to other factors. The preparation described in the *Experimental* section has independently confirmed the existence of α-WCl_6.

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Precision Neutron Diffraction Structure Determination of Protein and Nucleic Acid Components.

XIV. Crystal and Molecular Structure of the Amino Acid L-Cystine Dihydrochloride*

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A neutron diffraction study of L-cystine dihydrochloride, $C_6H_{12}S_2N_2O_4.2HCl$, has been carried out. The structure is monoclinic, space group $C2$; $a=18{\cdot}595$ (6), $b=5{\cdot}243$ (2), $c=7{\cdot}231$ (3) Å, $\beta=103{\cdot}738$ (9)°; $Z=2$. The structure has been refined by full-matrix least-squares techniques with a type II anisotropic extinction correction; the conventional R value is 0·034. All atoms have been located with a precision of better than 0·006 Å. The C–S–S–C torsion angle is −81·7 (2)°. Comparisons of the geometries of 15 molecules containing aliphatic C–S–S fragments show that the S–S and C–S bond lengths decrease as the magnitude of the C–S–S–C torsion angle increases from 0 to 90°. The L-cystine.2HCl structure is stabilized by a three-dimensional network of one O–H···Cl bond and three N–H···Cl hydrogen bonds. Normal probability plots and χ^2 tests have been employed to compare atomic coordinates and temperature parameters from this study with those obtained in an independent neutron diffraction investigation [Gupta, Sequeira & Chidambaram (1974). *Acta Cryst.* B**30**, 562–567]. These comparisons indicate that there are significant differences between the two studies. The errors are normally distributed and pooled standard deviations are underestimated by a factor of 1·4–1·6.

Introduction

A neutron diffraction study of L-cystine dihydrochloride has been carried out as part of a series of investigations of amino acids, small peptides, nucleosides and nucleotides. The aim of this work is to provide precise information about hydrogen-atom stereochemistry and hydrogen bonding in such systems.

The structure of L-cystine dihydrochloride has previously been studied by X-ray diffraction techniques (Steinrauf & Jensen, 1956; Steinrauf, Peterson & Jensen, 1958). After completing the present work, we learned of a similar independent study by Gupta, Sequeira & Chidambaram (1974).

Crystal data

L-Cystine dihydrochloride,
$C_6H_{12}S_2N_2O_4.2HCl$; F.W. 313·23.

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Monoclinic; $a = 18{\cdot}595$ (6), $b = 5{\cdot}243$ (2), $c = 7{\cdot}231$ (3) Å, $\beta = 103{\cdot}738$ (9)°.
Space group $C2$; $Z = 2$.
Density $\varrho_{\text{calc}} = 1{\cdot}518$, $\varrho_{\text{obs}} = 1{\cdot}520$ g cm^{-3} (Steinrauf & Jensen, 1956).
Absorption coefficient $\mu = 1{\cdot}75$ cm^{-1}.

Experimental

Large single crystals of L-cystine dihydrochloride were grown by evaporation of aqueous 1*M* hydrochloric acid saturated with L-cystine. The crystals are colorless prisms elongated in the **b** direction with major bounding planes {100} and {001}. A sample 5·70 mm^3 in volume and with maximum and minimum linear dimensions 2·8 and 1·3 mm was selected for data collection and mounted on a four-circle diffractometer at the Brookhaven High-Flux Beam Reactor. Unit-cell constants $a = 18{\cdot}62$ (1), $b = 5{\cdot}249$ (6), $c = 7{\cdot}239$ (5) Å and $\beta = 103{\cdot}72$ (3)° were obtained by least-squares techniques from the observed diffractometer setting angles for 28 reflections well distributed in reciprocal space. The neutron wavelength was found to be $\lambda = 1{\cdot}0142$ (3) Å, based on KBr ($a = 6{\cdot}600$ Å) as a standard. Our cell parameters agree to within 0·2 %with those obtained by Gupta *et al.* (1974). The two sets of cell constants were averaged and the weighted mean values (see *Crystal data*) are used in the following discussion.

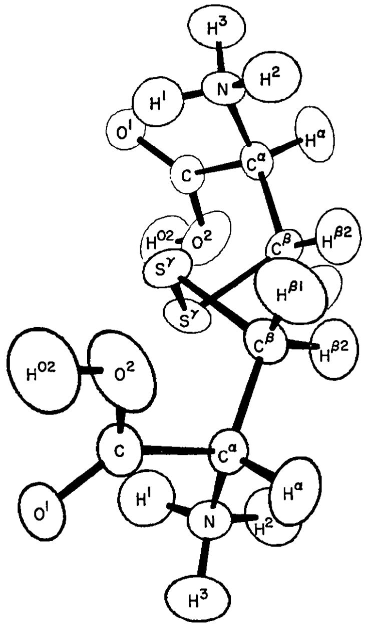

Fig. 1. L-Cystine dication with standard atomic nomenclature.

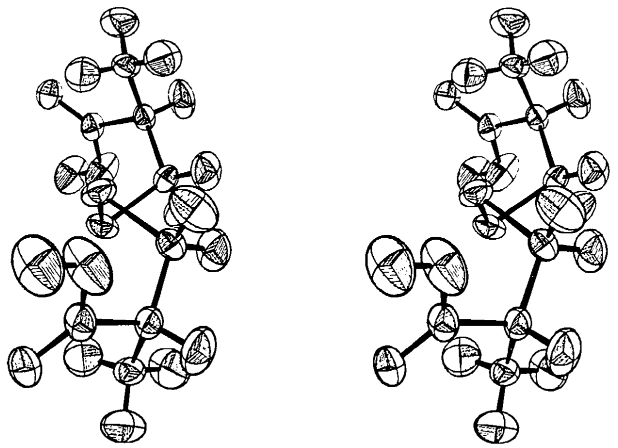

Fig. 2. Stereoview of the L-cystine molecule.

