A rotator can be expected to require more space than a stationary group; perhaps the short distance in this case indicates that the group is really stationary.) This comparison of C---C and H---H distances emphasizes the necessity of considering the positions of any hydrogen atoms involved in intermolecular contacts. The shortest intermolecular distances involving hydrogen atoms [other than those given in Fig. 2(b)] are, with their e.s.d.'s: O---H, 2·49 (6) Å; N---H, 3·25 (6) Å; H---H, 2·30 (9) Å. None of these distances is significantly less than the sum of appropriate van der Waals radii. It therefore seems unlikely that the exceptional distances given in Fig. 2(b) represent a reduction in the van der Waals radii resulting from the low temperature.

A more plausible explanation of the unusual proximity is that the hydrogen atom H(34) participates in a bifurcated bond, joining O(34) not only to O(35) but also to O(35) (1). The combined pull of the two weak symmetry-related bonds O(34)–H(34)---O(35) (1) and O(34) (1)–H(34) (1)---O(35) is sufficient to balance the repulsion between O(35) and O(35) (1). However, there are some objections to this hypothesis. The distance O(34)---O(35) (1) is 3·028 Å, and thus is readily explicable as a normal van der Waals contact. Also, if H(34) were even weakly bonded to O(35) (1), it could be expected to move towards that atom, with a consequent increase in the angle C(22)–O(34)–H(34). In fact this angle is 99°, compared with the corresponding value of 106° in molecule A. The e.s.d. of these angles is about 4°, so that the difference is probably not significant; however such evidence as is available does not support the hypothesis. Finally, it can be seen in Fig. 2(b) that the opposing attractive and repulsive forces are not in equilibrium; O(34)---O(35) (1) could be reduced, and O(35)---O(35) (1) increased by a translation of the molecule parallel to the long axis of the phenazine nucleus. In spite of these objections, the hypothesis of the bifurcated hydrogen bond is probably the best that can be advanced at this time. It is hoped that work now in progress in this laboratory on the crystal structure of iodinin (II) will throw additional light on the problem.

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The Crystal and Molecular Structure of L-Cysteine

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The structure of L-cysteine, $HSCH_2.CH(NH_2).COOH$, has been determined from three-dimensional X-ray diffraction data, and refined until $R = 0.127$. The crystals are monoclinic, $P2_1$, with $a = 11.51$, $b = 5.240$, $c = 9.517$ Å, $\beta = 109.13°$. The bond lengths and angles in the two cysteine molecules (zwitterions) in the asymmetric unit are not significantly different from each other or from expected values, but their conformations differ by twists of 118° around the $C_\alpha - C_\beta$ bond and 33° around $C - C_\alpha$ bond.

The crystal structure of L-cysteine,
$$HS.CH_2.CH(NH_2).COOH,$$
has been determined. The free amino acid was obtained from L-cysteine hydrochloride by neutralization with sodium hydroxide and crystallization from hot water.

Table 1. *Observed and calculated structure amplitudes in the form hkl, 10 $|F_{obs}|$, 10 $|F_{calc}|$*

Table 1 (cont.)

