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A Refinement of the Crystal Structure of Glycine*

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The crystal structure of glycine, originally determined by Albrecht & Corey in 1939, has been refined on the basis of complete three-dimensional intensity data obtained from molybdenum X-radiation. The structural parameters for the heavy atoms, including anisotropic temperature factors, were refined by difference maps and least-squares methods; the positions of the hydrogen atoms were located from a difference map. The final R factor was 0·063 for 1867 observed reflections and the standard deviations in the positional parameters of the heavy atoms are about 0·001 Å.

The bond distances and angles are close to those reported by Albrecht & Corey, with the exception of the C–N bond, which is found to be 1·474 Å rather than 1·39 Å. The apparent C–H and N–H distances are about 0·9 Å.

Introduction

The crystal structure of glycine, $H_3^+NCH_2COO^-$, was first determined by Albrecht & Corey (1939). The structure was solved by Patterson and Patterson–Harker maps, and was refined by trial-and-error methods. Although three-dimensional intensity data (copper radiation) were used for the Patterson maps, the refinement was based entirely on zonal data. Unfortunately, for a small molecule glycine is surprisingly ill-suited for two-dimensional refinement, since there is no direction of projection which does not involve serious overlap.

A surprising result obtained by Albrecht & Corey was the value 1·39±0·02 Å for the C–N distance—a value shorter by about 0·08 Å than that normally found in amino acids and peptides. Furthermore, their results indicated that, although two of the hydrogen atoms of the NH_3 group are involved in normal hydrogen bonding with neighboring oxygen atoms, the third hydrogen atoms forms a 'bifurcated' bond with two adjacent oxygen atoms. In view of these surprising features, a redetermination of the structure of this simplest of all amino acids was in order.

It has seemed worth while to put some special effort into this redetermination, with a view not only towards obtaining accurate parameters for the heavier atoms and locating, if possible, the hydrogen atoms, but also towards learning something concerning the accuracy to which ordinary X-ray diffraction techniques may be pushed.

Experimental

(i) *Refinement of the unit-cell parameters*

Large single crystals of glycine (the usual, or α, form) were readily grown by slow evaporation of aqueous solutions. They were elongated in the c direction and showed pronounced cleavage perpendicular to b. One crystal was ground to a cylinder about 3 mm. in length and 1·2 mm. in diameter; this was used for photographs about the c axis. A second crystal was shaped into an approximate sphere about 1 mm. in diameter by rolling it between thumb and forefinger, the slight moisture on the fingers being sufficient to dissolve the rough edges; this crystal was used for photographs about the a, b, and [101] axes.

Accurate values for the unit-cell dimensions were obtained from three Straumanis-type rotation photographs taken about the b, c, and [101] axes, respectively. The copper X-ray tube was badly contaminated with iron, so that a number of the reflections used in the determination of cell constants were due to iron rather than copper radiation. The photographs were measured with the help of a traveling microscope and a calibrated steel scale; the effective camera radius varied from 4·981 to 5·002 cm. for the three photographs. No eccentricity or absorption effect was apparent.

Two or three high-angle reflections were chosen on each film and were indexed on the basis of the unit-cell dimensions reported by Albrecht & Corey. In all, seven reflections having Bragg angles greater than 70° were chosen; of these, three were of copper radiation and

Table 1. *Spacing data for glycine*

Rotation axis	hkl	Radiation	$(\sin^2\theta)_o$	$(\sin^2\theta)_c$	Weight
c	470	Fe $K\alpha_1$	0·98760	0·98759	81
	1,12,0	Fe $K\alpha_1$	0·98330	0·98326	38*
	1,15,0	Cu $K\alpha_1$	0·95783	0·95794	24
[*101*]	$2,14,\bar{2}$	Cu $K\alpha_1$	0·93646	0·93636	17
	$4,10,\bar{4}$	Cu $K\alpha_1$	0·91352	0·91356	13
b	204	Fe $K\alpha_1$	0·98058	0·98058	52
	$50\bar{3}$	Fe $K\alpha_1$	0·93797	0·93797	17

* This reflection was very weak and the reported weight includes a factor of 0·64 as well as the standard factor $1/\sin^2 2\theta$.

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four were of iron. The spacings of the $K\alpha_1$ components were measured and used in a least-squares determination of the four unit-cell parameters. Values of $\sin^2\theta$ for these seven reflections and their assigned weights are listed in Table 1; the output cell parameters are listed in Table 2, together with the values reported by Albrecht & Corey.

Table 2. *Unit-cell dimensions for glycine*

(λ (Cu $K\alpha_1$) = 1·54051 Å; λ (Fe $K\alpha_1$) = 1·93597 Å)

	This investigation	Albrecht & Corey
a	5·1020 ± 0·0008* Å	5·10 Å
b	11·9709 ± 0·0017* Å	11·96 Å
c	5·4575 ± 0·0015* Å	5·45 Å
β	111° 42·3′ ± 1·0′*	111° 38′

* Estimated limits of error set at about five times the standard deviations calculated in the least-squares treatment.

The density calculated on the basis of four molecules in the unit cell is 1·610 g.cm.$^{-3}$; the observed density has been reported in the literature as 1·606 (Low & Richards, 1952) and as 1·607 (Curtius, 1882) g.cm.$^{-3}$.

(ii) *Collection of intensity data*

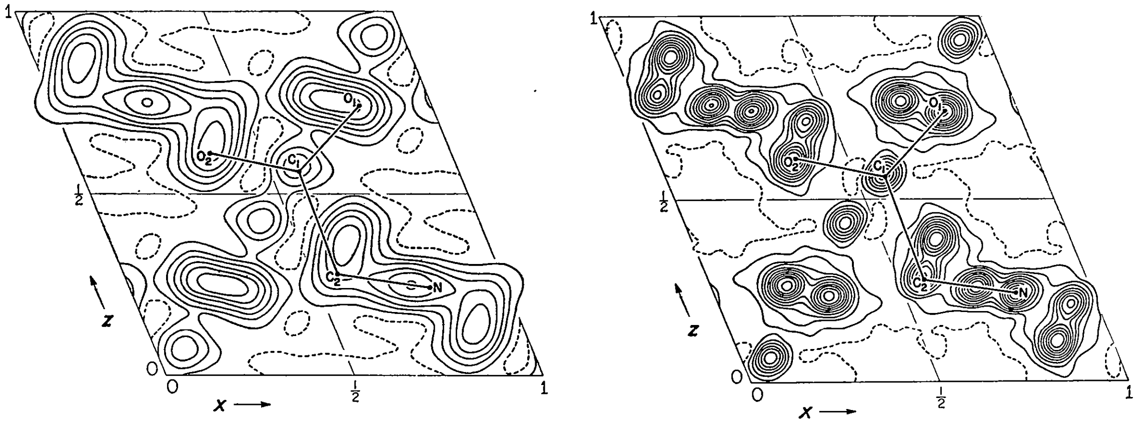
Equi-inclination Weissenberg photographs were taken with Mo $K\alpha$ radiation for layer lines zero through seven from crystals rotated about c, a, and [101]. Three films were used for each exposure, with thin copper foil interspersed to bring the film factor up to about 3·5; for most layer lines, two exposures of different duration were taken. Intensities were estimated by visual comparison with intensity strips prepared from the same crystals. Empirical film factors were obtained, and found to vary in the expected manner with the equi-inclination angle.

The intensities were corrected for Lorentz and polarization effects. Correlation factors for the various exposures were then obtained by comparing intensity values from each set of films with those from all sets from the other two rotation axes and taking subjectively-weighted averages. Finally, F^2 values, on an arbitrary scale, were obtained by taking averages (again, subjectively weighted) of the values observed about the three different axes. All reflections within the molybdenum sphere—about 5400—were covered, of which 1919 were strong enough to be observed. Of these, 965 were observed on photographs taken about all three axes, 588 were observed about two axes, and 366 were observed about only one axis. Values for the observed intensity ranged from about 2 to 11,000.

In order to assess the uncertainties in the observed structure factors, comparisons were made among the F^2 values for all reflections which were observed about more than one axis. The estimated relative standard deviations averaged about 5% for reflections of moderate intensity, increasing to about 10% for the strong reflections and to about 20% for the very weak reflections. This pattern of observational discrepancies was the basis of the weighting function used in the least-squares refinement of the positional parameters.

Refinement of the atomic parameters

The atomic positional parameters were refined by means of electron-density and difference projections on to (010), (100), and (101); through six three-dimensional structure-factor and difference-map cycles; and, finally, through two structure-factor least-squares cycles. Individual anisotropic temperature factors were included for the heavy atoms, beginning with the two-dimensional calculations; they were not optimized in the final least-squares treatments. Positional parameters for the hydrogen atoms were obtained from a three-dimensional difference map.



(*a*) (*b*)

Fig. 1. Electron-density projections on to (010): (*a*) calculated from the copper intensity data of Albrecht & Corey; (*b*) calculated from the molybdenum data of the present investigation. The contours are at intervals of 2 e.Å^{-2}; the 2 e.Å^{-2} contour is broken.

Table 3. *Atomic parameters obtained from two-dimensional refinements*

	x	y	z	α	β	γ	δ	ε	η
C_1	0·0760	0·1247	0·0642	0·0125	0·0025	0·0100	0	0·0125	0
C_2	0·0655	0·1453	0·7880	0·0125	0·0030	0·0105	0	0·0130	0
N	0·3030	0·0905	0·7410	0·0120	0·0035	0·0075	0	0·0075	0
O_1	0·3060	0·0936	0·2350	0·0145	0·0040	0·0115	0	0·0120	0
O_2	0·8538	0·1400	0·1082	0·0175	0·0045	0·0150	0	0·0175	0

(i) *Two-dimensional refinements*

The starting parameters for the two-dimensional refinements were those of Albrecht & Corey (1939). From these parameters, signs for the structure factors of the type $h0l$ were calculated; these signs were used in the preparation of an electron-density projection on to (010), in which all observed $h0l$ terms were included. This projection is shown in Fig. 1(*b*). For comparison, a second electron-density projection on to (010), based on the structure factors observed by Albrecht & Corey and listed in their Table 2, was calculated; it is shown in Fig. 1(*a*). The increased resolution obtained from the molybdenum intensity data of the present investigation, as compared with the copper data of Albrecht & Corey, is clearly apparent.