Intensities of Bragg reflections were measured automatically under the Multi-Spectrometer Control System (Beaucage, Kelley, Ophir, Rankowitz, Spinrad & van Norton, 1966) with a θ–2θ step-scanning technique. Intensities were measured for 2192 reflections with $d^* < 1{\cdot}36$ Å^{-1} and were corrected for background by a method described by Lehmann, Hamilton & Larsen (1972). An absorption correction computed by numerical integration over a Gaussian grid was applied to the observed intensities. The linear absorption coef-

Table 1. *Fractional coordinates and temperature parameters* (× 10^4)

The Debye–Waller factor is given by exp $\{-2\pi^2[u_{11}(ha^*)^2 + u_{22}(kb^*)^2 + u_{33}(lc^*)^2 + 2u_{12}(ha^*kb^*) + 2u_{13}(ha^*lc^*) + 2u_{23}(kb^*lc^*)]$.

	x	y	z	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Cl	0·15332 (4)	0·08900 (27)	0·88532 (12)	401 (4)	436 (4)	481 (4)	85 (4)	173 (3)	206 (4)
O^1	0·19402 (7)	0·26764 (34)	0·42896 (21)	420 (7)	341 (7)	534 (8)	102 (6)	108 (6)	159 (7)
O^2	0·12009 (11)	0·48264 (47)	0·57551 (22)	906 (12)	623 (11)	389 (8)	337 (11)	276 (8)	199 (9)
N	0·17721 (4)	0·60165 (27)	0·14240 (27)	264 (3)	361 (5)	513 (5)	39 (4)	139 (3)	184 (5)
C	0·15602 (5)	0·44890 (28)	0·44246 (15)	326 (5)	291 (5)	311 (5)	23 (5)	−18 (4)	66 (5)
C$^\alpha$	0·14491 (5)	0·67206	0·30437 (15)	255 (4)	237 (5)	341 (5)	−14 (4)	−21 (4)	44 (4)
C$^\beta$	0·06419 (5)	0·75062 (29)	0·23899 (15)	294 (5)	297 (5)	318 (5)	60 (5)	47 (4)	29 (4)
S$^\gamma$	0·00024 (12)	0·50000 (60)	0·14107 (38)	216 (9)	434 (15)	452 (13)	−44 (11)	35 (10)	113 (13)
H^1	0·15703 (15)	0·43272 (65)	0·07636 (40)	585 (14)	538 (18)	541 (14)	0 (15)	239 (12)	1 (14)
H^2	0·16692 (15)	0·74598 (66)	0·03978 (42)	635 (15)	625 (18)	676 (17)	161 (14)	315 (13)	352 (15)
H^3	0·23350 (11)	0·57804 (69)	0·18176 (44)	326 (11)	677 (19)	991 (22)	48 (13)	161 (12)	176 (18)
H$^\alpha$	0·17717 (13)	0·83220 (56)	0·37921 (40)	514 (13)	359 (12)	711 (18)	−109 (11)	−130 (12)	−2 (12)
H$^{\beta1}$	0·04571 (15)	0·82595 (68)	0·36211 (36)	688 (15)	728 (19)	502 (15)	189 (16)	175 (13)	−99 (14)
H$^{\beta2}$	0·05839 (13)	0·90970 (51)	0·13581 (37)	535 (12)	412 (13)	574 (14)	58 (11)	0 (11)	175 (12)
H^{02}	0·12953 (17)	0·34000 (68)	0·66906 (41)	877 (19)	693 (19)	465 (14)	213 (17)	178 (13)	189 (15)

ficient was calculated with an incoherent scattering cross section for hydrogen of 40b, and transmission coefficients ranged from 0·71 to 0·81.

Squared observed structure factors were obtained as $F_o{}^2 = I \sin 2\theta$ and were averaged for symmetry-related reflections. The agreement index is $R_c = \sum|F_o^2 - \bar{F}_o^2|/\sum F_o^2 = 0{\cdot}049$, where $\bar{F}_o^2$ is the mean value for the symmetry-related reflections. Of 1043 unique reflections measured, 121 reflections with $\bar{F}_o^2 < 3\sigma_{\text{count}}(\bar{F}_o^2)$ were omitted from subsequent refinements.

Table 2. *Observed and calculated squared structure factors.*

The columns are h, l, $100F_o^2$, $100\sigma(F_o^2)$, $100|F_c|^2$. The extinction correction has been applied to F_o^2.