h	k	l	Fo	Fc		h	k	l	Fo	Fc		h	k	l	Fo	Fc		h	k	l	Fo	Fc
6	2	-9	102.00	88.14		14	2	-2	29.00	62.36		6	3	4	64.00	49.68		2	4	2	124.00	132.66		11	4	-3	54.00	63.51
6	2	-8	46.00	39.42		0	3	1	273.00	266.20		6	3	5	54.00	68.14		2	4	3	93.00	96.79		11	4	-2	46.00	66.62
6	2	-7	43.00	34.41		0	3	2	222.00	211.18		6	3	6	72.00	67.62		2	4	4	52.00	50.35		11	4	-1	42.00	40.11
6	2	-6	38.00	49.03		0	3	3	39.00	34.95		6	3	7	43.00	57.49		2	4	5	62.00	59.46		11	4	0	27.00	44.38
6	2	-5	212.00	236.79		0	3	4	126.00	134.11		7	3	-10	40.00	24.61		2	4	6	31.00	24.55		12	4	-3	5.00	35.45
6	2	-4	103.00	90.78		0	3	5	131.00	110.42		7	3	-9	56.00	42.93		2	4	7	43.00	49.50		12	4	-1	78.00	72.06
6	2	-3	94.00	91.06		0	3	6	51.00	34.52		7	3	-8	50.00	40.43		2	4	8	25.00	30.32		12	4	2	74.00	72.00
6	2	-2	120.00	123.16		0	3	7	59.00	38.91		7	3	-7	105.00	108.59		3	4	-9	37.00	7.74		0	5	3	48.00	49.74
6	2	-1	160.00	154.45		0	3	8	31.00	19.49		7	3	-6	40.00	49.91		3	4	-8	94.00	77.65		0	5	4	129.00	143.45
6	2	0	259.00	261.14		0	3	9	93.00	83.25		7	3	-5	53.00	49.32		3	4	-7	76.00	67.55		0	5	6	51.00	46.95
6	2	1	130.00	131.93		0	3	10	48.00	47.46		7	3	-4	29.00	17.32		3	4	-6	95.00	94.41		0	5	7	18.00	13.91
6	2	2	246.00	283.03		1	3	-10	49.00	32.27		7	3	-3	122.00	120.67		3	4	-5	119.00	113.67		1	5	-8	20.00	33.92
6	2	3	36.00	29.34		1	3	-9	40.00	25.35		7	3	-2	170.00	206.75		3	4	-4	139.00	144.98		1	5	-7	22.00	16.52
6	2	4	65.00	57.61		1	3	-8	32.00	23.35		7	3	-1	30.00	29.16		3	4	-3	170.00	187.60		1	5	-5	27.00	26.03
6	2	5	45.00	39.44		1	3	-7	118.00	119.96		7	3	0	102.00	118.94		3	4	-2	58.00	45.31		1	5	-4	81.00	81.99
6	2	6	68.00	69.05		1	3	-6	159.00	137.86		7	3	1	54.00	56.21		3	4	-1	90.00	81.27		1	5	-3	34.00	20.30
6	2	7	66.00	74.86		1	3	-5	40.00	21.72		7	3	2	84.00	97.64		3	4	0	13.00	12.32		1	5	-2	102.00	88.92
6	2	8	25.00	21.71		1	3	-4	149.00	139.53		7	3	3	60.00	60.76		3	4	1	137.00	147.07		1	5	0	101.00	106.21
7	2	-11	27.00	20.38		1	3	-3	176.00	188.04		7	3	4	62.00	46.86		3	4	2	50.00	37.04		1	5	1	83.00	70.29
7	2	-10	65.00	47.28		1	3	-2	88.00	75.35		7	3	5	89.00	99.96		3	4	3	93.00	90.40		1	5	2	107.00	76.77
7	2	-9	22.00	36.10		1	3	-1	100.00	60.27		7	3	6	35.00	32.55		3	4	4	83.00	96.34		1	5	4	74.00	68.68
7	2	-8	62.00	46.00		1	3	0	163.00	164.07		8	3	-10	13.00	16.54		3	4	5	90.00	79.57		1	5	5	71.00	74.07
7	2	-7	65.00	63.85		1	3	1	117.00	129.36		8	3	-9	83.00	82.29		3	4	6	18.00	11.35		1	5	6	79.00	76.80
7	2	-6	69.00	67.35		1	3	2	264.20	273.93		8	3	-8	71.00	65.78		3	4	7	37.00	35.98		1	5	7	43.00	40.54
7	2	-5	115.00	132.84		1	3	3	144.00	145.49		8	3	-7	52.00	36.15		4	4	-8	26.00	27.79		2	5	-8	44.00	51.43
7	2	-4	106.00	87.32		1	3	4	47.00	27.19		8	3	-6	121.00	115.49		4	4	-9	111.00	84.09		2	5	-7	67.00	59.40
7	2	-3	183.00	184.28		1	3	5	142.00	140.69		8	3	-5	129.00	147.59		4	4	-8	50.00	22.88		2	5	-6	86.00	62.69
7	2	-2	105.00	114.14		1	3	6	68.00	79.95		8	3	-4	27.00	20.71		4	4	-7	151.00	136.47		2	5	-5	40.00	36.40
7	2	-1	190.00	212.19		1	3	7	95.00	92.19		8	3	-3	112.00	110.44		4	4	-6	99.00	92.02		2	5	-4	149.00	102.53
7	2	0	144.00	146.70		1	3	8	25.00	27.87		8	3	-2	40.00	52.62		4	4	-5	81.00	72.52		2	5	-3	72.00	52.75
7	2	1	90.00	89.90		1	3	9	47.00	30.99		8	3	-1	163.00	184.12		4	4	-4	73.00	70.61		2	5	-2	74.00	73.90
7	2	2	175.00	202.27		1	3	10	41.00	58.04		8	3	0	107.00	109.53		4	4	-3	174.00	179.36		2	5	-1	45.00	48.39
7	2	3	50.00	43.06		2	3	-10	51.00	24.94		8	3	1	56.00	67.31		4	4	-2	106.00	102.37		2	5	0	165.00	170.05
7	2	4	61.00	64.61		2	3	-9	76.00	79.71		8	3	2	54.00	64.64		4	4	-1	94.00	94.11		2	5	1	55.00	46.57
7	2	5	36.00	41.33		2	3	-8	45.00	51.86		8	3	3	86.00	111.55		4	4	0	31.00	36.44		2	5	2	66.00	59.71
7	2	6	64.00	74.28		2	3	-7	87.00	77.32		8	3	4	93.00	124.78		4	4	1	129.00	134.24		2	5	3	26.00	59.71
7	2	7	42.00	62.34		2	3	-6	169.00	184.52		9	3	-10	41.00	39.71		4	4	2	92.00	90.31		2	5	4	139.00	136.67
8	2	-11	7.00	21.79		2	3	-5	209.00	222.84		9	3	-9	23.00	31.07		4	4	3	52.00	55.97		2	5	5	20.00	23.12
8	2	-10	65.00	48.67		2	3	-4	193.00	212.69		9	3	-8	43.00	49.24		4	4	4	28.00	36.71		2	5	6	31.00	36.40
8	2	-9	34.00	27.53		2	3	-3	102.00	115.69		9	3	-7	66.00	54.57		4	4	6	97.00	112.56		3	5	-8	45.00	50.70
8	2	-8	48.00	45.56		2	3	-2	241.00	260.15		9	3	-6	96.00	94.54		4	4	7	31.00	46.97		3	5	-7	17.00	9.72