The x and z parameters indicated by the (010) projection were used in the calculation of $h0l$ structure factors, and approximate scale and isotropic temperature factors were assigned. The R factor for these 69 reflections was 0·149. A subsequent (010) difference projection showed only small shifts for the positional parameters, but gave indications of highly anisotropic temperature factors, particularly for the oxygen atoms. Accordingly, preliminary values for the individual temperature-factor anisotropies were assigned, the temperature factors being expressed in the form

$$T_i = \exp -(\alpha_i h^2+\beta_i k^2+\gamma_i l^2+\delta_i hk+\varepsilon_i hl+\eta_i kl)\,.$$

Attention was then turned to the $0kl$ reflections, from which an electron-density projection on to (100) and two structure-factor difference-map cycles were calculated. A second difference projection on to (010) and a structure-factor difference-map cycle, using data of the type $hk\bar{h}$, completed the two-dimensional work. The atomic parameters at this stage of refinement are listed in Table 3.

(ii) *Three-dimensional refinements*

With the exception of the final structure-factor least-squares cycles, which were carried out on a Datatron computer, the three-dimensional calculations were made on conventional IBM equipment, including a 604 Electronic Calculating unit. The first set of structure factors, calculated from the parameters in Table 3, led to an R factor of 0·131 for the observed reflections; they were used in the calculation of the first three-dimensional difference map. This and the subsequent difference maps were evaluated at intervals of $a/30$, $b/60$, and $c/30$, by use of the M-card system; accordingly, it was necessary to omit about 100 observed reflections having h or l greater than 10 or k greater than 20.

The first difference map indicated shifts in the positional parameters averaging about 0·003 Å; more significant were the indicated changes in the individual temperature factors. In particular, it was evident that the temperature-factor anisotropies should be markedly increased for the oxygen atoms. Approximate values for the changes in the scale and temperature-factor parameters were obtained by the method of Leung, Marsh & Schomaker (1957)*, and a second set of structure factors led to an R factor of 0·117. Another difference-map structure-factor cycle reduced R to 0·109.

At this point, the contributions of the hydrogen atoms were calculated. The parameters chosen for the two methylene hydrogen atoms were calculated on the basis of tetrahedral bond angles and C–H distances of 1·00 Å; the parameters for the ammonium hydrogen atoms were those indicated by the first three-dimensional difference map, which led to N–H distances of about 0·88 Å and to a roughly tetrahedral configuration about the nitrogen atom. An isotropic temperature factor with $B = 2·0$ Å^2 was assigned to each of the five hydrogen atoms. The inclusion of these hydrogen-atom contributions led to a significant improvement in the agreement of the low-order data.

It was now apparent that the observed structure factors for a number of strong reflections were too small, indicating extinction effects. Accordingly, the F_o values were multiplied by the correction factor $\sqrt{\{1/(1-KI_o)\}}$, where I_o is the observed intensity; the value for K was determined empirically. This correction was applied to 119 observed structure factors, of which 63 were changed by more than 1% and 8 by more than 10%. After including these extinction corrections and the hydrogen-atom contributions, the R factor was 0·092.

A third difference map was then calculated; it was much flatter than the first two, but again indicated that the major source of the discrepancies between observed and calculated structure factors lay in the assignment of temperature-factor parameters. These were re-adjusted and the structure factors were recalculated; R dropped to 0·077. A fourth difference map indicated only small changes in the temperature-

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* The equations for the temperature-factor corrections are not exact when the input atoms are not isotropic.

factor and positional parameters; the next set of structure factors led to an R factor of 0·072.

A difference map was then calculated with F_c values from which the hydrogen-atom contributions had been omitted, and including only those terms with h and l less than 5 and k less than 10. The positions of the five hydrogen atoms were clearly apparent on this map; they lay in regions with maximum electron density ranging from 0·75 to 0·90 e.Å^{-3}, whereas there were no other regions of density greater than 0·3 e.Å^{-3}. A composite drawing of this map is shown in Fig. 2, and the indicated hydrogen-atom parameters are listed in Table 4.

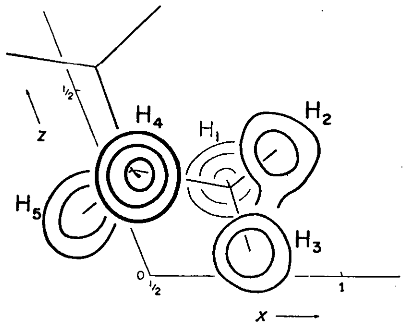

Fig. 2. A composite drawing of the three-dimensional difference map in which the hydrogen-atom contributions were omitted from the F_c values. The contours are at intervals of ¼ e.Å^{-3}, beginning with the ¼ e.Å^{-3} contour.

Table 4. *The final hydrogen-atom parameters*

Atom	x	y	z
H_1	0·286	0·100	0·570
H_2	0·457	0·119	0·837
H_3	0·298	0·020	0·763
H_4	0·080	0·220	0·771
H_5	0·898	0·118	0·671

At this stage of the investigation, a Datatron digital computer became available. The computer had previously been programmed for structure-factor and least-squares calculations on structures with point groups 2 or m (Pasternak, 1956), and the program was readily modified to accommodate the remaining monoclinic space groups. This program accepts complete anisotropic temperature factors for each atom, but only the positional parameters are optimized.

The weighting function used in the least-squares calculations was derived from the estimated standard deviations in the F_o values (see section 'Experimental'), the values for $\sqrt{w}$ being taken inversely proportional to the expected uncertainty in F_o. The explicit weighting function was:

$$\sqrt{w} = 35/F_o(1+0{\cdot}0032F_o^2) \quad \text{for} \quad F_o \geq 5{\cdot}3\,,$$
$$\sqrt{w} = 6{\cdot}0 \quad \text{for} \quad F_o \leq 5{\cdot}3\,.$$

Two additional factors were included in $\sqrt{w}$: the factor $\sqrt{n}$, where n (= 1, 2, or 3) is the number of rotation axes about which the observation was made, and a subjective factor (sometimes equal to zero) for observations which, for reasons of extinction, spot shape, contamination with white-radiation streaks, or extreme weakness, were of doubtful validity. Finally, for computational convenience, the values of $\sqrt{w}$ were rounded off to a single integer.

The first set of structure factors calculated on the Datatron computer led to an R factor—including only those reflections with $\sqrt{w} \neq 0$—of 0·076. The structure factors differed slightly from those of the previous set for three reasons: (1) the hydrogen-atom parameters had been changed slightly; (2) the atomic form factors of Hoerni & Ibers (1954) were used in place of those of McWeeny; (3) the atomic form factors were stored in the computer as linear interpolation tables, and for a few very small regions in reciprocal space the interpolated form factors could be in error by nearly 5%. Because of a programming error, the indicated least-squares shifts from this calculation were not sensible; accordingly, the structure factors were used in the calculation of a final three-dimensional difference map. This map indicated shifts in the positional parameters averaging about 0·001 Å and shifts in the temperature-factor parameters averaging about 2%; furthermore, it indicated that the change to Hoerni–Ibers form factors had somewhat improved the over-all pattern of agreement. The most significant feature of this map—and one which was also apparent on the previous maps—was the presence of a negative region of about 0·6 e.Å^{-3} at the position of the nitrogen atom and of two smaller positive regions at the positions of the oxygen atoms, indicating that the use of form factors for neutral N and O atoms was inappropriate. The implied charge effect was not taken into account in the final structure-factor calculations, although it would apparently account for the relatively poor agreement in some low-order reflections.

The improved temperature-factor parameters were

Table 5. *Final positional and temperature-factor parameters*

(The temperature factor for each atom is of the form

$$T_i = \exp -(\alpha_i h^2+\beta_i k^2+\gamma_i l^2+\delta_i hk+\varepsilon_i hl+\eta_i kl))$$

Atom	x	y	z	$10^4\alpha$	$10^4\beta$	$10^4\gamma$	$10^4\delta$	$10^4\varepsilon$	$10^4\eta$
C_1	0·07542	0·12478	0·06605	157	22	115	−10	150	−10
C_2	0·06536	0·14499	0·78711	156	32	118	20	130	16
N	0·30135	0·08980	0·74113	164	38	108	34	130	12
O_1	0·30583	0·09427	0·23553	205	50	115	45	138	28
O_2	0·85224	0·14154	0·10711	185	56	190	8	230	−20

Table 6. *Observed and calculated structure factors*

The three columns in each group contain the values, reading from left to right, of k, $100F_o$, and $100F_c$. Reflections indicated by a dagger (†) were given zero weight in the final least-squares calculation

0,k,0

0	----	16000
2	----	1217
4	7812	-8080†
6	1314	-1250
8	1890	1953
10	<135	136
12	<153	16
14	450	432
16	216	-215
18	414	-420
20	<171	30
22	225	197

0,k,1

1	2493	2811
2	531	-279
3	2862	-2959†
4	261	-183
5	1116	-1100
6	684	717
7	1611	1655
8	216	252
9	279	279
10	252	-299
11	765	-796
12	270	-273
13	<135	-81
14	288	296
15	351	364
16	234	224
17	<135	50
18	198	-195
19	153	-163

0,k,2

0	3663	-4164†
1	2115	-2101
2	1269	-1259
3	1899	-1849
4	1575	1676
5	1224	1193
6	1683	1695
7	756	712
8	297	299
9	477	-502
10	738	-627
11	225	-219
12	855	-915
13	252	267
14	<171	-87
15	126	104
16	639	652
17	198	-192
18	261	264
19	<153	-89
20	315	-306
21	171	133
22	171	-152

0,k,3

1	810	-740
2	2403	-2342
3	801	810
4	828	802
5	216	175
6	1305	1353
7	504	-458
8	801	-853
9	<135	188
10	675	-688
11	198	192
12	585	610
13	270	-290
14	261	249
15	<153	-20
16	351	-357
17	216	220
18	153	-121
19	<153	-54
20	153	150
21	126	-119

0,k,4

0	1296	1276
1	954	-928
2	738	709
3	297	-292
4	585	-572
5	1206	1273
6	1179	-1269
7	<108	72
8	171	-244†
9	972	-1034
10	675	711
11	<108	-88
12	513	540
13	531	560
14	<135	-96
15	<135	88
16	369	-368
17	153	-192
18	153	-145
19	<171	-59
20	153	124

0,k,5

1	108	-112
2	171	-202
3	225	204
4	<81	-92
5	108	110
6	234	277
7	171	195
8	153	157
9	171	-159
10	270	-298
11	130	139†
12	171	-184
13	198	193
14	216	258
15	<153	-104
16	180	160
17	180	-161

0,k,6

0	1503	-1528
1	171	154
2	297	-276
3	324	-285
4	1134	1116
5	567	-565
6	549	529
7	378	373
8	387	-369
9	576	524
10	306	-310
11	252	-248
12	<135	-55
13	252	-249
14	<135	4
15	171	145

0,k,7

1	531	-483
2	171	186
3	549	506
4	171	-156
5	351	320
6	153	-160
7	459	-404
8	198	170
9	126	-122
10	<153	80
11	270	252
12	<216	-67
13	<216	6
14	<216	7
15	<216	-125
16	<216	-19

