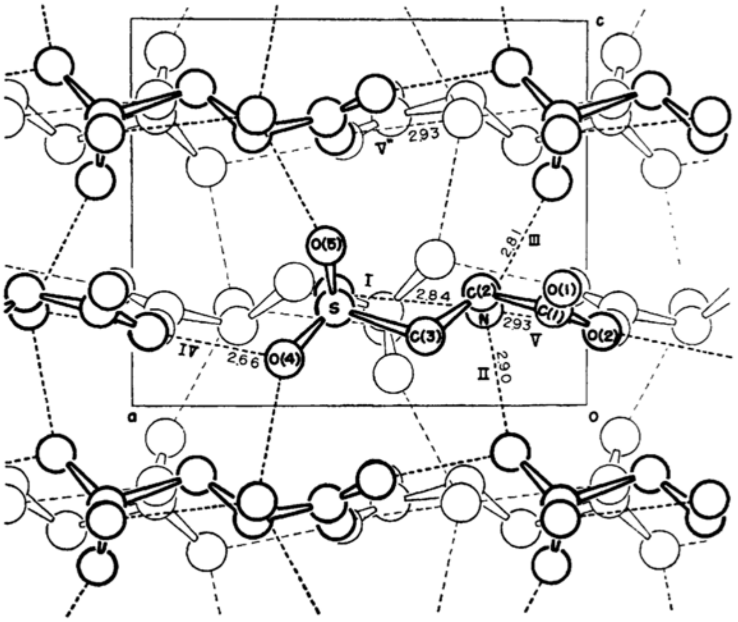

Fig. 4(a). The crystal structure viewed down the *b* axis. Chain lines show the close contacts available for hydrogen bonding.

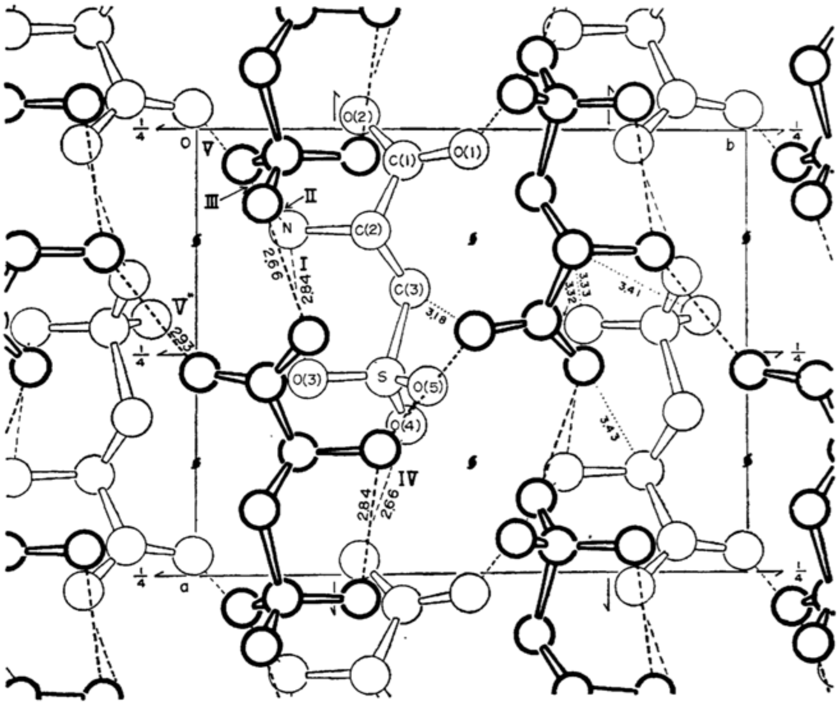

Fig. 4(b). The crystal structure viewed down the *c* axis. Some van der Waals contacts are shown by dotted line.

TABLE 4. THE HYDROGEN BONDS

(a) Short N···O, and O···O contacts.

No.	From	To	Distance	Hydrogen atom involved
I	N	O(3)	2.84 Å	H(7)
II	N	O(4)	2.90	H(6)
III	N	O(5)	2.81	H(5)
IV	O(4)	O(2)	2.66	H(4)
V	N	O(1)	2.93	

(b) Configuration around N.

Angle between	C–N	and	I	80°
	C–N		II	111
	C–N		III	110
	C–N		V	131
	I		II	107
	I		III	112
	II		III	133
	I		V	150
	II		V	67
	III		V	66

and sulfonic groups, together with the hydrogen-bond system in the crystal, the cysteic acid molecule can be said to have the zwitter ion form:

$$^{-}O_3SCH_2CH(NH_3{}^{+})COOH\,.$$

This could be expected from the difference between the dissociation constants of the carboxyl and the sulfonic groups. On the other hand, it has been expected, in the study of the optical resolution,1) that cysteic acid is weaker than usual sulfonic acid. This seems reasonable if the molecule takes such a zwitter ion structure. It is also expected that, in an asymmetric hydrogenation,3) this acid will be absorbed on the Raney nickel catalyst in a fairly different manner from common amino acids. This would explain the characteristic result obtained in the hydrogenation with the catalyst modified by this acid.

Fairly close van der Waals contacts are shown in Fig. 4(b). The molecules are at nearly $z=1/4$, and form a sheet parallel to the (010) plane by the three hydrogen bonds, II, III, and IV. No hydrogen bond seems to contribute to the contacts among these sheets.

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