H	L	FO	SIG	FC
*** K= -7 ***				
-5	1	330	69	194
-5	2	287	38	262
-3	-2	215	53	239
-3	-1	58	19	59
-1	-2	287	59	281
-1	-1	144	28	173
-1	2	169	44	192
1	-2	154	37	192
1	1	150	29	173
3	-1	184	37	113
5	-2	332	59	262
5	-1	313	46	194
*** K= -6 ***				
-14	0	110	37	222
-12	-1	457	58	336
-12	0	210	37	231
-12	1	316	36	323
-12	3	140	32	138
-12	4	91	10	7
-10	-1	261	30	228
-10	1	1047	83	987
-10	2	76	29	12
-10	3	361	32	359
-10	4	151	33	156
-8	-2	439	47	407
-8	-1	503	37	410
-8	0	1595	83	1576
-8	4	526	78	454
-6	-4	1797	84	1650
-6	-3	421	53	390
-6	-2	438	36	428
-6	-1	637	35	593
-6	0	361	28	328
-6	1	724	36	725
-6	2	267	28	253
-6	3	560	39	542
-6	4	405	53	401
-4	-4	1011	61	925
-4	-3	2447	78	2253
-4	-2	295	29	257
-4	-1	562	68	540
-4	0	136	59	136
-4	4	1739	73	1630
-4	5	165	29	159
-2	-5	147	42	104
-2	-4	3818	228	3527
-2	0	257	67	257
-2	1	145	64	166
-2	2	767	36	734
-2	3	517	42	500
-2	4	571	142	494
-2	5	178	55	186
0	-5	59	19	59
0	-4	238	32	236
0	-3	584	71	578
0	-2	241	32	212
0	-1	61	24	93
0	0	1570	51	1508
0	1	77	24	93
0	2	242	30	212
0	3	513	33	578
0	4	304	37	236
2	-5	183	34	186
2	-4	459	32	494
2	-3	554	35	500
2	-2	761	37	734
2	-1	172	27	166
2	0	265	24	257
2	4	3642	102	3527
4	-5	171	34	159
4	-4	1638	58	1630
4	0	46	20	136
4	1	562	31	540
4	2	250	49	257
4	3	2456	75	2253
4	4	923	47	925
6	-4	366	31	401
6	-3	606	110	542
6	-2	300	27	253
6	-1	734	54	725
6	0	329	26	328
6	1	632	50	593
6	2	472	42	428
6	3	453	39	390
6	4	1736	83	1650
8	-4	411	32	454
8	-3	101	32	161
8	0	1610	56	1576
8	1	395	64	410
8	2	497	59	407
10	-4	155	39	156
10	-3	318	63	359
10	-1	1007	44	987
10	1	230	39	228
12	-3	152	29	138
12	-2	154	28	104
12	-1	340	34	323
12	0	242	32	231
12	1	366	61	336
14	0	257	41	222
*** K= -5 ***				
-17	-1	278	42	198
-17	0	997	75	1001
-17	1	140	28	110
-17	2	173	64	162
-17	3	178	30	161
-17	4	290	48	286
-15	-2	410	38	470
-15	-1	296	52	249
-15	0	88	90	100
-15	1	138	26	87
-15	2	199	26	200
-15	3	140	26	119
-13	-3	136	25	124
-13	-2	113	29	69
-13	-1	999	42	992
-13	0	392	42	338
-13	1	178	27	160
-13	2	285	27	313
-13	3	92	63	162
-13	4	466	39	418
-13	5	147	66	115
-13	6	762	59	658
-11	-4	93	20	90
-11	-3	193	32	155
-11	-1	308	24	334
-11	0	582	29	537
-11	2	1132	106	1159
-11	3	516	66	544
-11	4	99	26	77
-11	5	127	25	108
-11	6	299	35	276
-9	-5	393	48	487
-9	-4	333	50	280
-9	-3	355	34	330
-9	-2	54	20	62
-9	0	231	44	186
-9	1	445	46	459
-9	2	525	52	474
-9	3	1381	90	1415
-9	5	211	32	102
-9	6	413	73	436
-7	-5	1964	154	2011
-7	-4	592	42	963
-7	-3	78	25	73
-7	-2	469	55	666
-7	-1	916	34	918
-7	0	2328	169	2171
-7	1	113	20	106
-7	2	2663	69	2796
-7	3	299	30	300
-7	4	268	35	215
-7	6	140	39	124
-7	7	869	72	691
-5	-5	1746	153	1644
-5	-4	392	63	310
-5	-3	628	30	667
-5	-2	887	33	854
-5	-1	521	49	517
-5	0	140	22	106
-5	1	476	34	418
-5	2	1174	53	1198
-5	3	583	28	543
-5	4	217	22	206
-5	5	462	41	420
-5	6	165	30	133
-5	7	515	53	498
-3	-6	199	27	161
-3	-5	429	47	652
-3	-4	486	30	483
-3	-1	2088	78	1980
-3	0	2788	86	2689
-3	1	61	23	41
-3	2	207	19	166
-3	3	508	40	544
-3	4	133	31	80
-3	5	279	34	283
-3	6	590	37	538
-3	7	364	43	386
-1	-6	542	66	679
-1	-5	821	140	781
-1	-4	190	23	173
-1	-3	663	29	708
-1	-2	2332	94	2346
-1	-1	299	22	319
-1	0	453	24	399
-1	1	323	34	354
-1	2	992	38	987
-1	3	130	18	103
-1	4	454	79	397
-1	5	141	66	146
-1	7	1773	83	1708
1	-7	1765	83	1708
1	-6	49	18	48
1	-5	138	30	146
1	-4	388	25	397
1	-3	101	16	103
1	-2	959	44	987
1	-1	369	47	354
1	0	386	29	399
1	1	294	22	319
1	2	2900	73	2346
1	3	755	32	708
1	4	235	24	173
1	5	783	38	781
1	6	559	43	579
3	-7	302	47	385
3	-6	599	36	538
3	-5	249	22	283
3	-4	105	17	80
3	-3	564	27	544
3	-2	178	19	166
3	0	2767	145	2689
3	1	1998	54	1980
3	4	444	65	483
3	5	481	31	552
3	6	220	32	161
5	-7	447	45	496
5	-6	92	25	133
5	-5	331	33	420
5	-4	164	21	206
5	-3	608	28	543
5	-2	1220	94	1198
5	-1	426	70	418
5	0	96	14	106
5	1	509	23	517
5	2	791	46	854
5	3	712	32	667
5	4	322	26	310
5	5	1802	78	1644
7	-7	713	61	691
7	-6	179	29	124
7	-4	200	20	215
7	-3	320	31	300
7	-2	2683	110	2798
7	-1	106	26	106
7	0	2285	91	2171
7	1	916	34	916
7	2	684	70	666
7	3	126	22	73
7	4	976	41	963
7	5	1912	66	2011
9	-7	974	66	987
9	-6	443	103	436
9	-5	104	20	102
9	-3	1478	106	1415
9	-2	470	57	474
9	-1	467	30	469
9	0	174	21	186
9	1	69	19	30
9	2	77	22	62
9	3	368	56	330
9	4	298	99	280
9	5	475	56	487
11	-6	320	36	276
11	-5	107	29	108
11	-4	94	24	77
11	-3	495	30	544
11	-2	1138	62	1199
11	-1	68	20	77
11	0	529	54	537
11	1	339	27	334
11	2	75	20	65
11	3	204	28	155
11	4	165	57	90
13	-6	665	51	658
13	-5	116	29	118
13	-4	469	77	418
13	-3	176	55	162
13	-2	274	29	312
13	-1	187	29	160
13	0	392	30	338
13	1	1054	43	992
13	3	124	29	124
15	-4	218	31	137
15	-3	120	28	119
15	-2	264	35	200
15	-1	138	26	87
15	0	138	31	100
15	1	262	57	249
15	2	509	40	470
17	-4	202	38	286
17	-3	145	38	161
17	-2	176	30	162
17	-1	162	75	110