8	2	-7	131.00	117.02		2	3	-1	127.00	137.30		9	3	-5	89.00	73.09		5	4	-9	107.00	89.87		3	5	-6	56.00	42.70
8	2	-6	70.00	64.89		2	3	0	365.00	352.75		9	3	-4	92.00	84.26		5	4	-8	71.00	58.91		3	5	-5	70.00	54.36
8	2	-5	88.00	87.79		2	3	1	172.00	180.94		9	3	-3	129.00	123.60		5	4	-7	31.00	39.98		3	5	-4	127.00	125.09
8	2	-4	117.00	110.95		2	3	2	88.00	96.03		9	3	-2	170.00	176.98		5	4	-6	56.00	55.53		3	5	-3	68.00	75.29
8	2	-3	192.00	188.35		2	3	3	56.00	61.81		9	3	-1	70.00	73.94		5	4	-5	162.00	164.43		3	5	-2	148.00	161.63
8	2	-2	198.00	224.63		2	3	4	129.00	134.39		9	3	0	92.00	65.91		5	4	-4	76.00	81.42		3	5	-1	64.00	94.01
8	2	-1	143.00	140.52		2	3	5	157.00	159.93		9	3	1	57.00	51.37		5	4	-3	85.00	97.48		3	5	0	21.00	37.56
8	2	0	46.00	33.37		2	3	6	143.00	148.48		9	3	2	68.00	72.90		5	4	-2	107.00	97.26		3	5	1	75.00	87.19
8	2	1	54.00	60.82		2	3	7	79.00	70.66		9	3	3	56.00	64.74		5	4	-1	97.00	97.87		3	5	2	45.00	44.79
8	2	2	68.00	46.25		2	3	8	46.00	46.32		9	3	4	37.00	40.69		5	4	0	172.00	206.61		3	5	3	83.00	78.11
9	2	3	119.00	118.74		2	3	9	53.00	68.21		10	3	-9	16.00	26.65		5	4	1	66.00	75.12		3	5	4	47.00	52.57
9	2	4	39.00	44.48		3	3	-10	58.00	44.90		10	3	-8	51.00	49.69		5	4	2	38.00	17.65		4	5	-7	45.00	47.07
9	2	5	48.00	43.40		3	3	-9	37.00	26.42		10	3	-7	22.00	12.59		5	4	3	43.00	27.22		4	5	-6	36.00	31.59
9	2	6	30.00	41.05		3	3	-8	71.00	63.43		10	3	-5	36.00	26.78		5	4	4	106.00	107.35		4	5	-5	50.00	45.64
9	2	7	28.00	63.22		3	3	-7	29.00	28.98		10	3	-4	68.00	72.67		5	4	5	29.00	14.83		4	5	-4	88.00	67.18
9	2	-11	19.00	22.26		3	3	-6	81.00	58.90		10	3	-3	63.00	53.53		5	4	6	27.00	15.67		4	5	-3	95.00	73.04
9	2	-10	50.00	42.18		3	3	-5	45.00	37.45		10	3	-2	11.00	6.29		5	4	7	27.00	58.01		4	5	-2	44.00	32.64
9	2	-9	72.00	67.11		3	3	-4	77.00	65.92		10	3	-1	93.00	105.28		6	4	-9	37.00	31.79		4	5	-1	64.00	70.20
9	2	-8	77.00	63.11		3	3	-3	135.00	133.67		10	3	0	61.00	83.06		6	4	-8	85.00	63.02		4	5	0	55.00	65.88
9	2	-7	111.00	106.47		3	3	-2	72.00	64.20		10	3	1	25.00	16.38		6	4	-7	85.00	78.99		4	5	1	36.00	73.10
9	2	-6	75.00	55.32		3	3	-1	40.00	39.64		10	3	2	44.00	41.21		6	4	-6	47.00	45.38		4	5	2	26.00	40.51
9	2	-5	68.00	74.62		3	3	0	169.00	182.83		10	3	3	25.00	32.80		6	4	-5	104.00	79.07		4	5	3	74.00	76.93
9	2	-4	119.00	134.57		3	3	1	127.00	123.06		10	3	4	9.00	23.36		6	4	-4	116.00	118.93		4	5	4	57.00	62.23
9	2	-3	114.00	109.05		3	3	2	76.00	89.07		11	3	-8	21.00	9.84		6	4	-3	141.00	143.24		5	5	-8	27.00	39.37
9	2	-2	170.00	208.25		3	3	3	115.00	122.49		11	3	-7	39.00	51.78		6	4	-2	54.00	79.16		5	5	-7	32.00	30.61
9	2	-1	61.00	53.96		3	3	4	113.00	109.08		11	3	-6	43.00	61.92		6	4	-1	91.00	97.52		5	5	-6	29.00	25.54
9	2	0	46.00	46.37		3	3	5	77.00	71.66		11	3	-5	87.00	94.51		6	4	0	38.00	15.67		5	5	-5	42.00	18.86
9	2	1	82.00	81.63		3	3	6	74.00	69.00		11	3	-3	64.00	60.27		6	4	1	84.00	95.33		5	5	-3	46.00	38.00
9	2	2	176.00	190.35		3	3	7	108.00	116.11		11	3	-2	53.00	66.24		6	4	2	65.00	56.05		5	5	-1	55.00	35.26
9	2	3	33.00	29.11		3	3	8	39.00	29.20		11	3	-1	63.00	93.06		6	4	3	94.00	87.52		5	5	0	105.00	102.17
9	2	4	57.00	53.80		3	3	9	50.00	48.05		11	3	0	35.00	31.30		6	4	4	39.00	35.10		5	5	2	59.00	49.55
9	2	5	43.00	93.53		4	3	-11	42.00	17.57		11	3	1	35.00	31.30		6	4	5	27.00	27.44		5	5	4	77.00	100.45
9	2	6	42.00	78.39		4	3	-10	0.00	18.65		11	3	2	50.00	70.05		6	4	6	31.00	58.89		5	5	5	30.00	43.54
10	2	-10	48.00	44.23		4	3	-9	107.00	97.99		12	3	-7	41.00	48.38		7	4	-9	52.00	30.31		5	5	-7	23.00	28.99
10	2	-9	64.00	56.26		4	3	-8	49.00	39.12		12	3	-6	42.00	52.89		7	4	-8	67.00	53.81		6	5	-6	51.00	54.74
10	2	-8	36.00	38.60		4	3	-7	86.00	64.77		12	3	-4	26.00	33.57		7	4	-7	42.00	28.44		6	5	-5	54.00	60.81
10	2	-7	136.00	131.92		4	3	-6	82.00	96.35		12	3	-3	56.00	58.72		7	4	-6	91.00	97.52		6	5	-3	117.00	117.74
10	2	-6	73.00	61.73		4	3	-5	184.00	196.67		12	3	-2	67.00	110.46		7	4	-5	59.00	46.18		6	5	-1	84.00	91.17
10	2	-5	190.00	175.74		4	3	-4	69.00	72.31		12	3	-2	37.00	41.64		7	4	-4	111.00	107.42		6	5	0	85.00	93.43
10	2	-4	90.00	77.08		4	3	-3	61.00	63.08		12	3	-1	45.00	55.19		7	4	-3	127.00	127.58		6	5	1	54.00	62.35
10	2	-3	79.00	70.11		4	3	-2	155.00	148.54		12	3	0	32.00	51.60		7	4	-2	57.00	60.64		6	5	3	43.00	49.21
10	2	-2	111.00	91.36		4	3	-1	215.00	222.61		12	3	1	37.00	71.56		7	4	-1	84.00	74.55		6	5	3	15.00	41.72