0,k,8

0	288	301
1	180	139
2	180	188
3	351	319
4	<198	-138
5	<225	161
6	423	-376
7	279	-218
8	198	-154
9	333	-271
10	360	278
11	<216	49
12	342	289
13	<216	158
14	<216	-58
15	<216	20
16	252	-223

0,k,9

1	<216	125
2	<216	68
3	171	-156
4	171	84
5	<216	-20
6	<171	-28
7	<216	105
8	<216	-88
9	<216	-91

0,k,10

0	171	-162
1	<216	7
2	171	-132
3	171	-118
4	<216	109
5	216	-200
6	324	296
7	<216	69
8	<216	-8
9	288	265
10	270	-254
11	<216	51
12	<216	-36
13	198	-156

1,k,0

1	1836	1790†
2	3429	-3851†
3	3240	-3367†
4	3078	-3106
5	<81	-31
6	585	517
7	2277	2319
8	2079	2118
9	<108	-107
10	432	447
11	1251	-1337
12	666	-658
13	<135	33
14	450	-444
15	549	576
16	<153	-30
17	<171	24
18	153	129
19	171	-173
20	180	135

1,k,1

0	3753	3976†
1	945	795
2	801	-614
3	126	-115
4	2205	-2291
5	603	-584
6	1260	1226
7	342	369
8	1062	1035
9	234	250
10	864	-874
11	486	-478
12	324	-323
13	<135	-33
14	486	529
15	387	395
16	<135	83
17	<135	-101
18	216	-253
19	252	-257

1,k,2

1	1233	1171
2	1620	1571
3	909	-863
4	1620	1567
5	720	-724
6	234	234
7	486	432
8	1116	-1087
9	216	269
10	936	-1003
11	<135	-53
12	225	239
13	<135	-99
14	873	946
15	<153	2
16	171	181
17	<153	33
18	477	-523
19	<153	-33
20	171	-191
21	<153	-19
22	198	205

1,k,3

0	72	32
1	1422	-1528
2	108	111
3	882	-913
4	180	-127
5	1413	1402
6	270	-258
7	441	423
8	<108	5
9	891	-982
10	270	258
11	171	-153
12	<108	-37
13	504	549
14	216	-217
15	<126	72
16	<126	48
17	234	-247
18	153	120

1,k,4

1	315	-306
2	2898	-2946†
3	234	255
4	468	-459
5	297	297
6	1386	1455
7	180	-195
8	270	257
9	261	-272
10	234	-217
11	<108	78
12	126	149
13	198	201
14	198	-202
15	<135	-17
16	297	-319
17	126	-119
18	108	125
19	<153	9
20	216	222

1,k,5

0	333	-344
1	477	-453
2	<81	-47
3	378	-360
4	369	369
5	387	373
6	126	134
7	153	151
8	324	-367
9	225	-229
10	198	-187
11	<108	-10
12	315	328
13	130	127
14	180	185
15	<135	-20
16	216	-240
17	<135	-73
18	<135	-118
19	<135	0
20	171	141

1,k,6

1	495	-489
2	1008	1027
3	414	418
4	441	433
5	396	372
6	432	-389
7	270	-265
8	378	-394
9	171	-178
10	153	-181
11	216	220
12	<135	79
13	<135	75
14	297	328
15	180	-195
16	126	130
17	<153	-57
18	180	-198
19	153	142
20	126	-127

1,k,7

0	675	-679
1	261	287
2	<108	81
3	216	227
4	558	573
5	252	-232
6	198	-213
7	<108	-81
8	324	-340
9	108	128
10	252	249
11	<108	-35
12	180	155
13	<126	-52
14	216	-218

1,k,8

1	<180	-109
2	333	-320
3	234	273
4	261	-302
5	<198	15
6	<198	42
7	342	-346
8	288	330
9	<198	-30
10	198	226
11	225	236
12	<198	-111
13	<198	53
14	279	-262

1,k,9

0	<198	66
1	<198	38
2	<198	-6
3	<198	34
4	<198	-31
5	<198	-68
6	<198	30
7	<198	-71

1,k,10

1	<198	-6
2	423	434
3	<198	-132
4	<198	153
5	<198	71
6	225	-244

$\bar{1}$,k,1

0	1377	1165
1	423	-230†
2	<81	-82
3	486	-456
4	1557	-1468
5	576	496
6	297	-269
7	108	-39
8	765	769
9	180	-194
10	180	187
11	<135	6
12	531	-539
13	<135	14
14	153	-169
15	<153	55
16	369	359
17	<171	-38
18	171	115
19	<180	-59
20	216	-196

$\bar{1}$,k,2

1	756	748
2	4752	-5200†
3	1368	1238
4	1539	-1515
5	1575	-1483
6	1710	1685
7	1386	-1422
8	945	958
9	900	888
10	<108	27
11	801	811
12	234	-199
13	522	-534
14	315	-345
15	171	-167
16	153	-165
17	315	313
18	135	135
19	153	-127
20	171	177
21	180	-193
22	<189	29
23	171	156

$\bar{1}$,k,3

0	1080	-1107
1	1908	-1802
2	486	423
3	1287	-1200
4	891	896
5	1287	1323
6	603	-608
7	513	469
8	126	-181
9	747	-762
10	468	476
11	<108	-49
12	108	-127
13	378	384
14	180	-211
15	<135	-60
16	198	225
17	153	-137
18	<153	46
19	<153	37
20	198	-215

$\bar{1}$,k,4

1	981	-939
2	1080	1000
3	198	143
4	1071	1015
5	828	766
6	<81	47
7	504	520
8	909	-939
9	153	-145
10	603	-622
11	567	-557
12	378	379
13	108	-146
14	567	589
15	234	254
16	<135	29
17	135	151
18	288	-299
19	<153	-30
20	135	-122

$\bar{1}$,k,5

0	108	32
1	630	577
2	126	-95
3	261	238
4	<81	-106
5	522	-480
6	162	140
7	180	180
8	108	122
9	234	241
10	126	-123
11	351	-384
12	<135	-80
13	<135	-25
14	<135	38
15	342	371
16	<153	-14
17	<153	-92
18	<153	9
19	216	-255
20	<153	62
21	<153	110
22	<153	-11
23	135	142

$\bar{1}$,k,6

1	414	419
2	324	-317
3	180	138
4	864	-834
5	513	-513
6	72	82
7	603	-586
8	936	972
9	126	141
10	<108	43
11	513	520
12	549	-578
13	<153	132
14	<135	8
15	216	-215
16	171	171
17	153	-157

$\bar{1}$,k,7

0	279	-276
1	171	-171
2	81	81
3	225	-226
4	315	300
5	108	112
6	171	-156
7	234	232
8	216	-295
9	108	-83
10	153	103
11	171	-177
12	198	216

$\bar{1}$,k,8

1	495	-472
2	<135	8
3	<135	37
4	396	379
5	549	565
6	153	130
7	306	301
8	459	-462
9	315	-308
10	207	-220
11	306	-290
12	306	307
13	<153	73
14	180	174

$\bar{1}$,k,9

0	<198	41
1	<198	-45
2	<198	-119
3	<198	23
4	<198	-36
5	<198	89
6	270	262
7	<198	-78
8	<198	5
9	<198	-89
10	270	-223

$\bar{1}$,k,10

1	261	235
2	<198	-53
3	<198	-18
4	171	-135
5	198	-193
6	<198	-27
7	198	-208
8	198	170
9	<198	-14
10	171	94
11	225	249

$\bar{1}$,k,11

0	153	-145
1	<198	43
2	<198	58
3	<198	28
4	171	158
5	<198	-55
6	<198	-122
7	<198	-17
8	198	-152

$\bar{1}$,k,12

1	234	-246
2	<189	83
3	153	132
4	<189	73
5	198	205

2,k,0

0	1800	-1762
1	1494	1319
2	1566	-1423
3	2124	2029
4	621	575
5	81	138
6	1674	1751
7	657	-687
8	660	624
9	738	-718
10	909	-926
11	<135	-111
12	738	-766
13	567	553
14	225	209
15	261	311
16	396	406
17	225	-216
18	<171	71
19	198	-228
20	171	-110

2,k,1

1	1215	1125
2	1188	1079
3	1566	-1470
4	675	-662
5	495	-441
6	423	-448
7	900	904
8	567	588
9	<108	-9
10	81	-95
11	504	-505
12	405	-403
13	153	156
14	261	284
15	171	174
16	180	175
17	171	-129
18	270	-304
19	<153	-5
20	<153	-58
21	126	75
22	198	222

2,k,2

0	2484	2558
1	<81	-59
2	675	644
3	972	-1003
4	1476	-1449
5	657	-640
6	864	-851
7	936	965
8	<108	-2
9	648	662
10	405	415
11	612	-659
12	477	502
13	306	-320
14	<135	46
15	360	360
16	315	-345
17	<135	-8
18	171	-176
19	198	-189
20	<189	96
21	180	136

2,k,3

1	126	-150
2	756	-770
3	225	217
4	<108	-14
5	234	182
6	630	635
7	198	-196
8	<81	21
9	171	-171
10	441	-447
11	171	190
12	<108	-11
13	<108	107
14	297	294
15	126	-87
16	<153	18
17	<135	-57
18	153	-155
19	<153	7
20	<153	-4
21	<153	26
22	<144	69

2,k,4

0	1206	-1260
1	594	-607
2	486	-494
3	108	-109
4	792	805
5	882	866
6	873	884
7	153	-155
8	126	-116
9	801	-828
10	522	-580
11	180	185
12	180	-179
13	504	524
14	<153	121
15	<153	-102
16	135	84
17	198	-222

2,k,5

1	108	-79
2	450	-484
3	108	-99
4	225	230
5	216	227
6	270	288
7	126	133
8	297	-305
9	261	-272
10	<135	-76
11	<135	-53
12	261	285
13	225	242
14	<135	-26
15	<135	-53
16	153	-177
17	189	-182
18	<153	24
19	153	98

2,k,6

0	414	420
1	<108	1
2	270	236
3	<108	-63
4	171	-160
5	<108	-69
6	450	-478
7	<108	82
8	306	-305
9	135	137
10	279	288
11	<135	-52
12	441	486
13	108	-143
14	<153	-13
15	<153	5
16	324	-355
17	<153	84
18	<153	-92
19	<153	23
20	153	159

2,k,7

1	270	-275
2	252	242
3	360	393
4	<108	-51
5	153	141
6	153	-171
7	378	-393
8	<108	90
9	<108	-64
10	<153	87
11	270	296
12	<135	-103
13	<135	29
14	<135	-43
15	153	-150