17	0	950	52	1001
17	1	205	45	198
*** K= -4 ***				
-20	0	133	23	116
-20	1	731	43	766
-20	2	117	23	144
-20	3	442	35	596
-20	4	128	32	80
-18	-2	172	63	191
-18	-1	93	23	71
-18	0	134	28	44
-18	1	854	61	875
-18	2	977	45	896
-18	3	929	44	904
-18	4	94	26	94
-18	5	380	57	496
-18	6	293	43	345
-16	-2	479	35	439
-16	0	1093	56	1124
-16	1	810	104	875
-16	2	140	22	158
-16	3	233	42	214
-16	4	110	32	128
-16	5	182	27	175
-16	6	983	48	981
-14	-4	422	55	459
-14	-3	863	41	888
-14	-2	194	23	203
-14	-1	802	49	639
-14	0	467	26	432
-14	1	358	23	333
-14	2	142	29	163
-14	3	368	55	450
-14	4	136	21	147
-14	5	112	67	130
-14	6	134	63	148
-14	7	238	32	212
-12	-5	127	83	179
-12	-3	121	26	79
-12	-2	753	33	723
-12	-1	165	46	191
-12	0	509	34	540
-12	1	3441	222	3518
-12	2	1935	99	1926
-12	3	291	20	314
-12	4	757	74	887
-12	5	226	22	226
-12	6	619	35	617
-10	-5	160	26	176
-10	-4	695	38	708
-10	-3	43	36	70
-10	-2	610	27	600
-10	-1	893	31	881
-10	0	146	16	188
-10	1	2814	84	2784
-10	2	2928	91	2992
-10	3	393	22	394
-10	4	311	51	319
-10	5	1201	93	1265
-10	6	207	24	197
-10	7	667	71	695
-10	8	746	60	586
-8	-6	1072	151	1165
-8	-5	549	63	516
-8	-4	434	26	426
-8	-3	1327	102	1418
-8	-2	499	53	546
-8	-1	1205	100	1240
-8	0	818	28	850
-8	1	1049	32	1078
-8	2	1396	39	1467
-8	4	432	22	494
-8	6	592	43	628
-8	7	401	63	370
-8	8	490	56	536
-6	-6	799	89	802
-6	-5	99	19	78
-6	-4	266	21	265
-6	-3	778	69	781
-6	-2	2247	136	2220
-6	-1	4700	186	4479
-6	0	1353	72	1295
-6	1	3432	79	3368
-6	2	395	23	370
-6	3	491	29	476
-6	4	613	26	590
-6	5	812	48	792
-6	6	689	75	672
-6	8	665	40	628
-4	-6	114	45	106
-4	-5	34	9	44
-4	-4	652	31	688
-4	-3	762	49	787
-4	-2	1448	98	1494
-4	-1	4324	119	4262
-4	0	332	15	344
-4	1	4120	92	4091
-4	2	589	23	591
-4	3	1933	70	1978
-4	4	119	17	120
-4	5	665	42	635
-4	6	167	27	158
-4	7	118	24	134
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10	1	1462	41	1468
10	2	1502	43	1497
10	3	64	10	87
10	4	4774	126	5001
10	5	1343	54	1372
10	7	239	41	172
12	-9	303	41	325
12	-8	813	49	810
12	-6	91	19	80
12	-5	4974	129	5204
12	-4	2715	74	2734
12	-3	648	26	660
12	-2	3438	84	3447
12	-1	514	20	507
12	0	1181	31	1139
12	1	175	15	179
12	2	7246	172	7504
12	3	5516	141	5525
12	4	167	29	90
12	5	344	32	343
12	6	181	27	177
12	7	373	61	439
14	-8	338	45	236
14	-6	415	31	445
14	-5	277	25	287
14	-3	647	29	626
14	-2	3202	84	3196
14	-1	1562	48	1514
14	0	1688	43	1701
14	1	70	14	35
14	3	316	27	316
14	4	409	33	517
16	-5	2443	80	2527
16	-4	766	38	699
16	-3	165	19	196
16	-2	3270	91	3137
16	-1	1074	42	1124
16	1	118	20	110
16	2	616	35	612
18	-7	583	59	549
18	-6	134	43	96
18	-5	440	39	474
18	-4	66	14	114
18	-3	266	29	225
18	-2	2089	68	2075
18	-1	978	44	981
18	2	2299	81	2306
18	3	339	40	347
20	-6	123	36	76
20	-4	396	36	336
20	-3	301	31	276
20	-1	339	37	287
20	0	750	45	710
20	1	243	31	226
20	3	474	51	419
22	-6	866	61	829
22	-5	433	46	468
22	-4	189	31	111
22	-3	109	29	169
22	-2	1707	72	1668
22	-1	484	36	471
22	1	249	40	208
22	2	929	65	922
24	-2	2342	95	2329
24	-1	483	43	451
24	0	339	67	374
*** K= 1 ***				
-23	-1	396	53	328
-23	0	418	43	420
-23	1	1436	70	1390
-23	2	241	61	168
-23	3	1004	57	1058
-23	4	662	58	720
-23	5	264	39	282
-21	-3	556	54	569
-21	0	85	22	36
-21	1	182	34	182
-21	3	169	20	291
-21	4	385	45	373
-21	6	384	48	303
-19	-4	1145	65	1055
-19	-2	182	30	209
-19	-1	423	24	424
-19	0	271	34	196
-19	1	738	38	748
-19	2	235	26	179
-19	3	92	23	38
-19	4	332	32	365
-19	5	308	33	354
-19	7	495	48	371
-17	-4	1627	75	1666
-17	-3	278	40	163
-17	-1	1356	52	1351
-17	0	1082	43	1008
-17	1	978	40	1046
-17	3	4360	117	4327
-17	4	1058	44	1014
-17	5	261	26	322
-17	6	91	28	96
-17	7	483	44	847
-17	8	879	63	763
-15	-6	322	40	330
-15	-5	480	49	530
-15	-3	287	27	207
-15	-2	134	21	128
-15	-1	439	27	461
-15	0	981	38	987
-15	1	932	37	924
-15	2	2438	70	2382
-15	3	1097	42	1024
-15	4	2347	70	2271
-15	5	327	27	301
-15	6	545	38	515
-15	7	335	40	318
-13	-8	464	45	474
-13	-4	1342	53	1387
-13	-2	1119	43	1070
-13	-1	1402	44	1413
-13	0	795	30	758
-13	1	3044	77	2989
-13	2	185	14	126
-13	3	3137	81	3179
-13	4	88	13	92
-13	5	595	32	587
-13	6	576	37	569
-11	-6	303	31	358
-11	-5	104	25	90
-11	-4	1992	66	2006
-11	-3	2367	69	2238
-11	-2	111	14	97
-11	-1	10116	220	9404
-11	5	107	25	64
-11	6	3249	94	3256
-11	7	690	43	643
-11	8	880	50	768
-11	9	176	81	10
-9	-7	165	31	182
-9	-6	364	35	343
-9	-5	187	23	158
-9	-4	1823	59	1801
-9	-3	194	15	92
-9	6	1817	60	1777
-9	9	201	40	228
-7	-8	784	67	709
-7	-7	634	43	518
-7	-6	1431	55	1541
-7	-5	693	24	699
-7	-4	3474	90	3327
-7	7	269	26	260
-7	8	748	47	773
-5	-8	184	36	90
-5	-7	212	30	257
-5	-6	664	38	632
-5	-5	2830	81	2780
-5	8	223	29	194
-3	-8	581	45	650
-3	-7	808	46	825
-3	-6	1535	55	1543
-3	8	384	35	258
-3	9	210	49	88
-1	-7	563	34	589
-1	9	155	31	142
1	-9	216	62	142
3	-8	275	29	258
3	9	204	40	144
5	-9	168	48	41