10	2	-1	90.00	86.83		4	3	0	60.00	64.54		13	3	-5	40.00	60.70		7	4	0	31.00	30.20		6	5	4	36.00	51.04
10	2	0	132.00	101.50		4	3	1	86.00	90.95		13	3	-4	46.00	75.74		7	4	1	44.00	32.13		0	6	1	76.00	78.95
10	2	1	78.00	84.11		4	3	2	140.00	148.22		13	3	-2	40.00	75.74		7	4	2	27.00	45.06		0	6	2	27.00	32.13
10	2	2	48.00	55.48		4	3	3	86.00	85.07		0	4	1	96.00	83.63		7	4	3	44.00	45.30		0	6	3	50.00	57.17
10	2	3	33.00	30.22		4	3	4	73.00	75.71		0	4	1	102.00	100.59		7	4	4	44.00	48.16		0	6	4	21.00	33.79
10	2	4	60.00	79.50		4	3	5	63.00	56.85		0	4	2	90.00	81.31		7	4	5	37.00	60.46		0	6	5	7.00	34.76
10	2	5	30.00	43.05		4	3	6	37.00	37.16		0	4	3	170.00	196.37		8	4	-9	91.00	71.44		1	6	-5	21.00	45.54
11	2	-10	42.00	84.15		4	3	7	42.00	35.68		0	4	4	90.00	73.90		8	4	-8	56.00	45.06		1	6	-2	35.00	20.64
11	2	-9	24.00	35.54		4	3	8	18.00	11.57		0	4	5	73.00	67.19		8	4	-7	82.00	79.87		1	6	-1	73.00	56.08
11	2	-7	40.00	29.08		5	3	-10	26.00	24.99		0	4	6	94.00	94.95		8	4	-6	36.00	23.94		1	6	1	79.00	81.51
11	2	-6	48.00	43.60		5	3	-9	44.00	22.99		0	4	7	90.00	83.71		8	4	-5	80.00	70.16		1	6	3	67.00	57.12
11	2	-5	157.00	163.54		5	3	-8	32.00	24.04		0	4	8	91.00	74.31		8	4	-4	64.00	49.80		1	6	4	66.00	64.30
11	2	-4	90.00	86.10		5	3	-7	92.00	83.83		1	4	-9	31.00	25.38		8	4	-3	92.00	72.25		2	6	-4	28.00	24.43
11	2	-3	37.00	29.12		5	3	-6	133.00	137.89		1	4	-9	98.00	105.24		8	4	-2	32.00	29.82		2	6	-3	52.00	57.86
11	2	-2	39.00	39.88		5	3	-5	54.00	37.07		1	4	-8	60.00	33.04		8	4	-1	95.00	93.79		2	6	-1	34.00	35.64
11	2	-1	148.00	142.91		5	3	-4	90.00	94.11		1	4	-7	68.00	57.99		8	4	0	76.00	79.05		2	6	0	38.00	30.61
11	2	0	111.00	93.58		5	3	-3	154.00	134.32		1	4	-6	26.00	31.25		8	4	1	75.00	66.93		2	6	2	44.00	51.79
11	2	1	40.00	38.60		5	3	-2	127.00	129.63		1	4	-5	177.00	191.74		8	4	2	48.00	53.04		2	6	3	26.00	33.95
11	2	2	63.00	91.83		5	3	-1	47.00	41.64		1	4	-4	113.00	124.93		8	4	4	44.00	49.78		2	6	4	44.00	46.96
11	2	3	42.00	52.29		5	3	0	118.00	127.75		1	4	-3	216.00	232.55		9	4	-7	35.00	41.20		3	6	-5	12.00	15.73
11	2	4	24.00	27.01		5	3	1	82.00	90.37		1	4	-2	61.00	48.35		9	4	-6	61.00	69.60		3	6	-4	21.00	20.27
12	2	-9	29.00	44.20		5	3	2	164.00	184.35		1	4	-1	190.00	216.27		9	4	-5	30.00	28.76		3	6	0	79.00	82.14
12	2	-8	46.00	51.60		5	3	3	31.00	42.18		1	4	0	136.00	148.54		9	4	-4	41.00	61.07		3	6	1	28.00	28.29
12	2	-7	59.00	70.65		5	3	4	31.00	33.16		1	4	1	41.00	61.07		9	4	-3	93.00	94.25		3	6	2	32.00	26.33
12	2	-6	34.00	37.54		5	3	5	95.00	102.00		1	4	2	89.00	88.26		9	4	-2	59.00	65.14		3	6	3	24.00	31.37
12	2	-5	50.00	59.59		5	3	7	81.00	87.84		1	4	3	79.00	67.99		9	4	-1	105.00	104.50		3	6	3	32.00	57.65
12	2	-4	52.00	54.97		5	3	7	37.00	45.22		1	4	4	107.00	110.98		9	4	0	25.00	29.50		4	6	-5	24.00	35.28
12	2	-3	64.00	55.02		5	3	8	19.00	20.79		1	4	5	66.00	65.01		9	4	1	65.00	69.88		4	6	-4	27.00	22.74
12	2	-2	99.00	108.89		6	3	-10	60.00	50.10		1	4	6	62.00	56.02		9	4	3	74.00	91.68		4	6	-3	53.00	55.36
12	2	0	52.00	36.67		6	3	-9	31.00	10.69		1	4	7	44.00	46.19		9	4	3	9.00	15.84		4	6	-2	15.00	34.68
12	2	-2	25.00	51.70		6	3	-8	86.00	81.09		1	4	8	89.00	77.73		10	4	-7	22.00	24.30		4	6	0	22.00	26.87
13	2	-7	39.00	34.36		6	3	-7	68.00	62.98		2	4	-9	73.00	39.07		10	4	-5	25.00	14.66		4	6	1	71.00	78.80
13	2	-6	25.00	31.35		6	3	-6	125.00	126.16		2	4	-8	81.00	59.91		10	4	-4	88.00	105.79		4	6	-3	31.00	29.45
13	2	-5	81.00	97.09		6	3	-5	127.00	123.98		2	4	-7	69.00	72.56		10	4	-2	53.00	21.23		4	6	-4	22.00	29.45
13	2	-4	82.00	57.37		6	3	-4	126.00	116.93		2	4	-6	42.00	44.51		10	4	-2	8.00	6.63		5	6	-4	33.00	39.53
13	2	-3	61.00	61.44		6	3	-3	27.00	10.65		2	4	-5	77.00	56.41		10	4	-1	34.00	22.55		5	6	-3	27.00	27.01
13	2	-2	42.00	43.02		6	3	-2	163.00	163.59		2	4	-4	77.00	64.36		10	4	0	33.00	47.63		5	6	-2	43.00	51.04
13	2	-1	33.00	27.90		6	3	-1	119.00	116.64		2	4	-3	136.00	145.08		10	4	1	46.00	53.00		5	6	-1	26.00	33.39
13	2	0	25.00	31.54		6	3	0	34.50	11.02		2	4	-2	120.00	115.45		10	4	2	19.00	15.49		5	6	0	35.00	31.50
14	2	-5	18.00	34.52		6	3	1	52.00	44.03		2	4	-1	91.00	75.46		11	4	-6	35.00	63.16		5	6	-3	22.00	40.74
14	2	-4	44.00	69.30		6	3	2	56.00	34.35		2	4	0	23.00	12.29		11	4	-5	27.00	41.38		5	6	-2	27.00	38.58
14	2	-3	36.00	56.17		6	3	3	41.00	47.04		2	4	1	46.00	47.55		11	4	-4	13.00	23.64		0	7	-1	34.00	67.28