2,k,8

0	738	-760
1	<189	113
2	<189	-101
3	<189	126
4	540	553

2,k,9

1	<189	-40
2	<189	82
3	<189	13
4	<189	27

2,k,10

0	315	374
1	<189	99
2	<189	73
3	<189	100
4	261	-265

$\bar{2}$,k,1

1	684	-587
2	1071	935
3	1377	1303
4	<81	-71
5	243	-151
6	711	-612
7	639	-684
8	<108	-60
9	459	462
10	414	379
11	207	240
12	<108	-60
13	468	-471
14	180	-201
15	<135	57
16	<135	12
17	324	327
18	<153	54
19	135	-152
20	<153	13
21	198	-198

$\bar{2}$,k,2

0	<126	227
1	1377	1306
2	1881	1690
3	2628	2390
4	225	139
5	477	463
6	2259	-2372
7	1206	-1223
8	306	-323
9	819	-842
10	1404	1511
11	261	255
12	135	121
13	477	474
14	549	-590
15	<153	96
16	153	152
17	<171	-81
18	<189	109
19	<189	-90
20	261	-266
21	<189	-73
22	<189	19
23	<189	16
24	243	213

$\bar{2}$,k,3

1	288	303
2	378	-316
3	108	39
4	216	157
5	648	-621
6	306	277
7	180	-128
8	108	-92
9	621	594
10	198	-205
11	<108	-56
12	126	117
13	387	-430
14	<135	82
15	117	111
16	<135	-26
17	252	273

$\bar{2}$,k,4

0	180	-51
1	387	-435
2	684	-640
3	1413	-1368
4	315	-289
5	711	-691
6	963	1004
7	990	1007
8	657	669
9	819	883
10	711	-699
11	315	-332
12	585	-625
13	423	-459
14	288	278
15	<135	1
16	315	330

$\bar{2}$,k,5

1	261	345
2	459	515
3	477	-541
4	675	-612
5	108	-101
6	252	-258
7	513	521
8	675	673
9	<108	-38
10	<108	-30
11	333	-363
12	441	-473
13	<135	75
14	198	222
15	198	209
16	198	206
17	<153	-52
18	234	-269
19	126	-108
20	<171	-57
21	<171	5
22	207	207

$\bar{2}$,k,6

0	603	592
1	558	543
2	198	198
3	783	754
4	378	-395
5	144	139
6	396	-370
7	225	-246
8	<108	55
9	549	-535
10	288	268
11	333	-340
12	126	109
13	414	439
14	<135	-75
15	459	488
16	<135	-64
17	180	-196
18	<153	-33
19	288	-324

$\bar{2}$,k,7

1	<108	36
2	612	-620
3	<81	-18
4	234	231
5	<81	-16
6	594	572
7	<81	-28
8	279	-274
9	<108	15
10	459	-462
11	<108	50
12	189	176
13	<108	-19
14	261	276
15	<126	-54
16	126	-68
17	<126	4
18	144	-118

$\bar{2}$,k,8

0	<153	-133
1	891	-894
2	126	-149
3	981	-983
4	108	110
5	405	410
6	333	337
7	531	537
8	<135	-68
9	<135	-42
10	297	-297
11	<135	-6
12	<171	54
13	<153	-17
14	171	166
15	198	-198
16	<198	-69
17	<198	-52
18	<198	-53
19	153	144

$\bar{2}$,k,9

1	<135	- 66
2	297	-276
3	<135	-2
4	108	-30
5	180	180
6	144	151
7	<171	13
8	<171	4
9	252	-260
10	<153	-26
11	<153	10
12	<153	36
13	252	240
14	<153	-8
15	<153	-29
16	<153	-56
17	198	-163

Table 6 (*cont.*)

$\bar{2},k,10$

0	216	-219
1	324	307
2	<198	32
3	459	452
4	252	214
5	<198	-20
6	<198	-78
7	270	-263
8	198	-196
9	198	-194
10	<198	87
11	<198	-2
12	180	172

$\bar{2},k,11$

1	216	-206
2	<198	136
3	252	253
4	<198	62
5	<180	100
6	<180	-68
7	216	-231
8	<180	-60
9	<153	1
10	<180	7
11	180	156

$\bar{2},k,12$

0	<180	-142
1	<180	-117
2	<180	27
3	216	-190
4	<180	136
5	<180	-49
6	<180	-60
7	153	96
8	<180	-101
9	171	152

$\bar{2},k,14$

0	<135	30
1	153	138
2	<135	-11
3	171	173
4	<135	-24
5	<135	-9
6	<135	28
7	135	-104

3,k,0

1	1314	1175
2	<81	4
3	459	392
4	1116	1069
5	1278	-1296
6	594	582
7	1017	-1048
8	846	-845
9	567	563
10	792	-815
11	756	752
12	432	377
13	<153	26
14	531	541
15	297	-286
16	<153	-28
17	198	-171
18	198	-213

3,k,1

0	<126	19
1	72	80
2	189	-141
3	297	-247
4	<81	10
5	162	-173
6	180	159
7	513	494
8	<81	-36
9	108	96
10	216	-205
11	414	-465
12	<135	84
13	<135	20
14	126	137
15	351	360
16	153	-140
17	<153	-44
18	<153	-55
19	198	-219
20	171	137

3,k,2

1	936	-1025
2	72	-41
3	198	238
4	1143	-1192
5	1017	1065
6	198	-222
7	342	332
8	1125	1172
9	558	-564
10	261	267
11	351	-376
12	585	-641
13	153	134
14	<135	-40
15	126	132
16	171	166
17	<153	22
18	171	-157
19	<153	52
20	<153	10
21	<153	-13
22	189	188

3,k,3

0	495	-554
1	324	336
2	<108	26
3	<135	109
4	459	495
5	342	-345
6	<108	-42
7	<108	74
8	396	-389
9	180	211
10	<135	62
11	153	-145
12	261	255
13	<153	-27
14	<126	-40
15	135	119
16	144	-125
17	<153	-84

3,k,4

1	333	326
2	288	293
3	<81	17
4	576	607
5	324	-330
6	99	89
7	351	-344
8	594	-634
9	<135	67
10	333	-335
11	387	404
12	297	317
13	117	143
14	243	244
15	252	-248
16	<135	-43
17	171	-192

3,k,5

0	171	177
1	225	-217
2	<135	-89
3	<135	-40
4	<135	-105
5	297	299
6	180	196
7	<135	-80
8	<135	-4
9	234	-240
10	189	-193

3,k,6

1	198	-205
2	288	-319
3	<135	-38
4	279	-309
5	324	350
6	<135	-20
7	189	196
8	288	297
9	324	-311
10	252	288
11	180	-192
12	<153	-94
13	198	183
14	261	-275
15	<153	71
16	<153	-58
17	<153	-71
18	153	130

3,k,7

0	171	-186
1	153	155
2	<108	16
3	<108	102
4	180	179
5	180	-201
6	<135	-34
7	<135	-83
8	180	-149
9	180	180

3,k,8

1	<189	-16
2	351	352
3	<189	136
4	216	226
5	<189	-93
6	<189	-147
7	234	-199
8	234	-243
9	<189	135
10	<189	-37
11	180	187

$\bar{3},k,1$

0	1719	-1702
1	1170	1141
2	666	602
3	729	720
4	1251	1212
5	1035	-1029
6	828	-877
7	243	-225
8	378	-393
9	729	738
10	675	737
11	<108	49
12	<108	-61
13	450	-431
14	369	-403
15	<135	22
16	207	232
17	252	251
18	135	144
19	<153	3
20	198	-223
21	153	-130

$\bar{3},k,2$

1	2349	-2363
2	1791	1786
3	1206	1078
4	603	553
5	1458	1455
6	873	-796
7	315	263
8	342	-346
9	<135	-45
10	180	151
11	567	-634
12	<135	118
13	612	-633
14	<135	-65
15	342	317
16	<135	55
17	549	593
18	135	122†
19	<153	-111
20	<153	-70
21	297	-313
22	135	-131

$\bar{3},k,3$

0	1215	1247
1	657	638
2	288	-243
3	567	558
4	1062	-1082
5	495	-459
6	252	265
7	324	-304
8	801	789
9	<153	174
10	252	-238
11	207	189
12	513	-509
13	<153	-60
14	<153	116
15	171	-169
16	252	270
17	<171	11
18	<171	-27
19	153	103
20	135	-122

$\bar{3},k,4$

1	2700	2672
2	333	276
3	1800	-1772
4	756	-674
5	1944	-1963
6	297	-285
7	585	592
8	630	656
9	621	594
10	198	182
11	108	-115
12	342	-372
13	189	181
14	<135	-34
15	126	108
16	<153	107
17	297	-285
18	<153	-66
19	153	-152
20	<171	-7
21	135	116

$\bar{3},k,5$

0	1332	1335
1	243	214
2	<81	-29
3	108	-111
4	1062	-1063
5	306	-295
6	171	154
7	396	351
8	558	572
9	207	202
10	162	-193
11	441	-457
12	252	-255
13	<135	-53
14	135	167
15	369	395
16	135	142†
17	<153	-22
18	<153	-98
19	225	-234

$\bar{3},k,6$

1	765	-722
2	522	-496
3	<126	29
4	153	129
5	801	740
6	513	499
7	567	602
8	108	-128
9	153	-162
10	441	-425
11	540	-588
12	<108	63
13	288	-294
14	315	315
15	279	277
16	<135	-8
17	333	334
18	180	-186
19	<153	-60
20	<153	-6
21	180	-174

$\bar{3},k,7$

0	<153	-120
1	810	-822
2	108	-73
3	567	-548
4	72	56
5	819	812
6	108	112
7	225	201
8	<81	46
9	594	-630
10	<108	-60
11	<108	38
12	<108	-88
13	378	379
14	<135	-15
15	<135	-94
16	<135	63
17	198	-210

$\bar{3},k,8$

1	621	609
2	711	-725
3	171	-191
4	180	214
5	531	-539
6	549	567
7	270	-262
8	279	-282
9	<171	84
10	315	-326
11	351	340
12	198	216
13	225	244
14	153	154
15	171	-167
16	<153	-106
17	252	-259

$\bar{3},k,9$

0	<171	-53
1	<171	-112
2	<171	31
3	<171	-96
4	<171	101
5	<171	130
6	<171	-61
7	<171	124
8	189	-191
9	135	-111
10	<171	9
11	153	-150
12	198	202
13	<189	57
14	<189	36
15	171	132
16	171	-154

$\bar{3},k,10$

1	666	-660
2	<171	22
3	414	405
4	<171	-129
5	576	568
6	<153	-36
7	<153	-79
8	171	150
9	225	-224