Structure refinement

The starting parameters for the full-matrix least-squares refinement were the coordinates from the X-ray study (Steinrauf *et al.*, 1958). Neutron scattering lengths were taken to be $b_S = 0{\cdot}2847$, $b_{Cl} = 0{\cdot}9584$, $b_O = 0{\cdot}575$, $b_N = 0{\cdot}920$, $b_C = 0{\cdot}6626$ and $b_H = -0{\cdot}3723$ (all $\times 10^{-12}$ cm). These are the values given by Shull (private communication) except for the nitrogen scattering length, which is the mean value from several recent neutron diffraction studies in which b_N was allowed to vary during the refinement process (Kvick, Koetzle, Thomas & Takusagawa, 1974). The function minimized in our refinements was $\sum w|F_o^2 - |F_c|^2|^2$; weights were chosen as $w = 1/\sigma^2(F_o^2)$ with $\sigma^2(F_o^2) = \sigma^2_{\text{count}}(F_o^2) + (0{\cdot}02\ F_o^2)^2$. Anisotropic thermal parameters were used for all atoms, and an extinction correction was introduced following Zachariasen's (1967) model.

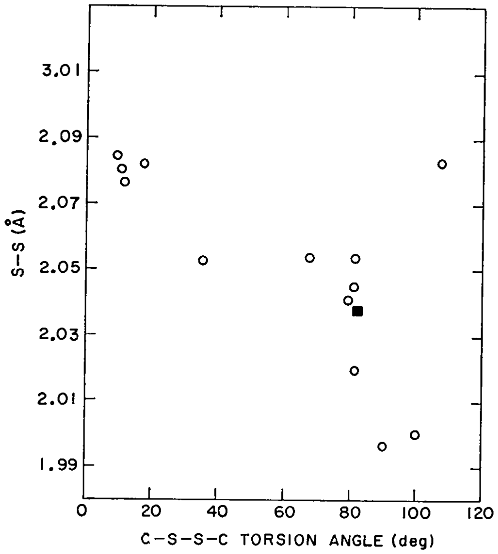

Fig. 3. Plot of S–S distance *vs.* C–S–S–C torsion angle. Results for hexagonal L-cystine not included. Square point identifies present results.

The crystal exhibited severe extinction effects and a type II anisotropic extinction correction (Coppens & Hamilton, 1970) was introduced in the final refinement cycles, which were based on the full, unaveraged data set of 1834 reflections with $F_o^2 > 3\sigma_{\text{count}}(F_o^2)$. A total of 173 parameters were varied in these final cycles. The extinction correction factor E, which multiplies the calculated structure factor, is

$$E = \left[1 + \frac{2\bar{T}|F_c|^2 g\lambda^3)\,(10^4)}{V^2 \sin 2\theta}\right]^{-1/4}$$

where $\bar{T}$ is the absorption-weighted average beam path length through the crystal, V is the unit-cell volume and F_c is the calculated structure factor on absolute scale. For type II anisotropic extinction, $g = (\mathbf{N}'\mathbf{W}'\mathbf{N})^{-1/2}$ where $\mathbf{W}'$ is a symmetric tensor describing the anisotropy of domain size and $\mathbf{N}$ is a unit vector in the diffraction plane and perpendicular to the incident beam. The refined atomic parameters are given in Table 1 and final values for the squared structure factors are shown in Table 2 for those reflections included in the refinement. The anisotropic extinction tensor, defined above, is $W'_{11} = 0{\cdot}093$ (6), $W'_{22} = 3{\cdot}5$ (2), $W'_{33} = 0{\cdot}13$ (1), $W'_{12} = -0{\cdot}09$ (3), $W'_{13} = -0{\cdot}004$ (5), $W'_{23} = 0{\cdot}23$ (4). These values correspond to an average particle size described by an ellipsoid with principle axes as follows (direction cosines refer to the crystal axis system $\mathbf{a}, \mathbf{b}, \mathbf{c}^*$).

R.m.s. (μ)	Direction cosines		
0·54	0·024	−0·998	−0·064
2·76	−0·419	0·048	−0·907
3·71	0·908	0·049	−0·417

Table 3. *Covalent bond distances* (Å)

	Neutron			
	BNL*		BARC†§	X-ray‡§
	Uncorrected	Corrected for thermal motion	Uncorrected	Uncorrected
O^2–H^{O2}	0·996 (4)	0·996	0·966 (10)	
O^1–C	1·202 (2)	1·208	1·204 (5)	1·237
O^2–C	1·307 (2)	1·318	1·309 (6)	1·308
N–C^α	1·484 (2)	1·496	1·488 (4)	1·484
N–H^1	1·034 (4)	1·037	1·030 (8)	
N–H^2	1·045 (3)	1·050	1·041 (8)	
N–H^3	1·025 (2)	1·032	1·017 (6)	
C–C^α	1·520 (2)	1·527	1·511 (4)	1·472
C^α–C^β	1·525 (2)	1·533	1·526 (3)	1·558
C^α–H^α	1·097 (3)	1·105	1·116 (6)	
C^β–S^γ	1·816 (3)	1·832	1·811 (7)	1·862
C^β–$H^{\beta1}$	1·094 (3)	1·103	1·093 (6)	
C^β–$H^{\beta2}$	1·091 (3)	1·095	1·092 (7)	
S^γ–$S^{\gamma'}$	2·038 (6)		2·041 (14)	2·044

* Present work

† Gupta *et al.* (1973).

‡ Steinrauf *et al.* (1958).

§ Recalculated with the mean cell parameters used in this paper.

The extinction is quite anisotropic, and is greater along **a** and **c*** than along **b**. This latter axis corresponds to the long dimension of the crystal. The agreement between observed and calculated squared structure factors was markedly improved by the introduction of the anisotropic extinction correction: the weighted agreement index $R_{wF2}=\{[\sum w|F_o^2-|F_c|^2|^2]/\sum wF_o^4\}^{1/2}$ dropped from a value of 0·085 with an isotropic extinction correction to the final value of 0·061. No parameter shifted by more than $0{\cdot}1\sigma$ in the last cycle of refinement. Final unweighted agreement indices are

$$R_{F2}=\sum|F_o^2-|F_c|^2|/\sum F_o^2=0{\cdot}074$$

and

$$R_F=\sum|F_o-|F_c||/\sum F_o=0{\cdot}034\,.$$

The standard error of fit is

$$S=\{\sum w|F_o^2-|F_c|^2|^2/(n_o-n_v)\}^{1/2}=1{\cdot}31\,.$$

All calculations were carried out on CDC 6600 computers with programs that have been described briefly by Schlemper, Hamilton & La Placa (1971).