Table 2. *Positional and vibrational parameters*

The numerals in parentheses are 10^4 times the estimated standard deviations of the positional parameters. The vibrational parameters, $\bar{U}$, are mean square vibration amplitudes (Å^2), with estimated standard deviations ~ 0.002. The hydrogen parameters are those used in the structure factor calculation; they have not been refined.

	x	y	z	$\bar{U}$
S(1)	0·0947 (3)	1·1768*	0·1199 (4)	†
S(11)	0·9194 (3)	0·6101 (10)	0·3244 (5)	†
C(3)	0·1960 (9)	1·0123 (23)	0·2892 (11)	0·030
C(13)	0·8370 (10)	0·9005 (22)	0·2770 (11)	0·028
C(2)	0·3286 (8)	0·9912 (19)	0·2968 (9)	0·020
C(12)	0·6969 (8)	0·8745 (19)	0·2145 (9)	0·018
C(1)	0·3439 (8)	0·8840 (18)	0·1571 (9)	0·016
C(11)	0·6454 (8)	0·7849 (19)	0·3317 (9)	0·016
N(1)	0·3918 (7)	1·2455 (16)	0·3299 (8)	0·016
N(11)	0·6437 (7)	1·1261 (18)	0·1563 (8)	0·022
O(1)	0·3970 (6)	1·0079 (15)	0·0857 (7)	0·020
O(11)	0·6253 (6)	0·9523 (15)	0·4154 (7)	0·022
O(2)	0·3004 (6)	0·6629 (17)	0·1203 (7)	0·031
O(12)	0·6260 (7)	0·5519 (17)	0·3405 (8)	0·031
H	0·383	0·833	0·370	0·018
H	0·163	0·787	0·270	0·018
H	0·173	0·080	0·345	0·018
H	0·677	0·773	0·125	0·018
H	0·867	0·987	0·325	0·018
H	0·877	0·987	0·185	0·018