$\bar{3},k,11$

0	459	-443
1	<189	29
2	<189	15
3	<189	8
4	351	368
5	<189	-58
6	<189	-52
7	<189	-23
8	207	-197

$\bar{3},k,12$

1	180	137
2	<189	89
3	<189	37
4	<180	83
5	189	-156
6	<180	-38
11	216	191

4,k,0

0	630	-590
1	2079	-1987
2	396	345
3	2133	-2099
4	639	618
5	864	880
6	576	-597
7	1008	1087
8	495	-513
9	171	-175
10	333	350
11	<153	-92
12	288	309
13	<135	33
14	<189	-70
15	288	-283
16	<135	-92
17	<153	-105
18	<135	-38
19	207	208
20	<153	-10
21	126	117

4,k,1

1	423	-436
2	414	-428
3	432	439
4	135	93
5	414	407
6	378	356
7	270	-277
8	135	-97
9	315	-319
10	261	-264
11	117	166
12	108	66
13	297	294
14	171	162
15	<135	-80
16	<135	-17
17	225	-219
18	<135	-86
19	<135	39
20	<135	-1
21	144	118

4,k,2

0	864	-914
1	909	987
2	198	-182
3	1008	1056
4	657	661
5	306	-306
6	315	307
7	459	-476
8	279	-273
9	153	-150
10	153	-144
11	135	-157
12	153	114
13	198	214
14	<171	-40
15	369	386
16	180	-140
17	135	-92
18	126	82
19	270	-286
20	180	155

4,k,3

1	378	-444
2	522	617
3	441	479
4	252	-248
5	261	268
6	360	-393
7	414	-413
8	315	317
9	108	-96
10	108	131
11	315	305
12	234	-242
13	<135	-9
14	<135	30
15	216	-206
16	135	111
17	<171	19
18	135	-80
19	135	126

4,k,4

0	<135	-66
1	207	-200
2	216	195
3	414	-434
4	180	181
5	189	-201
6	351	-381
7	288	303
8	315	-347
9	342	389
10	234	248
11	<153	-1
12	288	315
13	270	-275
14	<171	-37
15	162	-170
16	126	-157
17	<171	87
18	<171	-47
19	144	156

4,k,6

0	<135	-9
1	270	282
2	162	-184
3	378	422
4	<135	-59
5	<135	-45
6	342	390
7	324	-354
8	<153	156
9	<153	-102
10	261	-289
11	153	159

4,k,7

1	<135	34
2	198	211
3	<135	-81
4	<135	-27
5	<135	0
6	171	-173

4,k,8

0	144	129
1	126	-56
2	<171	107
3	<171	-123
4	<171	-60
5	<171	-55
6	180	-221
7	<171	97
8	<171	-54
9	<171	124

$\bar{4},k,1$

1	459	-426
2	1512	1620
3	630	618
4	324	-265
5	81	-71
6	1098	-1143
7	504	-548
8	369	359
9	297	288
10	576	608
11	279	304
12	261	-270
13	342	-363
14	297	-311
15	<153	-117
16	171	163
17	225	254
18	153	177
19	<153	24
20	144	-69
21	153	-111

$\bar{4},k,2$

0	279	343
1	261	-261
2	117	-94
3	882	-901
4	387	-390
5	981	-925
6	<108	77
7	423	457
8	387	389
9	1080	1070
10	<108	31
11	288	253
12	288	-297
13	657	-691
14	<153	-95
15	513	-504
16	135	167
17	252	259
18	126	70
19	360	361
20	<189	-77
21	<189	-68
22	<189	-17
23	189	-151

$\bar{4},k,3$

1	1026	1013
2	423	350
3	1287	-1308
4	108	-140
5	351	-386
6	369	-347
7	1053	1105
8	<108	80
9	<108	16
10	297	287
11	675	-685
12	<108	13
13	171	169
14	225	-226
15	333	355
16	<153	-56
17	126	-128
18	171	153
19	171	-168

$\bar{4},k,4$

0	1719	1748
1	1080	1104
2	297	-271
3	1440	1456
4	1440	-1432
5	<108	-32
6	675	637
7	720	-739
8	819	840
9	468	-444
10	594	-619
11	<135	-36
12	414	-414
13	333	312
14	423	405
15	315	327
16	225	191
17	<153	-55
18	153	-176
19	189	-223
20	144	-92

$\bar{4},k,5$

1	522	522
2	<108	60
3	603	-585
4	<108	66
5	414	-391
6	<108	61
7	486	492
8	<108	-23
9	324	313
10	153	-148
11	297	-324
12	<135	-57
13	279	-278
14	162	159
15	153	168
16	126	66
17	216	203

$\bar{4},k,6$

0	198	218
1	1251	-1210
2	126	149
3	1377	-1374
4	198	-201
5	459	465
6	369	-349
7	738	760
8	126	146
9	<108	46
10	351	333
11	<108	-52
12	135	-142
13	<135	-77
14	234	-204
15	198	-216
16	144	150
17	<153	-50
18	<153	78
19	153	147
20	135	-135

$\bar{4},k,7$

1	72	44
2	1143	-1135
3	72	52
4	198	195
5	99	-93
6	765	760
7	108	-93
8	306	-308
9	<108	65
10	333	-358
11	<108	41
12	279	283
13	<108	-32
14	<108	106
15	<135	39
16	171	-180

$\bar{4},k,8$

0	198	-202
1	<135	-8
2	108	-112
3	342	337
4	126	123
5	495	499
6	261	237
7	261	-231
8	<153	27
9	612	-629
10	180	-192
11	<153	-63
12	<153	-81
13	378	422
14	<171	82
15	216	199
16	<153	44
17	126	-140
18	<153	-7
19	153	-154

$\bar{4},k,9$

1	153	-158
2	126	128
3	126	110
4	<135	-36
5	135	120
6	<135	-9
7	<135	-47
8	126	85
9	<153	-26
10	<153	-120
11	<153	25
12	153	-111
13	<153	-23
14	153	166

$\bar{4},k,10$

0	144	-138
1	144	-130
2	135	146
3	378	-383
4	198	175
5	216	-201
6	261	-307
7	315	343
8	207	-210
9	279	300
10	225	250
11	171	-162
12	171	182
13	180	-181
14	144	-106

$\bar{4},k,11$

1	<171	-118
2	126	-119†
3	189	199
4	<171	-58
5	<171	59
6	<171	75
7	225	-219
8	<171	62
9	<171	-50
10	<171	-32
11	171	146

$\bar{4},k,12$

0	180	-190
1	<171	83
2	<171	-86
3	180	185
4	<171	132
5	<171	86
6	180	174
7	153	-140
8	<171	-28
9	171	-165
10	153	-145

5,k,0

1	1242	-1257
2	1134	-1117
3	594	591
4	387	386
5	1062	1038
6	747	744
7	<108	90
8	567	-580
9	378	-388
10	387	-378
11	234	-237
12	495	509
13	144	-109
14	180	172
15	144	82
16	270	-292
17	153	176
18	135	-84
19	117	56

5,k,1

0	288	-307
1	540	-555
2	<81	3
3	297	-315
4	279	303
5	522	552
6	<108	0
7	<108	22
8	252	-265
9	369	-381
10	<108	-45
11	144	157
12	225	229
13	198	218
14	<135	57
15	171	-166
16	180	-179
17	126	-108†
18	<171	-39
19	<171	86
20	153	128

5,k,2

1	324	344
2	153	178
3	135	157
4	<81	12
5	324	-357
6	<108	-61
7	531	-552
8	<135	65
9	<108	-9
10	<135	-35
11	522	570
12	135	-141
13	279	297
14	<135	18
15	279	-308
16	<171	122
17	288	-303
18	<153	15
19	<189	98
20	<153	-47
21	153	162

5,k,3

0	558	-679
1	351	390
2	<108	64
3	216	249
4	504	520
5	342	-379
6	126	-160
7	<135	-43
8	369	-380
9	261	276
10	153	170
11	126	-94
12	225	223
13	153	-157
14	126	-125

5,k,4

1	594	-699
2	198	241
3	423	449
4	117	-154
5	495	560
6	243	-278
7	126	-99
8	<135	122
9	162	-170
10	198	247
11	<153	-57
12	<153	-6
13	153	-116
14	<153	-134
15	<153	21
16	<135	-60

5,k,5

0	<153	-26
1	<153	77
2	<153	2
3	<153	91
4	<153	18
5	<153	-86
6	<153	-2
7	171	-137
8	<153	0
9	<153	76
10	<153	1
11	180	162
12	<153	-8
13	<153	-47
14	<153	-1
15	153	-142

5,k,6

1	333	405
2	189	230
3	198	-253
4	<153	101
5	270	-327

5,k,7

0	144	182
1	126	125
2	<135	-22
3	<135	100
4	126	-153

$\bar{5},k,1$

0	405	-412
1	630	660.
2	<108	18
3	504	515
4	315	330
5	657	-653
6	<81	-61
7	342	-339
8	171	-201
9	477	499
10	<108	93
11	252	246
12	<108	79
13	288	-296
14	<135	-84
15	189	-189
16	<135	-14
17	135	139
18	<153	37
19	126	110

$\bar{5},k,2$

1	1278	1426
2	540	572
3	675	-738
4	315	310
5	981	-1028
6	414	-414
7	<108	-60
8	441	-414
9	207	231
10	270	293
11	261	275
12	351	340
13	261	273
14	216	-219
15	<153	-111
16	207	-177
17	261	-289
18	162	170
19	<126	-41

$\bar{5},k,3$

0	1341	1548
1	<108	23
2	252	-218
3	81	129
4	1089	-1201
5	126	61
6	504	467
7	171	-194
8	594	633
9	<108	-39
10	477	-503
11	171	182
12	171	-191
13	<135	-34
14	315	345
15	135	-137
16	<135	2
17	<153	99
18	153	-158
19	126	113

$\bar{5},k,4$

1	252	-247
2	234	-206
3	612	-580
4	279	-255
5	486	460
6	<108	-6
7	1080	1084
8	315	316
9	126	-152
10	180	205
11	801	-841
12	198	-203
13	171	-164
14	216	-218
15	351	382
16	<135	58
17	198	200
18	153	135

$\bar{5},k,5$

0	<135	-140
1	126	-132
2	<108	37
3	<108	-83
4	<108	26
5	<108	55
6	117	-116
7	<108	-49
8	126	146
9	<135	43
10	180	169
11	<153	126
12	225	-244
13	<153	-31
14	153	-147
15	<153	-114
16	234	239
17	<171	-11
18	<153	79
19	<153	52
20	189	-177