Table 4. *Covalent bond angles* (°)

	Neutron		X-ray
	BNL	BARC	
C—O^2–H^{02}	111·1 (2)	111·6 (7)	
C$^\alpha$—N–H^1	114·0 (1)	113·7 (5)	
C$^\alpha$—N–H^2	109·9 (2)	109·5 (5)	
C$^\alpha$—N–H^3	112·9 (2)	113·0 (5)	
H^1—N–H^2	107·9 (3)	108·5 (6)	
H^1—N–H^3	105·0 (3)	105·1 (6)	
H^2—N–H^3	106·7 (2)	106·7 (6)	
O^1—C—O^2	125·4 (1)	124·9 (4)	119·1
O^1—C—C$^\alpha$	123·1 (1)	122·8 (3)	122·6
O^2—C—C$^\alpha$	111·5 (1)	112·4 (3)	118·2
N—C$^\alpha$–C	108·0 (1)	108·3 (2)	111·0
N—C$^\alpha$–C$^\beta$	112·3 (1)	112·0 (2)	111·2
N—C$^\alpha$–H$^\alpha$	107·7 (2)	106·8 (4)	
C—C$^\alpha$–C$^\beta$	113·1 (1)	113·1 (2)	111·4
C—C$^\alpha$–H$^\alpha$	107·0 (2)	108·8 (4)	
C$^\beta$—C$^\alpha$–H$^\alpha$	108·6 (2)	107·5 (4)	
C$^\alpha$—C$^\beta$–S$^\gamma$	114·7 (1)	114·7 (3)	112·8
C$^\alpha$—C$^\beta$–H$^{\beta1}$	108·7 (2)	108·3 (4)	
C$^\alpha$—C$^\beta$–H$^{\beta2}$	110·7 (1)	110·1 (4)	
S$^\gamma$—C$^\beta$–H$^{\beta1}$	105·4 (2)	105·4 (5)	
S$^\gamma$—C$^\beta$–H$^{\beta2}$	109·4 (2)	109·9 (4)	
H$^{\beta1}$–C$^\beta$–H$^{\beta2}$	107·6 (3)	108·1 (6)	
C$^\beta$—S$^\gamma$–S$^{\gamma'}$	103·7 (1)	104·0 (4)	103·7

Discussion

The L-cystine dication is shown in Fig. 1 with the standard atom names for amino acids and peptides. The crystallographic twofold axis relating the two halves of the cystine molecule is oriented nearly horizontally in Fig. 1. A similar view in stereo with full thermal ellipsoids is given in Fig. 2. As might be expected for a strongly hydrogen-bonded structure, there is no indication of disorder or abnormally large thermal motion. Tables 3 and 4 present a comparison of bond distances and angles from the present work with the corresponding bonding parameters from the neutron study of Gupta *et al.* (1974) and with those from the X-ray work (Steinrauf *et al.*, 1958). Torsion angles from the present study agree to within 0·7° with those given by Gupta *et al.* (1974). These authors have described the conformation of the cystine molecule in some detail. Here we restrict our discussion to some remarks concerning the C–S–S–C fragment, which is of particular interest because of the importance of the cystine disulfide bond in proteins.

Table 5. *Mean bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *for molecules containing aliphatic* C–S–S *fragments*

Compound	Distance C–S	S–S	Angle C–S–S	Torsion angle C–S–S–C*	Reference
Acetylaranotin	1·88	2·082	97	17	Cosulich, Nelson & Van den Hende (1968)
t-Butyl-*N*,*N*-dimethyltrithiopercarbamic acid	1·83	2·00	106	100	Mitchell (1969)
Chaetocin	1·88	2·077	98	+11	Weber (1972)
L-Cystine (hexagonal)	1·82	2·03	115	+106	Oughton & Harrison (1959)†
L-Cystine dihydrobromide	1·86	2·02	104	−81	Peterson, Steinrauf & Jensen (1960)
L-Cystine dihydrochloride	1·82	2·038	104	−82	present work
N,*N*′-Diglycyl-L-cystine.2H_2O	1·87	2·041	103	−79	Yakel & Hughes (1954)
Gliotoxin	1·88	2·084	98	−9	Fridrichsons & Mathieson (1967)
1,2,3,6,7,8-Hexathiecane	1·86	2·054	105	81‡	Lemmer, Fehér, Gieren, Hechtfischer & Hoppe (1970)
2-(2-Pyridylmethyldithio)benzoic acid	1·82	2·045	104	81	Karle, Karle & Mitchell (1969)
Sporidesmin	1·90	2·08	98	−10	Fridrichsons & Mathieson (1965)
Tetraethylthiuram disulfide	1·82	1·997	103	90	Karle, Estlin & Britts (1967)
1,2,3,4-Tetrathiadecalin	1·80	2·054	103	67‡	Fehér, Klaeren & Linke (1972)
DL-6-Thioctic acid	1·81	2·053	94	35	Stroud & Carlisle (1972)
3,3′Trithiobis-(2,4-pentanedione)	1·80	2·083	104	107‡	Power & Jones (1971)

* Calculated according to the IUPAC-IUB (1970) conventions. Quantities carrying a sign indicate that the absolute configuration of the molecule is known.

† This structure appears to be incorrect. The S–S distance calculated from the sulfur coordinates given by these authors is only 1·32 Å and the C–S–S–C torsion angle is +116°. A Patterson map calculated by one of us (IB) from values of F_o given by Oughton & Harrison does not fit their solution for the sulfur position. Further details will be published elsewhere.

‡ C–S–S–S.