* y of S(1) was not refined, since the origin along y is defined by it.
† Anisotropic vibration parameters of sulphur, relative to the crystallographic axes:

	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
S(1)	0·0300	0·0653	0·0573	−0·0065	0·0119	0·0024
S(11)	0·0468	0·0614	0·0880	0·0182	0·0317	0·0133
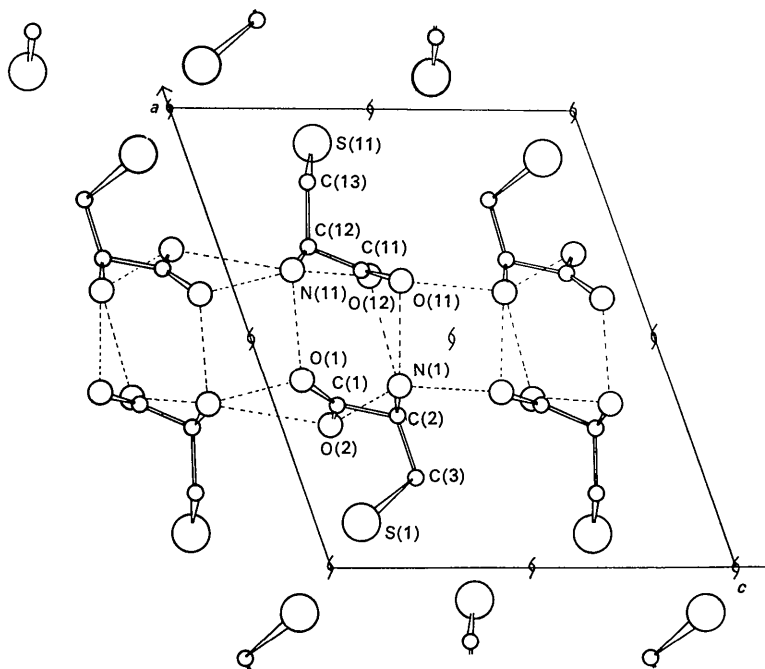
Fig. 1. The structure seen along the b axis.

Crystal data

L-Cysteine, $C_3H_7NO_2S$, M.W.121. Monoclinic needles, elongated along b. $a=11\cdot51\pm0\cdot01$, $b=5\cdot240\pm0\cdot005$, $c=9\cdot517\pm0\cdot01$ Å, $\beta=109°8'$, $V=542\cdot4$ Å³. $D_m=1\cdot483$ (by flotation), $Z=4$, $D_{calc}=1\cdot483$. Space group $P2_1$. Cu $K\alpha$ radiation, $\mu=61\cdot1$ cm⁻¹.

Experimental

Cell dimensions were determined from $h0l$ and $0kl$ Weissenberg photographs calibrated with copper powder lines $(a=3\cdot615$ Å). The intensities of 1239 re-flexions were estimated visually from multiple-film Weissenberg photographs of the layers $h0l$ to $h4l$ and $0kl$ to $6kl$ of crystals with cross section dimensions $\sim0\cdot2$ mm. Lorentz and polarization corrections, and a spot-shape correction (Phillips, 1956) were applied, and all the intensities placed on a common scale. 84 reflexions within these layers were too weak to observe. Although the layers $7kl$ to $9kl$ were recorded, the re-flexions were very blurred; we presume that this crys-tal was decomposing – by air oxidation to cystine. This decomposition slightly affected the layers $5kl$ and $6kl$, but elsewhere the reflexions were sharp, with no blurring and no suggestion of disorder.

Table 3. *Interatomic distances, bond angles, and angles between planes*

Bond lengths

					σ
S(1)–C(3)	1·86 Å		S(11)–C(13)	1·77 Å	0·012
C(3)–C(2)	1·51		C(13)–C(12)	1·53	0·014
C(2)–C(1)	1·51		C(12)–C(11)	1·50	0·013
C(2)–N(1)	1·50		C(12)–N(11)	1·48	0·012
C(1)–O(1)	1·24		C(11)–O(11)	1·26	0·012
C(1)–O(2)	1·27		C(11)–O(12)	1·25	0·012

Bond angles $(\sigma=0\cdot8-0\cdot9°)$

S(1)–C(3)–C(2)	114·4°	S(11)–C(13)–C(12)	115·5°
C(3)–C(2)–C(1)	113·2	C(13)–C(12)–C(11)	111·2
C(2)–C(1)–O(1)	120·7	C(12)–C(11)–O(11)	116·9
C(2)–C(1)–O(2)	115·8	C(12)–C(11)–O(12)	118·6
C(3)–C(2)–N(1)	111·0	C(13)–C(12)–N(11)	108·6
C(1)–C(2)–N(1)	109·1	C(11)–C(12)–N(11)	109·9
O(1)–C(1)–O(2)	123·4	O(11)–C(11)–O(12)	124·5