$\bar{5},k,6$

1	513	510
2	171	-161
3	198	180
4	540	532
5	729	-744
6	207	215
7	621	-590
8	621	-628
9	486	504
10	216	-251
11	477	502
12	387	410
13	189	-207
14	135	138
15	153	-136†
16	126	-143

Table 6 (*cont.*)

$\bar{5},k,7$		
0	171	203
1	360	-351
2	81	76
3	153	-157
4	153	-182
5	477	478
6	171	-179
7	<108	31
8	153	157
9	369	-403
10	126	145
11	<108	-4
12	126	-142
13	180	202

$\bar{5},k,8$		
1	279	-267
2	405	-404
3	<135	-82
4	324	-345
5	297	300
6	171	190
7	396	395
8	378	386
9	<135	-65
10	<153	-1
11	378	-392
12	243	-237
13	135	-117
14	<153	-26
15	180	183

$\bar{5},k,9$		
0	<135	-86
1	135	129
2	<135	-11
3	<135	-74
4	<153	53
5	279	-277
6	<153	23
7	198	194
8	<153	17
9	225	244
10	<153	-15
11	198	-200
12	<153	-52
13	135	-82
14	<153	7
15	171	164
16	<153	50
17	<153	-42
18	<153	-7
19	126	-118

$\bar{5},k,10$		
1	135	151
2	297	302
3	<153	88
4	126	129
5	225	-220
6	<153	-37
7	279	-257
8	135	-110
9	<153	114
10	171	-198
11	234	230
12	<153	3
13	<153	4
14	243	242
15	<153	-83
16	<153	63
17	<135	-37
18	162	-163

$\bar{5},k,11$		
0	<153	9
1	<153	-104
2	<153	16
3	<153	-47
4	<153	5
5	198	180
6	<153	-32
7	<153	54
8	<153	-29
9	216	-187
10	<153	20
11	<153	-72
12	<153	38
13	144	120

$\bar{5},k,12$		
1	<153	-95
2	378	-345
3	<153	-41
4	153	-115
5	171	161
6	153	176
7	153	138
8	135	114
9	135	-139
10	<153	-10
11	<135	-123

$\bar{5},k,14$		
1	<108	-4
2	180	152

$6,k,0$		
0	<108	19
1	72	-90
2	<153	107
3	351	357
4	<81	44
5	630	638
6	261	-249
7	288	-297
8	<153	-163
9	721	-752
10	225	245
11	<171	42
12	198	221
13	423	436
14	153	-128
15	<171	88
16	171	-191
17	126	-117

$6,k,1$		
1	72	-117
2	549	-544
3	<81	37
4	216	236
5	144	163
6	342	355
7	<108	12
8	288	-336
9	108	-150
10	144	-123
11	<135	8
12	207	262
16	144	-144

$6,k,2$		
0	270	-241
1	288	-311
2	<108	-75
3	441	-456
4	252	236
5	<108	-76
6	189	196
7	216	211
8	207	-202
9	270	294
10	252	-224
11	126	115
12	126	138
13	243	-226
14	180	159
15	225	-218

$6,k,3$		
1	162	-181
2	279	312
3	252	237
4	<135	-67
5	<153	119
6	261	-254
7	243	-231
8	<135	95
9	<153	-89
10	171	170
11	153	175

$6,k,4$		
0	261	270
1	315	369
2	<135	70
3	414	478
4	180	212
5	<135	-87
6	153	-193
7	261	-308
8	<171	-99
9	<171	-96
10	216	239
11	<153	49
12	<153	32
13	<171	78
14	189	-195

$\bar{6},k,1$		
1	72	-67
2	<81	-20
3	117	83
4	<81	63
5	126	115
6	<108	-51
7	144	-145
8	<108	-102
9	162	-162
10	108	124
11	153	140
12	<153	83
13	153	158
14	162	-147
15	<153	-80
16	<153	-36
17	<153	-101
18	135	128

$\bar{6},k,2$		
0	117	-79
1	108	121
2	288	-296
3	603	634
4	<81	39
5	504	511
6	612	653
7	567	-588
8	<108	20
9	612	-600
10	558	-563
11	270	283
12	<135	-38
13	288	309
14	270	283
15	135	-99

$\bar{6},k,3$		
1	261	255
2	<135	98
3	486	-471
4	198	179
5	<81	-1
6	153	-138
7	477	482
8	243	-211
9	117	-128
10	180	184
11	288	-301
12	171	170
13	144	137
14	180	-186

$\bar{6},k,4$		
0	486	543
1	126	-124
2	234	236
3	378	-377
4	378	-373
5	405	-383
6	477	-485
7	108	139
8	<108	63
9	567	573
10	378	376
11	153	172
12	108	109
13	342	-375
14	144	-130
15	198	-247

$\bar{6},k,5$		
1	198	-195
2	90	64
3	477	468
4	<108	21
5	108	-116
6	153	-144
7	477	-481
8	<108	-28
9	243	261
10	171	180
11	288	294
12	<135	12
13	252	-248
14	144	-158
15	<117	-52
16	<153	10
17	180	189

$\bar{6},k,6$		
0	792	-767
1	153	149
2	108	-84
3	486	440
4	540	491
5	261	255
6	<153	137
7	396	-393
8	<108	27
9	360	-367
10	<135	-13
11	126	153
12	360	-345
13	126	173
14	<135	-119
15	<153	-23
16	324	338
17	<153	29
18	126	137
19	<153	17
20	171	-199

$\bar{6},k,7$		
1	117	125
2	72	117
3	198	-215
4	<108	34
5	126	-121
6	<135	-85
7	288	290
8	<108	-43
9	189	166
10	<108	53
11	261	-251
12	<135	36
13	162	-176
14	<135	-40
15	153	138

$\bar{6},k,8$		
0	909	945
1	<153	94
2	171	146
3	180	-184
4	720	-722
5	378	-357
6	306	-271
7	234	239
8	315	306
9	369	400
10	153	156
11	144	-147
12	<153	-24
13	198	-189
14	<153	29
15	<153	70
16	<153	-31
17	<153	13
18	135	-90

$\bar{6},k,9$		
1	225	246
2	144	139
3	144	-157
4	189	-191
5	207	-228
6	<135	-41
7	<153	62
8	252	267
9	135	121
10	<153	-81
11	<153	-42
12	216	-222
13	<153	-35
14	162	136
15	<153	65
16	144	127
17	<153	14
18	135	-122

$\bar{6},k,10$		
0	324	-317
1	<153	-35
2	153	-134
3	<153	10
4	171	179
5	126	148
6	261	262
7	<153	56
8	<126	73
9	207	-198
10	180	-186
11	153	-135
12	198	-201
13	180	145
14	<153	20
15	126	133
16	162	156

$\bar{6},k,11$		
1	<153	-22
2	306	-312
3	<153	-75
4	<153	80
5	<153	70
6	243	252
7	135	132
8	<153	-118
9	<153	-41
10	162	-154
11	<153	-95
12	<153	108
13	<153	8
14	117	89

$\bar{6},k,12$		
0	306	313
1	171	-190
2	<153	57
3	180	-173
4	189	-202
5	153	151
6	<153	-105
7	153	104
8	<126	-14
12	153	142

$\bar{6},k,14$		
0	324	-280
1	<108	25
2	<108	-33
3	<108	26
4	252	218

$7,k,0$		
1	126	152
2	306	-301
3	153	137
4	189	-212
5	<171	-167
6	<171	121
7	414	-381
8	270	245
9	<153	-40
10	<153	71
11	315	337
12	162	-126
13	162	174
14	153	-143
15	153	-139

$7,k,1$		
0	<153	8
1	153	-152
2	<108	-31
3	<108	-4
4	<108	17
5	234	227
6	<135	73
7	<135	-112
8	<135	-66
9	171	-182
10	<153	-89
11	126	146

$7,k,2$		
1	180	-166
2	180	181
3	<171	-120
4	198	214
5	243	269
6	171	-132
7	279	325
8	279	-297
9	171	-156
10	<153	66
11	234	-256
12	225	203

$7,k,4$		
1	<153	109
2	<153	15
3	<153	102
4	<153	-83
5	153	-174
6	<153	-37
7	225	-252
8	<153	124
9	<153	96

$\bar{7},k,1$		
0	171	-185
1	297	-299
2	<81	-19
3	117	-95
4	180	187
5	387	404
6	<108	36
7	90	-72
8	198	-186
9	297	-316
10	<135	-15
11	<171	128
12	180	159
13	162	136

$\bar{7},k,2$		
1	378	-346
2	783	-767
3	<81	-20
4	108	-97
5	459	452
6	387	370
7	234	274
8	<108	63
9	270	-280
10	<108	83
11	198	-191
12	<135	55
13	<135	98
14	252	-268
15	<153	-10
16	126	-124
17	<153	-50
18	216	213
19	144	113

$\bar{7},k,3$		
0	216	-165
1	<153	61
2	<135	-23
3	<81	49
4	189	164
5	117	-128
6	99	63
7	126	-102
8	171	-167
9	171	157
10	108	-83
11	144	146
12	153	152
13	144	-117

$\bar{7},k,4$		
1	<135	-64
2	909	1001
3	423	421
4	279	284
5	72	-127
6	594	-615
7	558	-591
8	279	-290
9	<108	80
10	198	175
11	369	385

$\bar{7},k,5$		
0	468	-502
1	333	362
2	135	146
3	378	393
4	387	397
5	252	-253
6	333	-352
7	279	-298
8	153	-152
9	171	166
10	342	350
11	126	157
12	<153	-52
13	153	-144
14	225	-260

$\bar{7},k,6$		
1	153	-137
2	198	-230
3	<108	24
4	324	-347
5	<108	46
6	108	-80
7	126	128
8	342	348
9	135	146
10	324	347
11	171	-140
12	153	-143
13	198	-232
14	333	-368
15	<153	64
16	<153	-39
17	126	167
18	198	227

$\bar{7},k,7$		
0	540	556
1	180	192
2	<135	-57
3	<108	60
4	459	-489
5	288	-287
6	126	135
7	<171	-15
8	333	335
9	252	271
10	180	-173
11	<135	36
12	180	-182
13	117	-144
14	180	141

$\bar{7},k,8$		
1	495	468
2	765	750
3	450	-442
4	135	151
5	333	-326
6	360	-353
7	315	329
8	126	-116
9	<153	109
10	<153	-66
11	216	-217
12	<153	-36
13	<153	15
14	189	207
15	180	163

$\bar{7},k,9$		
0	270	296
1	<198	108
2	<198	-21
3	<198	82
4	297	-279
5	<198	-37
6	<198	40
7	<198	35
8	252	230
9	<198	-28
10	<198	-21
11	<198	-131
12	198	-186
13	<198	42
14	<198	-8
15	171	127
16	162	121

$\bar{7},k,10$		
1	<153	69
2	621	-623
3	<153	-93
4	198	-177
5	<153	-67
6	342	356
7	153	104
8	171	171

$\bar{7},k,11$		
0	135	125†
1	306	-344
2	<153	-13
3	279	-291
4	<153	-94
5	279	281
6	<153	35
7	153	136
8	<153	34
9	189	-181
10	<153	-47

$\bar{7},k,12$		
1	<153	8
2	<153	19
3	<153	-38
4	198	192
5	<153	34
6	<153	87
7	<153	46
8	234	-220
9	<153	-60
10	171	-172
11	<153	-32
12	<153	116
13	<153	53
14	144	145
15	<153	13

$8,k,0$		
0	567	-559
1	<225	154
2	<225	-90
3	<225	4
4	450	438
5	315	-319
6	216	186
7	<225	-1
8	261	-174
9	324	306

$\bar{8},k,1$		
1	252	-242
2	450	-459
3	207	203
4	180	152
5	207	215
6	279	296
7	171	-149
8	234	-228
9	126	-143
10	126	-109
11	126	122
12	171	199

$\bar{8},k,2$		
0	171	194
1	207	-218
2	171	145
3	207	-208
4	<135	-51
5	<153	84
6	279	-277
7	<135	28
8	216	-212
9	<153	-3
10	198	194
11	<171	133
12	333	342
13	<189	19
14	<189	-16
15	153	-141
16	279	-278
17	<189	-45
18	<189	-60
19	<189	62
20	153	142†

$\bar{8},k,3$		
1	189	-185
2	315	344
3	279	271
4	<135	-67
5	<171	105
6	243	-245
7	279	-263
8	<171	109
9	<153	-93
10	<171	119
11	207	195
12	171	-123
13	171	95

$\bar{8},k,4$		
0	909	-1026
1	450	473
2	<153	-87
3	387	396
4	693	758
5	369	-381
6	144	145
7	153	-160
8	234	-245
9	261	277
10	<153	-38
11	<153	-32
12	<153	-84
13	216	-212
14	<153	-82
15	<153	70
16	<153	127
17	153	153

$\bar{8},k,5$		
1	252	-267
2	378	409
3	252	273
4	<153	-71
5	144	132
6	351	-353
7	171	-181
8	<153	83
9	<153	31
10	297	302
11	<171	94
12	<171	-42
13	126	-102
14	180	-207

$\bar{8},k,6$		
0	639	706
1	180	198
2	135	137
3	171	168
4	459	-508
5	225	-227
6	234	-269
7	171	-190
8	144	128
9	171	181
10	135	149
11	207	198
12	<153	103
13	135	-85
14	<153	31
15	171	-152

$\bar{8},k,7$		
1	414	472
2	306	327
3	441	-506
4	<108	-34
5	252	-276
6	180	-223
7	369	399
8	<135	57
9	<135	45
10	<135	99
11	198	-240
12	<135	-61
13	<135	75
14	<135	-41
15	126	135

$\bar{8},k,8$		
0	<252	63
1	<198	140
2	216	-213
3	<198	58
4	180	-158
5	<198	-165
6	423	435
7	<198	36
8	297	294
9	<198	142
10	333	-334
11	<198	-80
12	333	-317
13	<198	-103
14	<198	116
15	<198	50
16	207	185

$\bar{8},k,10$		
0	333	364
1	198	-208
2	153	129
3	<198	-80
4	252	-252
5	225	276
6	252	-267
7	<198	-31
8	<198	47
9	234	-235
10	198	185
11	<198	67
12	<189	45
13	198	156

$\bar{8},k,11$		
1	<153	117
2	216	-223
3	<153	-76
4	<153	112
5	<153	-98
6	198	191
7	<153	27
8	153	-141
9	<153	46
10	180	-136

$\bar{8},k,12$		
0	180	-236
1	<153	-140
2	<153	-106
3	153	-195
4	<153	141
5	<153	32
6	171	217
10	126	-132

$9,k,0$		
1	<243	-177
2	522	514
3	<243	165
4	<243	89
5	<243	87
6	333	-274

$\bar{9},k,1$		
0	216	-197
1	261	-255
2	<225	30
3	216	-190
4	252	193
5	252	233

$\bar{9},k,2$		
1	171	-132
2	270	298
3	171	160
4	180	188
5	180	140
6	<180	-79
7	207	-149
8	189	-190
9	189	-164
10	144	-123
11	<162	81
12	<162	61
13	162	149
14	162	164

$\bar{9},k,3$		
0	297	-323
1	297	318
2	<171	7
3	198	212
4	252	270
5	279	-310
6	<171	-22
7	<171	-41
8	171	-155
9	207	211
10	<153	26
11	126	-78
12	<153	73
13	153	-120

$\bar{9},k,4$		
1	153	-168
2	<153	78
3	216	220
4	315	-356
5	<153	54
6	198	-208
7	198	-212
8	387	416
9	<153	40
10	252	269
11	189	173
12	207	-233
13	<153	-54
14	207	-213
15	153	-121

$\bar{9},k,5$		
5	162	-142
9	144	128

$\bar{9},k,6$		
1	<153	109
2	360	399
3	207	-238
4	225	262
5	<153	60
6	189	-175
7	225	255
8	234	-282
9	144	-153
10	<153	-18
11	180	-204
12	162	139
13	153	147

$\bar{9},k,7$		
0	315	323
1	99	147
2	<135	-107
3	126	158
4	297	-284
5	<135	-94
6	198	234
7	<135	-110
8	198	196
9	<135	49
10	180	-226

$\bar{9},k,8$		
1	198	197
2	153	-135
3	<189	-142
4	171	-194
5	171	-184
6	<189	-30
7	<189	54
8	180	205

$\bar{9},k,10$		
1	<153	-101
2	<162	12
3	<162	54
4	225	230
5	<162	68
6	<162	66
7	<162	23
8	279	-264
9	<162	15
10	<162	-95
11	<162	-69
12	171	150

$\overline{10},k,2$		
0	297	-230
1	<216	35
2	<216	-93
3	<216	-52
4	216	153
5	<216	-88

$\overline{10},k,4$		
0	<153	70
1	162	135
2	<171	95
3	162	144
4	<153	2
5	126	-88
6	198	-195
7	<153	-103
8	153	-138

$\overline{10},k,6$		
0	<153	-41
1	<153	-138
2	<153	-149
3	<153	-142
4	<153	-4
5	<153	67
6	234	324
7	<153	70
8	<153	69
9	<153	17
10	189	-253

$\overline{10},k,8$		
0	<198	36
1	180	154
2	<198	108
3	225	225

$\overline{11},k,8$		
1	216	-262
2	153	182
3	180	221
4	<153	62
5	180	190

$\overline{11},k,11$		
0	225	183
1	<180	110
2	<180	4
3	<180	79
4	180	-148

$\overline{12},k,4$		
0	<180	-102
1	180	-187
2	<180	-22

used in two structure-factor least-squares cycles. After the first cycle the author exercised his privilege of checking the observed intensities of reflections showing poor agreement; a few of these observed intensities (or their indices) were found to be in error. The final structure-factor least-square calculation was then made; the maximum parameter shift was 0·0014 Å and the average shift was 0·0004 Å. The final parameters, which include the shifts indicated in the last least-squares calculation,* are listed in Table 5.

The observed and calculated structure factors are listed in Table 6.

Accuracy of the results

The final R factor, calculated for 1867 observed reflections of non-zero weight, is 0·063. Aside from the observational uncertainties, the major sources of disagreement between observed and calculated structure factors probably are, in order of importance: (1) residual-charge effects on the nitrogen and oxygen atoms; (2) incomplete refinement of the temperature-factor parameters, including those of the hydrogen atoms; (3) use of inappropriate form factors, due to bond effects (which could be partially, but not entirely, compensated for by the temperature-factor parameters) and to the linear interpolation scheme used in the Datatron program.

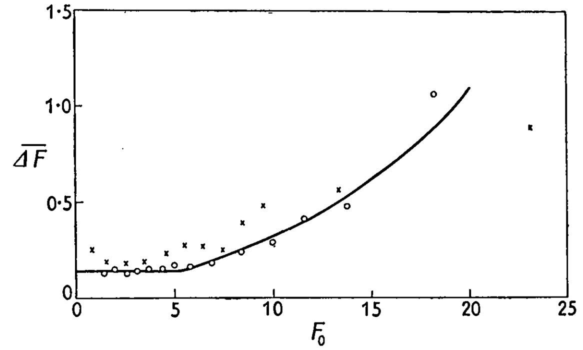

Fig. 3. Structure-factor discrepancies.

Discrepancies ΔF, averaged over all reflections within a range of F_o values, are plotted against the mean F_o value for that range. The crosses refer to the final structure-factor calculations; here, $\Delta F = |F_o - F_c|$. The circles refer to the observational discrepancies implied by the disagreements between F^2 values measured about three different crystal axes i; here, $\Delta F = |F_i^2 - \hat{F}^2| \div 2F_o$, where $\hat{F}^2$ ($\equiv F_o^2$) is the average of the three measurements F_i^2. The solid line is proportional to the inverse of the weighting function $\sqrt{\omega}$ used in the least-squares refinements. The units are electrons per unit cell.

A comparison of the final structure-factor agreement with that expected from the statistics of the observations is shown in Fig. 3. Here the discrepancy $|\Delta F|$ between F_o and F_c, averaged over a group of reflections, is plotted against F_o; for comparison, the discrepancies arising from the statistics of the observations (see section 'Experimental') are also plotted. In addition, the pattern of uncertainties used as the basis of the weighting function is shown as a solid line in Fig. 3; this curve is proportional to the inverse of the weighting function $\sqrt{w}$. It is apparent that the refinement is nearly, but not exactly, as complete as could be expected from the accuracies of the observations. Accordingly, the weighting scheme which was used in the least-squares refinement of the positional parameters, while not perfect, is clearly appropriate.

The standard deviations in the positional parameters of the carbon, nitrogen, and oxygen atoms, calculated from the residuals of the last structure-factor least-squares cycle, range from 0·0007 Å to 0·0010 Å, the larger values being associated with the y parameters. Since the heavier atoms have the larger temperature factors, the uncertainties are roughly the same for all five heavy atoms. It seems appropriate, then, to estimate the limit of error as 0·0035 Å; this corresponds to limits of error of about 0·005 Å in the apparent bond distances and 0·3° in the bond angles. The estimated limit of error in the apparent hydrogen-atom positions is 0·06 Å.

The limits of error in the temperature-factor parameters, judging from the appearances of the difference maps, are probably around 0·1 Å² in B units.