The C–S–S–C torsion angle χ^2 is −81·7 (2)°, which places L-cystine.2HCl in the class of disulfide compounds with torsion angles of magnitude near 90°. As has been discussed by Hordvik (1970), the S–S bond length is dependent on the value of the disulfide torsion angle probably because of variations in the lone-pair repulsions. These repulsions are largest when the torsion angle is 0°, *i.e.* in a *cis*-planar disulfide, and *cis*-planar disulfides have S–S bond distances about 0·07 Å longer than disulfides with torsion angles of 90°. Recent Raman spectroscopic results (van Wart, Lewis, Scheraga & Saeva, 1973) have indicated that the S–S and C–S stretching frequencies increase linearly with the C–S–S–C torsion angle. The effect of torsion angle on S–S and C–S bond lengths in molecules containing C–S–S fragments can be seen in Table 5, which also gives the C–S–S angle. Figs. 3 and 4 are plots of the S–S and C–S distances *vs* the magnitude of the C–S–S–C torsion angle and show an inverse correlation such that these distances become smaller as the torsion angle increases from 0 to 90°, as was previously noticed by Hordvik (1970). It should be pointed out that the X-ray data given in Table 5 are not of uniform precision. Some of the older data are from film rather than diffractometer studies and some are based on incomplete sets of measured intensities, so that they are not fully, or fairly, comparable. It is therefore not surprising that the plots in Figs. 3 and 4 show a certain amount of scatter. The correlation between the C–S–S–C torsion angle and the C–S–S bond angle is not as clear as that observed for the S–S and C–S bond lengths, but again approximately, the C–S–S angle increases with increasing torsion angle.

A comparison of disulfide torsion angles in five proteins is shown in Table 6. The disulfide bonds in question are divided equally between the two chiralities. With the exceptions of cystine 1-122 in tosyl-α-chymotrypsin, cystine 14–38 in basic pancreatic trypsin inhibitor, and cystine A6–A11 in insulin, the magnitudes of all these disulfide torsion angles are within 20° of 90°. As mentioned earlier, L-cystine.2HCl also falls in this category along with a majority of the small molecules listed in Table 5. The disulfide groups in acetylaranotin, chaetocin, gliotoxin and sporidesmin, which have torsion angles near zero, are sterically severely restricted by ring closure. Torsion angles near 90° generally should be favored in these systems since this conformation leads to minimum S–S lone-pair repulsions.

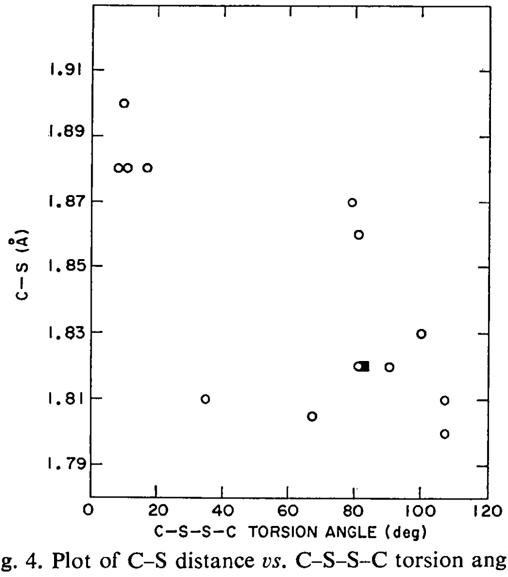

Fig. 4. Plot of C–S distance *vs*. C–S–S–C torsion angle.

Table 6. *Torsion angles for disulfide bonds in selected proteins**

Protein	Cystine residues	Torsion angle
Carboxypeptidase A (Quiocho & Lipscomb, 1971)	138–161	93·5°
Tosyl α-chymotrypsin (Birktoft & Blow, 1972)	1–122 136–201	113·2 105·1
Ribonuclease-S (Wyckoff, Tsernoglou, Hanson, Knox, Lee & Richards, 1970)	26–84 40–95 58–110 65–72	−100·8 −84·6 −84·6 104·4
Basic pancreatic trypsin inhibitor (Huber, Kukla, Rühlmann, Epp & Formanek, 1970)	5–55 30–51 14–38	−100·8 −77·1 37·9
Insulin (Blundell, Dodson, Dodson, Hodgkin & Vijayan, 1971)	A6–A11 A7–B7 A20–B19	31·9 110·2 −70·4

* Calculated according to the IUPAC-IUB (1970) conventions from atomic coordinates deposited in the Protein Data Bank (1973) at Brookhaven National Laboratory.

The structure of L-cystine.2HCl is extensively hydrogen bonded as shown in Fig. 5, a view of the molecular packing in one unit cell. Hydrogen bond distances and angles are given in Table 7. The chloride ion is the only hydrogen-bond acceptor and is coordinated to four protons arranged at the corners of a distorted trigonal pyramid. Each cystine molecule is linked to six neighbors *via* H···Cl···H bridges. Two such bridges connect two ammonium-group protons with the ammonium group of a single adjacent molecule, thus forming an eight-membered ring.

In order to obtain the best geometrical parameters, the non-hydrogen atoms of the half-cystine molecule were assumed to behave as a rigid body whose motion was described in terms of **T**, **L** and **S** tensors (Schomaker & Trueblood, 1968). The r.m.s. difference between observed and calculated thermal parameters u_{ij} was 0·0035 Å^2 and the screw translations were negligibly small. The calculated rigid-body librations were used to derive corrections to bond distances between non-hydrogen atoms, and these corrected values are included in Table 3. Bond distances involving hydrogen were corrected for the effects of thermal motion with the minimum correction of Busing & Levy (1964) which sets a lower bound on the corrected distance.

An additional rigid-body calculation was carried out for the ammonium group, yielding an r.m.s. difference between observed and calculated u_{ij} of 0·002 Å^2. The largest principal axis of **L** lies approximately 15° from the group's threefold axis and corresponds to an r.m.s. librational amplitude of 10·0°. With a harmonic oscillator approximation to a threefold cosine hindered rotor as described by Schlemper *et al.* (1971), the librational frequency ν and the height of the potential barrier V_o were estimated to be $\nu = 306$ cm^{-1} and $V_o = 5{\cdot}1$ kcal mole^{-1}. The barrier obtained here is only slightly larger than the average value of 4·8 kcal mole^{-1} for ammonium groups of four other α-amino acid hydrochlorides we have studied by neutron diffraction. By contrast, the average barrier for ten neutral amino acids is 8·0 kcal mole^{-1}. The ammonium groups in the neutral compounds have higher barriers than in the hydrochlorides, presumably because the N–H···O bonds formed in the neutral compounds are stronger than the N–H···Cl bonds predominating in the hydrochlorides.