Hydrogen bonds and close contacts between charged groups

N(1)···O(11)	at	$x,$	$y,$ z	2·97 Å
N(1)···O(11)	at	$1-x, \frac{1}{2}+y,$	$1-z$	2·72
N(1)···O(2)	at	$x, 1+y,$	z	2·91
N(1)···O(12)	at	$x, 1+y,$	z	3·11
N(11)···O(1)	at	$x,$	$y,$ z	2·77
N(11)···O(12)	at	$x, 1+y,$	z	2·89
N(11)···O(1)	at	$1-x, \frac{1}{2}+y,$	$-z$	2·97
N(11)···O(2)	at	$1-x, \frac{1}{2}+y,$	$-z$	2·91

Environment of sulphur atoms

S(1)···S(1)	at	$-x, \pm\frac{1}{2}+y,$	$-z$	3·68 Å (two)
S(1)···S(11)	at	$-1+x,$	$y,$ z	4·38
S(1)···S(11)	at	$-1+x,$ $1+y,$	z	3·95
S(1)···O(2)	at	$x,$ $1+y,$	z	3·48
S(11)···S(11)	at	$2-x, \pm\frac{1}{2}+y,$	$1-z$	4·17 Å (two)
S(11)···S(1)	at	$1+x,$	$y,$ z	4·38
S(11)···S(1)	at	$1+x,$ $1+y,$	z	3·95
S(11)···O(12)	at	$x,$	$y,$ z	3·44 (intramolecular)

Other intermolecular distances less than 3·3 Å

C(2)····O(11)	3·23 Å
C(11)···O(1)	3·26

Dihedral angles, between planes of

O(1), C(1), C(2)	and	C(1), C(2), N(1)	$-3\cdot0°$	$\psi2*$
O(11), C(11), C(12)	and	C(11), C(12), N(11)	$-36\cdot1$	$\psi2$
N(1), C(2), C(3)	and	C(2), C(3), S(1)	72·6	$\chi1*$
N(11), C(12), C(13)	and	C(12), C(13), S(11)	$-170\cdot1$	$\chi1$
C(1), C(2), C(3)	and	C(2), C(3), S(1)	$-50\cdot5$	
C(11), C(12), C(13)	and	C(12), C(13), S(11)	67·6	

* The signs, and symbols $\psi2, \chi1$ correspond to those used by Lakshminarayan, Sasikheran & Ramachandran (1967).

Solution and refinement of the structure

There are two cysteine molecules in the asymmetric unit. Solution of the structure from the three-dimensional sharpened Patterson series was not entirely straightforward. One sulphur atom was found correctly but the vector peaks from which a second position was deduced apparently arose from chance coincidences of oxygen vectors. The correct position for the second sulphur atom was found only after several electron-density distributions and Patterson superposition functions had been calculated. The remaining non-hydrogen atoms were located, and their positions adjusted by difference Fourier series until R reached 0·33.

Some refinement was done with a least-squares program using the block-diagonal approximation, but on account of the near special relationship between the two molecules in the asymmetric unit (see discussion) this approximation was poor. This refinement converged with $R=0·15$ and indicated some unreasonably anisotropic vibrations and unreasonable bond lengths. A difference electron density series calculated at this stage showed, by peaks and hollows of magnitude up to 2 e.Å^{-3} near sulphur and 1 e.Å^{-3} near other atoms, that the positional and vibrational parameters were still not quite correct; but there were no other features greater than 0·75 e.Å^{-3}. Subsequently the full-matrix least-squares program of Busing, Martin & Levy (1962) was used. Six hydrogen atoms were included in the structure factor calculations but their positions were not refined. Form factors were taken from *International Tables for X-ray Crystallography* (1962); the real part of the anomalous dispersion correction was made to that of sulphur; the oxygen atoms were treated as $O^{1/2-}$. For weighting purposes $\sigma(|F|)$ was taken as 0·025 $|F|$ when $|F| \geq 80$ and $160/|F|$ when $|F| < 80$, except that reflexions with $k=0$ or $k>4$ were given twice these σ values since their measurements seemed less reliable. Assuming isotropic vibration for all atoms

except sulphur the parameters converged, with $R=$ 0·127; the largest shift in the last cycle was two-thirds of the corresponding standard deviation, estimated from the least-squares matrix.

Results and discussion

Observed and calculated structure amplitudes are given in Table 1, positional and vibrational parameters in Table 2, and interatomic distances and angles in Table 3. The structure is illustrated in Figs. 1 and 2.

The two cysteine molecules in the asymmetric unit have different conformations, as shown by the dihedral angles in Table 3. The signs, and the names $\psi 2$ and $\chi 1$ correspond to those used by Lakshminarayanan, Sasisekharan & Ramachandran (1967), with whose tabulated data on amino acid conformations the present values may be compared. In the second molecule (atoms with numbers greater than 10) the C–N bond is twisted out of the plane of the carboxyl group so that N(11) is 0·82 Å from this plane, whereas in the first molecule N(1) is only 0·08 Å from the plane. However, both these torsion angles about C–C$_\alpha$ lie within the range found in other amino acids. Further, the first molecule has the more common *cis* conformation around the bond C(2)–C(3) already found in L-cystine and various derivatives whereas in the second molecule S(11) is *trans* with respect to N(11). Presumably this allows a more satisfactory packing in the crystal lattice. Perhaps it is significant that S(1) makes a close intermolecular contact, 3·48 Å, with an O(2) whereas S(11) is able to make a close intramolecular contact, of 3·44 Å, with O(12). Some (0·02 Å) of the large difference between the C–S bond lengths, which lie on either side of the expected value, may be due to a 'polar dispersion error' (Cruickshank & McDonald, 1967) in the sulphur coordinates. No other explanation can be found, but we think it must be the result of some systematic error in the data, rather than a real difference between the molecules. Otherwise the bond lengths in the two molecules are not significantly different from each other or from those in analogous compounds.