Discussion of the results

(i) *Bond distances and angles*

The bond distances and angles involving the heavy atoms are listed in Table 7 and shown in Fig. 4; the values in parentheses have been corrected for the rocking effects implied from the temperature-factor

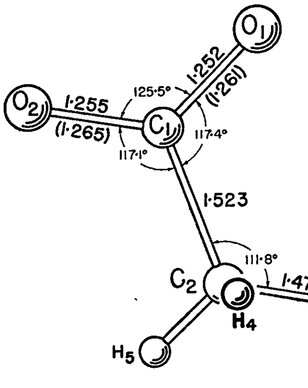

Fig. 4. Dimensions of the glycine molecule. The values in parentheses have been corrected for libration effects implied by the temperature-factor anisotropies.

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* Only the diagonal terms of the normal equations are calculated in the least-squares routine, although in the present case the x–z cross terms would be large and, in view of the large temperature-factor anisotropies, not easily predictable. In the first least-squares, the magnitude of the x–z cross term was estimated; the observed effects of the parameter shifts on the least-squares totals were then used to calculate more accurate values for the cross terms which were included in the normal equations of the second least-squares.

Table 7. *Bond distances and bond angles*

Bond	This investigation	Albrecht & Corey	Angle	This investigation	Albrecht & Corey
C_1–O_1	1·252 (1·261) Å	1·27 Å	C_2–C_1–O_1	117·4°	119°
C_1–O_2	1·255 (1·265)	1·25	C_2–C_1–O_2	117·1	119
C_1–C_2	1·523	1·52	O_1–C_1–O_2	125·5	122
C_2–N	1·474	1·39	C_1–C_2–N	111·8	112

anisotropics.* For comparison, the values reported by Albrecht & Corey are also listed in Table 7. With the exception of the C–N bond, the molecular dimensions found in the present investigation are close to those reported by Albrecht & Corey; the C–N bond, on the other hand, is longer by 0·08 Å and is close to the values reported for other amino acids.

Bond distances and angles involving the hydrogen atoms are listed in Table 8. Although all the bond angles involving hydrogen atoms are within 4° of the expected tetrahedral values, the average C–H distance —0·91 Å—and the average N–H distance—0·87 Å—are both 0·16 Å shorter than the normal single-bond distances. This difference is far greater than the estimated limit of error in the present determination (0·06 Å), and seems to indicate that the effective centers of electron density of the hydrogen atoms are significantly displaced toward the adjacent atoms. Similar effects were observed in a two-dimensional analysis of salicylic acid (Cochran, 1953); on the other hand, a two-dimensional analysis of α-pyridone (Penfold, 1953) indicated more normal C–H and N–H distances, in agreement with the later findings of McDonald (1956) and Cochran (1956).

Table 8. *Bond distances and angles involving the hydrogen atoms*

N–H_1	0·92 Å	C_2–N–H_1	110°
N–H_2	0·85	C_2–N–H_2	110
N–H_3	0·85	C_2–N–H_3	111
		H_1–N–H_2	106
		H_1–N–H_3	106
C_2–H_4	0·91	H_2–N–H_3	113
C_2–H_5	0·91		
		C_1–C_2–H_4	106
		C_1–C_2–H_5	108
		N–C_2–H_4	109
		N–C_2–H_5	110
		H_4–C_2–H_5	112

The electron densities associated with the hydrogen atoms in glycine (see Fig. 2) are roughly spherical; furthermore, the density distributions along the N–H and C–H bonds are approximately Gaussian. It is apparent that the negative region around the nitrogen atom in the difference map, caused by the failure to compensate for the charge effect, could alter only slightly the apparent positions of H_1, H_2, and H_3; no such effect pertains to H_4 and H_5. It is perhaps worth while to point out that in the present case, because the structure has a relatively small over-all temperature factor, it has been possible to obtain intensity data out to a relatively small spacing and the electron densities associated with the hydrogen atoms have been clearly separated from the temperature-factor effects of the heavy atoms; such a separation is often not possible with copper intensity data. Indeed, if the apparent shortening of the C–H and N–H bonds is anomalous, owing to incorrect collection or interpretation of the data, the reason for the anomaly is not readily apparent.

Atoms C_1, C_2, O_1 and O_2 are nearly coplanar, the central carbon atom C_1 being only 0·005 Å from the least-squares plane (calculated by the method of Schomaker, Waser, Marsh & Bergman (1958) with all four atoms weighted equally). The nitrogen atom is 0·436 Å out of this plane.

(ii) *The hydrogen bonding*

Hydrogen-bond distances and angles are given in Table 9. The hydrogen-bond arrangement is essentially that described by Albrecht & Corey. Strong N–H · · · O bonds involving H_1 and H_2 hold the molecules together in the *ac* plane (see Fig. 5); the third hydrogen atom of the ammonium group, H_3, is situated between two neighboring oxygen atoms, forming a weak, 'bifurcated' bond in the *b* direction. The geometry of the 'bifurcated' bond is essentially that pictured by Albrecht & Corey in their Fig. 13: although the nitrogen atom is closer to the neighboring O_1 atom than to the O_2 atom, the angle of attack is less favorable; accordingly, the hydrogen atom H_3 is appreciably closer to O_2 than to O_1.

Table 9. *Hydrogen-bond distances and angles*

N–O_1'	2·768 Å	C_2–N–O_1'	118·0°
H_1–O_1	1·87	N–H_1–O_1	168
N–O_2'	2·850	C_2–N–O_2'	116·1
H_2–O_2'	2·03	N–H_2–O_2'	163
N–O_1''	2·949	C_2–N–O_1''	155·8
N–O_2''	3·074	C_2–N–O_2''	93·0
H_3–O_1''	2·44	N–H_3–O_1''	120
H_3–O_2''	2·29	N–H_3–O_2''	155

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* The directions of maximum temperature factor for the two oxygen atoms lie within 5° of normal to the respective C_1–O bonds, and it has accordingly seemed appropriate to subtract the total temperature factor of C_1 from those of the oxygen atoms and to assume that the remainders represent the rocking motions of the oxygen atoms relative to C_1. For each oxygen atom the principal component of this remainder has a magnitude of approximately 2 Å^2 in *B* units and a direction approximately normal to the plane of the carboxyl group; only this principal component has been taken into account in calculating the bond shortening. No corrections were applied to the C_1–C_2 and C_2–N distances.

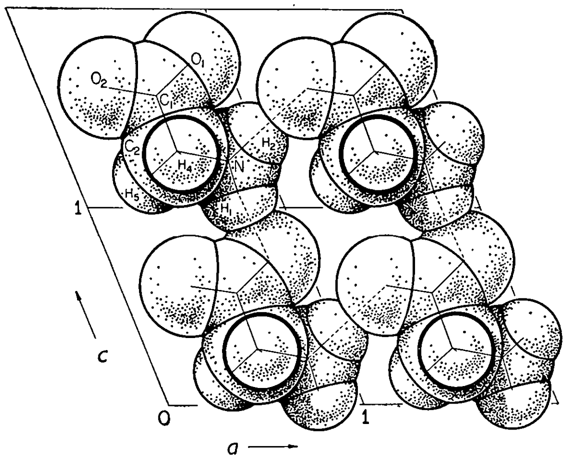

Fig. 5. A packing drawing showing the hydrogen bonds that link the molecules into layers parallel to (010).

(iii) *The temperature factors*

The temperature-factor parameters for the five heavy atoms were transformed into parameters related to the principal axes of the ellipsoids of vibration (Rollett & Davies, 1955); the magnitudes of these principal axes and their direction cosines relative to the unit-cell axes are listed in Table 10. Schematic drawings of the ellipsoids viewed down the *b* and *a* axes are shown in Fig. 6.

Table 10. *Magnitudes and directions of the principal axes of the vibration ellipsoids*

Atom	Axis i	B_i	g_i^1	g_i^2	g_i^3
C_1	1	1·564	0·833	−0·417	0·647
	2	1·200	0·426	0·903	0·213
	3	0·884	0·354	−0·105	−0·732
C_2	1	1·960	0·401	0·899	0·311
	2	1 320	0·876	−0·433	0·523
	3	1·052	0·268	0·067	−0·794
N	1	2·352	0·406	0·914	0·176
	2	1·324	0·889	−0·401	0·534
	3	0·964	0·213	−0·064	−0·827
O_1	1	3·084	0·378	0·923	0·206
	2	1·644	0·920	−0·366	0·209
	3	1·072	−0·104	0·119	−0·955
O_2	1	3·260	−0·002	0·984	−0·163
	2	2·136	0·751	0·118	0·882
	3	1·056	0·661	−0·130	−0·442

The vibrations implied by the temperature-factor parameters are in general agreement with those that would be expected on the basis of the geometry of the molecule and the intermolecular packing. The smallest component for each atom is in a direction approximately parallel to the main axis of the molecule and to the shortest N–H · · · O hydrogen bond; the largest component of vibration for each atom except C_1 is approximately perpendicular to the plane of the molecule—that is, perpendicular to the plane of the strong hydrogen bonding. The central carbon atom C_1, which is covalently bonded to three heavy atoms, has the smallest average vibration, followed by C_2 and the nitrogen atom; the oxygen atoms, which are each bonded (covalently) to only one atom, have the largest vibrations. Furthermore, O_2, which is involved in the longer and hence weaker of the two strong hydrogen bonds, has a larger vibration than O_1.

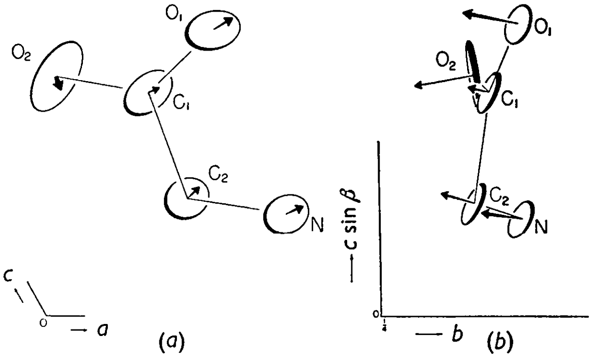

Fig. 6. (*a*) Schematic drawing of the ellipsoids of thermal vibration viewed along the *b* axis. The arrows are drawn in the directions of the principal axes most nearly perpendicular to the molecular plane; for all atoms except C_1, they correspond to the major axes. The lengths of the arrows are proportional to the magnitudes of the corresponding axes projected on to the plane of the drawing. (*b*) Schematic drawing of the ellipsoids of thermal vibration viewed along the *a* axis.

The relatively large anisotropy of C_1 in the *ac* plane is surprising; it is conceivable that it is an artifact caused by the electron density associated with the C_1–O_1 bond, although the use of extensive high-angle data has presumably minimized any such effect.

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