An examination of the bond distances and angles in Tables 3 and 4 indicates that the agreement between bonding parameters is quite good for the two neutron studies. [In the comparisons which follow, parameters from the present refinement are identified as BNL and those from the refinement of Gupta *et al.* (1974) are identified as BARC.] The largest discrepancies are 0·030 Å or 3σ(BARC) for the O^2–H^{02} distance and 1·8° or 4σ(BARC) for the C–C$^\alpha$–H$^\alpha$ angle. Larger discrepancies occur between the neutron and X-ray results; these are difficult to assess since no standard deviations were reported for the X-ray parameters and only *h*0*l* and *hk*0 intensities were used in the X-ray refinement. In order to analyze the differences between our atomic coordinates and thermal parameters and those of Gupta *et al.* (1974), we have compared the two parameter sets by the method of normal probability plots (Abrahams & Keve, 1971; Hamilton & Abrahams, 1972) and employing χ^2 tests as discussed by Hamilton (1969). Half-normal probability plots of the parameter differences

$$|\Delta p_i/\sigma(p_i)|$$

are shown in Fig. 6 for positional parameters and in Fig. 7 for thermal parameters. These plots are nearly linear, indicating that the errors are indeed approximately normally distributed. The slopes are 1·6 for positional parameters and 1·4 for thermal parameters, indicating that the pooled standard deviations $\sigma(p_i) = [\sigma^2(\mathrm{BNL}) + \sigma^2(\mathrm{BARC})]^{1/2}$ are underestimated by approximately 1·4–1·6. In comparisons of X-ray and neutron results for L-asparagine.H$_2$O (Verbist, Lehmann, Koetzle & Hamilton, 1972), pooled standard deviations were found to be underestimated by comparable factors.

The sums of the squares of parameter differences have been tested as χ^2 for all parameter classes (x, y, z, u_{11}, u_{22}, *etc.*). Significant values of χ^2 at the 0·01 probability level are found for all classes except z, u_{22}

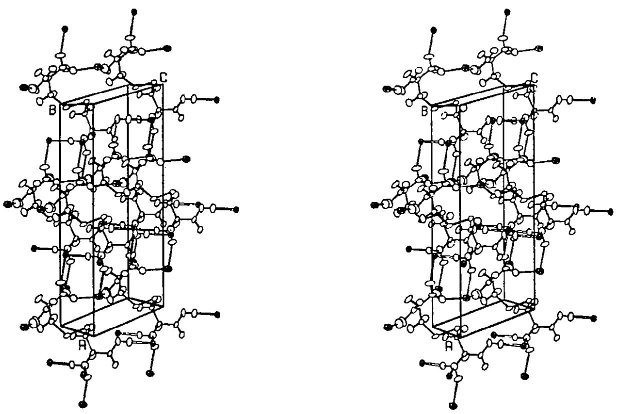

Fig. 5. Stereo view of the molecular packing in one unit cell. Cl$^-$ ions have been shaded.

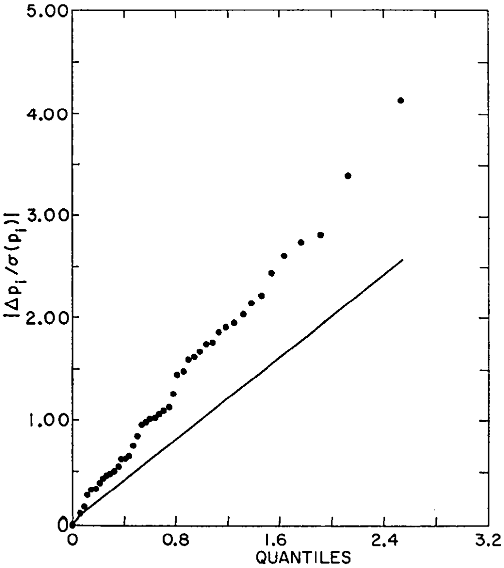

Fig. 6. Half-normal probability plot for differences between BNL and BARC positional parameters. The line with unit slope has been drawn.

Table 7. *Distances* (Å) *and angles* (°) *in hydrogen bonds*

X–H···Cl	X–H	H···Cl	X···Cl	∠X–H···Cl
N–H^1···Cl	1·034 (4)	2·262 (4)	3·238 (3)	156·9 (2)
N–H^2···Cl	1·045 (3)	2·100 (4)	3·129 (3)	167·4 (3)
N–H^3···Cl	1·025 (2)	2·270 (4)	3·206 (3)	151·1 (3)
O^2–H^{02}···Cl	0·997 (4)	2·011 (3)	3·004 (3)	172·1 (3)

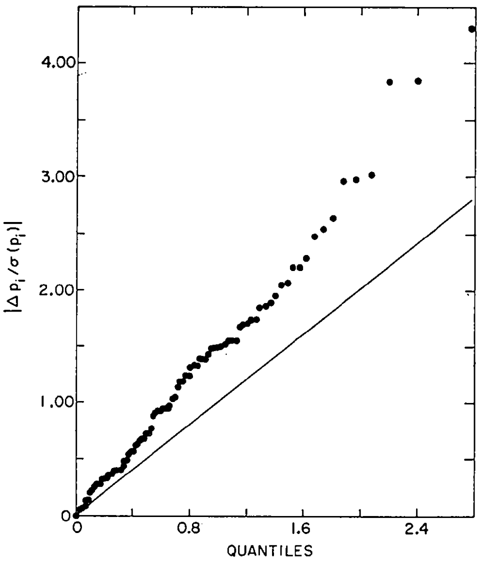

Fig. 7. Half-normal probability plot for thermal parameters.

and u_{12}. This strongly suggests some systematic difference between the two data sets. One would expect some difference in nitrogen thermal parameters due to the small difference in values used for the nitrogen scattering factor. An examination of the mean values of the differences of the various parameters for all atoms indicates that the largest differences occur for thermal parameters u_{11},u_{33} and u_{13}. For these three parameter classes, the mean difference divided by σ ranges from 3·9 to 4·8 with the BARC thermal parameters larger than the BNL values in each case. Quite possibly, these differences in thermal parameters for the two refinements are indicative of the correlation of thermal parameters and extinction. The BARC crystal showed moderate extinction effects (the minimum value of E^2 was 0·73) and an isotropic extinction correction was included in the BARC refinement. By contrast, the BNL crystal showed severe extinction (minimum E^2= 0·45), and we have included a type II anisotropic extinction correction in our refinement. Interestingly, we found the minimum extinction to occur along **b**, and values of u_{22} for the two refinements agree relatively well.

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