The molecules are arranged in the crystal lattice in layers parallel to (100); on one side of the layer are $-COO^-$ and $-NH_3^+$ groups, held by hydrogen bonds and electrostatic interaction to similar groups in the adjacent layer. On the other side are the $-SH$ groups, each of which makes van der Waals contacts with other sulphur atoms (Table 3).

Within the asymmetric unit there is an approximate twofold symmetry axis, along $\frac{1}{2},y,\frac{1}{4}$, relating all the atoms, except sulphur, of the first molecule to those of the second molecule. In the *b*-axis projection the average deviation from this extra twofold symmetry is 0·4 Å, and the sulphur atoms are consistent with it; the second molecule is displaced $\sim$0·5 Å down the
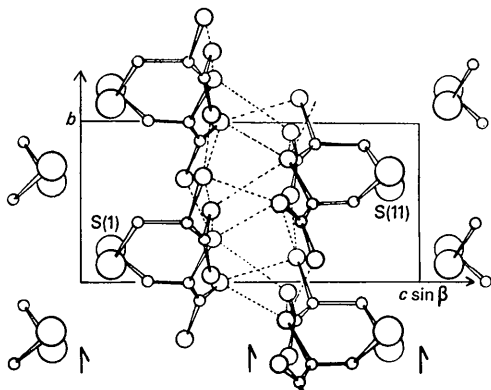

Fig. 2. The structure seen along the *c* axis.

b direction relative to the first, but its sulphur atom is displaced by $b/2+0\cdot3$ Å. These relationships are probably responsible for the difficulties encountered in solving and refining the structure.

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The Crystal Structures of Niobium(III) Selenide and Tantalum(III) Selenide

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The crystal structures of the monoclinic phases Nb_2Se_3 ($a=6\cdot503$, $b=3\cdot434$, $c=9\cdot215$ Å; $\beta=103\cdot39°$) and Ta_2Se_3 ($a=6\cdot495$, $b=3\cdot408$, $c=9\cdot206$ Å; $\beta=103\cdot63°$) have been determined and refined from single-crystal data. All atoms are in the special position $2(e)$: $\pm(x\frac{1}{4}z)$ of space group $P2_1/m$. The metal atoms are in octahedral holes of a *chh* close packing of selenium, but the structures are deformed in such a way that zigzag metal–metal chains are formed. These chains are of two kinds; the metal–metal distances in half of the chains are comparable to those in the pure metals, in the other half of the chains the distances are considerably longer. In the isotypic phase Mo_2S_3 short metal–metal distances are found in all chains.

The phases Nb_2Se_3 and Ta_2Se_3

In our study of the system Nb–Se (*cf.* Selte, Bjerkelund & Kjekshus, 1966) we found needle-shaped crystals of a new phase (together with polycrystalline material of the same phase) in samples of compositions around Nb_2Se_3 that had been prepared by heating the mixed elements at 1000–1200°C, followed by quenching to room temperature (Huisman, Kadijk & Jellinek, 1967). Weissenberg diagrams showed the phase to crystallize in the monoclinic system, the needle axis coinciding with the b axis. In a sample of composition $Nb_{1\cdot35}Se_2$ the new phase was contaminated by Nb_3Se_4 (Selte & Kjekshus, 1964a), while a sample of composition $Nb_{1\cdot33}Se_2$ contained a trace of $2s(a)$-$Nb_{1+x}Se_2$ (Kadijk, Huisman & Jellinek, 1964; Selte & Kjekshus, 1964b) in addition to the new phase. The unit-cell dimensions of the new phase were not significantly different in the two samples. This indicates that the homogeneity range of the new phase is very narrow and that its composition is very close to Nb_2Se_3. The phase is a metallic conductor.

Needles of the corresponding tantalum selenide Ta_2Se_3, together with polycrystalline material, were obtained by heating the mixed elements at 1140°C and quenching to room temperature (Huisman *et al.*, 1967). The unit-cell dimensions determined at room temperature from diffractometer data with the use of Cu $K\alpha$ radiation ($\lambda\alpha_1 = 1\cdot54050$ Å) and silicon ($a=5\cdot4306$ Å) as internal standard are:

Nb_2Se_3 $a=6\cdot503$, $b=3\cdot434$, $c=9\cdot215$ Å; $\beta=103\cdot39°$

Ta_2Se_3 $a=6\cdot495$, $b=3\cdot408$, $c=9\cdot206$ Å; $\beta=103\cdot63°$.

Assuming unit-cell contents of Nb_4Se_6 and Ta_4Se_6 the densities are calculated as $7\cdot012$ g.cm^{-3} and $10\cdot040$ g.cm^{-3} respectively, which are reasonable values.

The phases Nb_2Se_3 and Ta_2Se_3 may correspond to γ-$Nb_{1\cdot3}Se_2$ and γ-$Ta_{1\cdot3}Se_2$ mentioned by Revolinsky, Brown, Beerntsen & Armitage (1965), although the latter phases were thought to possess layer-like structures.

Structure determination

The axial ratio $a:b:c$ and the angle β of Nb_2Se_3 and Ta_2Se_3 are very similar to those of monoclinic Mo_2S_3 (Jellinek, 1961, 1963) as is evident from the following table: