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The Crystal Structures of Glycyl-L-phenylalanine *p*-Toluenesulfonate and Glycyl-L-phenylalanine *p*-Bromobenzenesulfonate*

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Glycyl-L-phenylalanine *p*-toluenesulfonate, $C_{11}H_{15}N_2O_3$. $C_7H_7O_3S$, and glycyl-L-phenylalanine *p*-bromobenzenesulfonate, $C_{11}H_{15}N_2O_3$. $C_6H_4O_3SBr$, both crystallize in the monoclinic space group C2 with unit-cell dimensions a=35.99 (1), b=6.005 (2), c=9.679 (5) Å, $\beta=109.12$ (5)° and a=35.91 (1), b=5.838 (2), c=9.679 (8) Å, $\beta=93.59$ (5)° respectively. There are four molecules in the unit cell with $D_m = 1.297$ g.cm⁻³ for the tosylate and 1.498 g.cm⁻³ for the brosylate. Preliminary crystallographic data are also reported for glycyl-L-phenylalanine. The structures of the two salts were solved by heavy atom methods using Cu K α peak-height data and refined by least squares to R values of 0.095 (tosylate) and 0.12 (brosylate). Peptide and sulfonate conformations in both structures are nearly identical. Molecular packing is characterized by sheets of peptide extended along **a** alternating with parallel sheets of benzenesulfonate ions. Within both tosylate (brosylate) and peptide sheets, the hydrophilic regions show extensive hydrogen bonding. The principal difference between the structures arises from the relative positions of the tosylate methyl and brosylate bromine with respect to the screw axes, which leads to different β angles in the two lattices. The peptide consists of an essentially planar region from the N(1) atom of Gly to the $C\beta(2)$ atom of the Phe with the carboxyl and phenyl groups twisted 74 and 99° respectively from this plane.

Introduction

Studies of the conformations of peptides in the solid state are seriously limited by difficulties frequently encountered in peptide crystallization. Even dipeptides may present problems, although some specific peptides crystallize with reasonable ease. Crystallization of these compounds as a class does not improve with size until 'protein' provides a better descriptive term.

Peptides are often more easily crystallized as salts. In such crystals, however, the packing arrangement may be determined by charge-charge interactions between peptide and counter-ion and/or by the bulk of the counter-ion. Intermolecular interactions may induce peptide conformation changes, therefore, if the potential energy barriers to free rotations about single bonds are low. In order to investigate these effects we have studied for one peptide (glycyl-L-phenylalanine) the crystal structures of the closely related (pseudoisomorphous) tosylate and the brosylate salts.

The primary purpose of this study was a comparative evaluation of peptide conformation in related salt structures. *p*-Toluenesulfonic acid and *p*-bromobenzenesulfonic acid were chosen as counter ions because of the general usefulness of the arylsulfonic acids in the crystallizations of amino acids (Crosby & Kirk, 1935; Stein, Moore & Bergman, 1944). A crystal structure analysis of the 'free' dipeptide for which preliminary data are given is in progress.

Experimental

Crystallization

Both tosylate and brosylate salts of glycyl-L-phenylalanine and the isolated peptide were crystallized by the vapor diffusion method with ethyl acetate in the vapor phase as precipitating agent.

To prepare the tosylate salt, equivalent amounts of *p*-toluenesulfonic acid and the peptide were dissolved in a minimal volume of glacial acetic acid. A beaker containing the solution was kept at room temperature in a closed vessel together with a second beaker of ethyl acetate. Crystals appeared in profusion after solutions were left standing overnight. In the preparation of the brosylate salt an aqueous solution of pbromobenzenesulfonic acid was used. It was prepared by dissolving commercially available sodium p-bromobenzenesulfonate in water and passing the solution through a Dowex 50 W-XB ion exchange column (200-400 mesh size) to remove sodium. The concentration was established as 0.34M by titration with a standard sodium hydroxide solution. An equimolar amount of peptide was added to 2 ml of this solution and needle-like crystals appeared rapidly. This solution was then evaporated to dryness and the residue dissolved by addition of the minimum amount of acetic acid required. Diffusion of ethyl acetate vapor into the solution led overnight to the formation of crystals.

Preparation of the glycyl-L-phenylalanine crystals followed the procedure used with the tosylate salt:

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solution in glacial acetic acid followed by vapor phase addition of ethyl acetate.

X-ray studies

Preliminary X-ray studies were made using both precession and Weissenberg film methods. Crystal densities were determined by the gradient column technique (Low & Richards, 1952).

A tosylate crystal of approximate dimensions $0.04 \times 0.4 \times 0.2$ mm was chosen and mounted with **b** along the φ axis of a General Electric computer controlled diffractometer. The brosylate was cut from a larger piece and had dimensions of $0.02 \times 0.5 \times 0.09$ mm. Cell dimensions were computed from the 2θ values of reflexions along each axial line.

Instrumental difficulties made it impossible to collect data unattended and/or continuously, and therefore the more rapid procedure of peak height data collection was used for both compounds. Nickel-filtered Cu Ka ($\lambda = 1.5418$ Å) radiation was used. A 30 sec count was employed at the peak position with background counted for 15 sec at $2\theta \pm \{1\cdot8(1\cdot0+0\cdot48)\}$ $\tan \theta$). Crystal alignment and possible decay were checked by monitoring three standard reflections after every 50 measurements. A 15% loss in the standard intensities occurred during the data collection. Reflections with $I_{net} < 2\sigma$ were taken as unobserved with I_{unobs} set equal to $2\sigma \ (\sigma = \sqrt{I_{peak} + I_{back}})$. An empirical (Alexander & Smith, 1962) peak-height to intensity conversion curve was used to transform measured peakheights into integrated intensities. The curve was established by measuring 50 integrated intensity/peak height ratios over the range 0 to 150° in 2θ .

Rotation about the φ axis showed a maximum absorption error of 28% for the 020 reflection of the tosylate (μ =17·3 cm⁻¹) and 17% for the smaller brosylate crystal (μ =42·0 cm⁻¹). The magnitude of the measured absorption effects were in agreement with calculations based on crystal dimensions. The intensities were corrected for Lorentz and polarization factors, but not for absorption. Absorption effects should be comparable in the two structures since the brosylate crystal was much smaller.

Crystal description and preliminary X-ray data

Crystals of the peptide tosylate are thin, uniterminal monoclinic plates approximately $0.04 \times 1.0 \times 1.0$ mm in size lying on (100) bounded by {001} and by (010) and {011} at opposite ends; they show perfect cleavage parallel to the (100) face, and are highly birefringent (+) with $\beta \parallel \mathbf{b}$ and γ approximately normal to the face. The brosylate crystals are morphologically similar monoclinic plates. Both crystals show absences for hkl, h+k=2n+1, appropriate to the space group C2. (There is no space group ambiguity. The molecules of glycyl-L-phenylalanine contain an asymmetric carbon atom and must therefore crystallize in the monoclinic class 2.)

Crystals of glycyl-L-phenylalanine are large blades elongated along **b**, lying on (100) and bounded by (010) (001), (101), (101), and {041}. The crystals show perfect cleavage on the (100) face with $\gamma \parallel \mathbf{b}$. The space group is $P2_1$ (systematic absences 0k0, k=2n+1absent).

The space group, cell dimensions, densities and some diffraction statistics are reported for all three crystals in Table 1.

Structure determination and refinement

The intensity data were put on an absolute scale using the *DATFIX* program (Stewart, 1970) which minimizes $\sum (E^2 - 1)^2$ and thus determines a *B* value and scale factor. The overall *B* value so determined was 6.5 for the brosylate and 4.0 for the tosylate salt.

Glycyl-L-phenylalanine brosylate

The close relationship (pseudo-isomorphism) between tosylate and brosylate structures as suggested by their cell dimensions and space group is evident also

	Gly-L-phe TsOH	Gly-L-phe BsOH	Gly-L-phe
Mol. formula	C18H22N2O6S	C17H10N2O6SBr	C11H14N2O3
M.W.	394.44	459.31	222.24
Space group	C2	C2	$P2_1$
a*	35·99 ±0·01 Å	35·91 <u>+</u> 0·01 Å	16∙74 <u>-</u> 0∙02 Å
b	6.005 ± 0.002	5.838 ± 0.002	5.505 ± 0.005
с	9.679 ± 0.005	9.679 ± 0.008	6.465 ± 0.005
β	$109.12 \pm 0.05^{\circ}$	$93.59 \pm 0.05^{\circ}$	97·76 ±0·05°
V	1976·67 Å ³	2025·15 Å ³	
Q _m	1.297g.cm^{-3}	1.498g.cm^{-3}	_
M.W. measured	386.0	446.8	
Radiation	Cu Kα, 1·5418 Å		
No. of independent reflections	2237	2294	1349
No. of observed reflections	2073	1684	885
Ζ	4	4	2
d _{mIn}	0·80 Å	0·80 Å	0·80 Å

Table 1. Physical data

* The limits of error cited for the unit-cell dimensions are mean-square deviations from the mean.

† Gradient column of water saturated bromobenzene/o-xylene.

‡ Gradient column of water saturated bromobenzene/o-xylene/carbon tetrachloride.

 Table 2. Observed and calculated structure factors for glycyl-L-phenylalanine tosylate

The columns are h, $10F_o$, $10F_c$, and α . Unobserved reflections are marked with an asterisk (*).

н FO Ка В. La	FC	H FO	FC	H FO -42 26	FC 24	H FO 13 186	FC 139	H FO	FC 148	N 40	fC	H FD 4 443	FC 362	H F7 -34 25	FC .18	H FO -18 67	50 59	H F	5 FC 5 238	н FD -31 18	FC • 16	н F а 12	D FC
2 1845 1 4 461 6 376 8 1316 1	394 542 398 613	2 34 4 286 6 385 8 35#	715 7 185 399 362	K= 8, L= 8 32 2 167	8 42 186	19 346 17 316 19 381 21 195 23 71	285 362 196 68	-35 191 -37 190 -39 47 -41 58	184 12 47 55	1 44 3 64 5 95	41 61 96	8 89 18 116 12 69 14 85	738 78 182 88	-36 34 -38 18 -48 56 -42 61	• 5 42 49	-28 68 -22 147 -24 113 -26 51 -28 42	131 185 41	-17 35 -19 27 -21 18 -23 36	349 263 89 343	-35 38 -37 48 K= 3,	24 36 34	12 18 14 16 16 9 18 4	1 179 1 179 1 159 3 78 1 41
18 827 12 388 14 333 16 824	007 1 275 1 402 1 730 1	245 2325 4157 6189	242 327 188 194	4 24 6 46 6 56 18 63	15 38 44 68	25 53 27 73 29 43 31 49	43 71 38 54	K* 1, L	587	7 57 9 59 11 43 13 95	58 49 41 92	16 10 18 122 20 118 22 59	22 192 97 54	K• 2, 1 8 260 2 353	268 325	-38 48 -32 65 K+ 2. L	51 73	-25 33 -27 17 -29 8 -31 8	330 149 70 83	1 33 3 78 5 39	32 83 34	28 14 22 16 24 4 26 7	4 152 3 152 8 59 8 79
18 73 28 175 22 83 24 93 24 47	76 1 176 2 59 2 43 2 58 2	227 353 2 206 4 22 4 114	228 372 198 28	12 19+ 14 81 16 159 18 17+ 28 75	82 118 2	33 63 35 58 87 37 39 16•	58 66 28 9	3 335 5 118 7 167 9 166	344 116 197 175 219	15 /3 17 64 -1 95 -3 54	55 103 53	24 153 26 31 28 19 38 68	149 34 28 53	4 387 6 172 8 74 18 124	295 165 63 121	8 63 -2 199 -4 286	57 176 271	-33 7 -35 6 -37 1 -39 4	78 53 53 53 7 53	7 181 9 72 11 18 13 92	114 78 • 23 94	28 38 32 -2 23	6 52 8 52 7 29 4 221
28 89 38 19• 32 35 34 19•	100 2. 78 3 42 3 14 3	100 31 2 37 4 49	98 38 38 58	22 58 -2 22 -4 31 -6 19•	46 18 21 15	-3 871 -5 787 -7 735 -9 588	837 621 739 522	13 147 15 133 17 191 19 121	158 148 284 183	-7 111 -9 74 -11 0 -13 223	181 44 76 196	34 24 36 38 38 16 -2 743	17 94 92 668	14 44 16 89 18 93 28 69	39 96 86 69	-8 118 -19 88 -12 39 -14 29	118 81 32 24	K• 3.	L. 4 5 248	17 51 -1 85 -3 65 -5 157	45 95 71 148	-6 45 -8 30 -18 19 -12 4	9 441 1 371 1 198 1 39
38 118 38 91 48 17• 42 75	175 - 04 - 17 - 27 -	2 16 4 238 6 373 8 337 421	245 393 356 483	-8 121 -18 147 -12 95 -14 235 -16 62	115 134 88 229 79	-11 469 -13 234 -15 137 -17 579	459 278 158 533	21 64 23 61 25 61 27 67 29 17	-55 68 58 67 7	-15 174 -17 127 -19 170 -21 270 -23 287	101 125 102 255	-4 314 -6 511 -8 834 -18 352	281 441 691 374	22 50 24 28 26 24 -2 434	54 29 21 388	-16 54 -16 92 -28 64 -22 35	58 91 68 37	3 11 5 32 7 31 9 6	188 389 329 77	-7 196 -9 41 -11 186 -13 76	154 48 97 67	-14 21 -16 20 -18 10 -28 10	9 193 8 266 5 118 1 171
K. B. L.	1 -1 -1 (4 -1 37 -1	4 189 6 437 8 34A	254 531 311	-18 73 -28 72 -22 195 -24 193	66 88 286 223	-21 85 -23 119 -25 98 -27 38	74 112 85 45	31 15 -1 342 -3 518 -5 489	316 446 416	-25 99 -27 67 -29 167 -31 61	186 71 166 73	-14 475 -18 527 -18 147 -22 225	428 489 145 219	-6 524 -8 219 -18 386 -12 542	451 286 753 481	-26 52 K= 3. L	8	13 10 15 22 17 9	5 171 4 243 5 103 5 70	-17 273 -19 34 -21 238 -23 256	244 39 283 216	-24 17 -26 7 -28 4	0 105 8 78 2 45 1 57
6 348 8 45 18 97 12 153	133 -2 381 -2 47 -2 86 -2 284 -2	2 185 4 44 6 37 1 1 A	47 238 68 46 1	-20 82 -28 105 -38 31 -32 21 -34 75	198 58 21 64	-29 10 -31 153 -33 168 -35 35 -37 43	24 149 113 34	-7 427 -9 218 -11 548 -13 169 -15 63	387 154 472 171 67	-33 /3 -35 41 -37 68	59 47 72	-24 419 -26 177 -28 154 -38 131 -32 113	383 183 142 199 188	-14 338 -16 318 -18 124 -26 357 -72 154	298 282 117 341 157	1 312 3 282 5 591 7 591 9 212	265 197 536 553	21 0 23 4 25 4 27 1 29 1	79 45 48 48 12	-25 114 -27 44 -29 182 -31 125 -33 32	181 51 184 116 32	-32 9 -34 7 -36 7	4 83 5 51 3 57
14 163 16 988 18 84 28 214	284 -3 584 -3 47 -3 184 -3 971 -3	134 2 37 4 89 6 190	145 23 188 21	-36 85 -38 58 -49 43	36 55 92	-39 49 -41 16• K# 1, L#	51 12 2	-17 274 -19 237 -21 60 -23 59	318 279 46 56	1 101	188 59 62	-34 95 -36 23 -38 31 -48 39	03 27 27 39	-24 17A -24 6R -28 74 -38 81	163 56 77 84	11 167 13 279 15 152 17 122	166 268 154 181	31 1 -1 18 -3 31 -5 47	14 85 292 428	-35 26 K* 3,	28	12 2 11 4 28	9 146 1 115 7 218
24 243 26 184 28 181 38 75	223 -4 111 -4 186 65 Km	19 17 17	82	8 154 2 57 4 28	162 52 38	1 612 3 1426 5 683 7 33	426 1261 659 43	-27 57 -29 126 -31 68 -33 189	58 155 66 187	9 21 11 32 -1 181 -3 65	27 25 189 65	-42 1V X= 2.1	• 2 • 3 • 452	-32 70 -34 97 -36 58 -38 29 -49 43	93 48 28 29	10 130 21 179 23 161 25 138 27 22	114 154 168 133 28	-7 19 -9 25 -11 9 -13 5 -15 5	196 224 94 5 65 48	1 129 3 46 5 49 7 89 9 68	136 51 98 69	6 13 8 6 18 5 12 7 14 8	8 141 7 59 5 38 3 87 8 82
32 19• 34 41 36 19• 38 48 48 22	28 44 9 42 26	8 761 2 476 4 164 4 21	754 421 155	6 190 8 190 18 180 12 59 14 170	6 21 5 54	9 285 11 12* 13 148 15 49 17 394	319 33 124 59	-35 61 -37 38 -39 52 -41 78	63 25 52 59	-3 47 -7 186 -9 385 -11 163	58 157 281 149	2 127 4 382 6 324 8 169	147 208 314 189	-42 57 X= 2, 1	42 	29 30 31 49 33 49 35 18	40 58 47 13	-17 26 -19 12 -21 22 -23 32	248 133 299 318	11 42 -1 256 -3 213 -5 83	44 248 228 89	16 7 18 11 29 4 22 2	4 77 8 128 8 37 2 18
-2 117 -4 178 -6 333 -8 241	198 273 1 394 1 361 1	8 195 8 291 2 145 4 117	199 318 158 127	16 15• -2 59 -4 184 -6 358	18 56 184 338	19 177 21 221 23 59 25 115	164 218 58 189	K* 1. L 1 271 3 199	256 199	-15 77 -17 79 -19 73 -21 44	73 67 72 46	12 213 14 98 16 73 18 161	222 188 75 183	2 237 4 227 6 67 8 77	244 239 78 .79	39 28 K+ 3, L	15	-27 9 -29 17 -31 13 -33 11	86 156 127 197	-9 221 -11 46 -13 141 -15 152	198 47 127 137	26 7 28 2 39 1 -2 28	7 66 9 27 48 7 2 267
-12 49 -14 254 -16 1845 1 -18 574	54 1 54 1 318 2 895 2 583 2	8 103 8 48 2 126 4 77	192 41 121 66	-18 72 -12 344 -14 462 -16 274	212 78 321 431 275	27 120 29 81 31 48 33 44 35 182	112 73 46 30 93	7 188 9 147 11 146 13 184	149 146 141 184	-23 117 -25 143 -27 35 -29 62 -31 57	114 134 44 68 57	20 105 22 75 24 39 26 43 28 57	191 77 36 38 52	18 141 12 84 14 148 16 138 18 72	159 94 161 139 68	1 261 3 301 5 519 7 328 9 77	256 389 453 281 71	-35 4 -37 2 -39 2 -41 7	26 31 52	-17 96 -19 52 -21 77 -23 183 -25 77	88 56 72 92 75	-4 28 -6 5 -8 5 -18 10	273 6 46 4 42 7 143 3 218
-25 2?1 -22 225 -24 366 -26 127	281 2 289 2 385 3 179 3	6 3A 8 38 8 47 2 28	38 39 88 29	-18 24 -28 174 -22 126 -24 43	21 188 138 37	37 66 39 22 -1 2185 -3 766	68 19 1969 632	15 56 17 158 19 164 21 19*	58 158 174 12	-33 30 -35 20 Ke 1,	37 37 L= 11	30 19 32 52 34 40 36 21	72 84 35 71	20 70 22 53 24 13 -2 164	68 46 19 159	11 316 13 301 15 52 17 66	382 292 39 62	K• 3. 1 12 3 28	110 272	-27 35 -29 34 -31 26 -33 14	37 39 29 28	-14 7 -16 5 -18 15 -28 29	3 71 2 47 9 177 4 297
-38 62 -32 62 -34 19- -36 54	68 - 56 - 78 - 69 -1	4 259 6 197 8 434 8 13*	226 146 438 38	-28 121 -38 67 -32 21 -34 58	122 78 13 38	-7 918 -9 764 -11 416 -13 372	853 775 386 291	25 29 27 28 29 13 -1 294	33 24 7 179	1 74 3 184 -1 31 -3 114	77 186 49 121	-4 311 -6 222 -8 658 -13 683	266 176 546 553	-4 196 -8 184 -18 47 -12 316	162 83 48 267	21 169 23 117 25 61 27 56	166 111 57 63	7 22 9 28 11 18 13 6	243 213 189 77	K* 3. 1 1 15 3 37	18 18	-24 12 -26 6 -28 5	2 113 9 48 7 27
-38 74 -48 38 -42 21 X= 8, L0	63 -1 7 -1 7 -1 2 -2	2 139 4 59 6 577 8 268 8 57	185 78 737 294 75	-36 160 -38 52 X+ 8, L+	47	-15 619 -17 681 -19 345 -21 162 -23 194	649 681 342 153 191	-3 169 -5 344 -7 181 -9 258 -11 94	158 381 196 241 89	-5 31 -7 126 -9 116 -11 51 -13 81	35 133 115 90 73	-12 319 -14 374 -16 378 -18 419 -28 16	297 384 338 395	-14 337 -16 143 -18 197 -28 282 -22 385	314 134 187 184 284	29 61 31 33 33 53 35 38 37 38	62 38 55 36	15 15 17 16 19 8 21 11	167 169 77 • 28	-1 38 -3 78 -5 17 -7 126	34 87 28 132	-32 -34 -36 -38 -38	9 54 7 35 9 21 9 43
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8 661 18 254 12 266 14 585	784 -3 248 -3 264 -3 636 -3	2 77 4 98 6 10• 8 34	91 116 34 38	18 15+ -2 23 -4 19+ -6 68	2 24 18 58	-35 21 -37 30 -39 24 -41 17+	12 39 29 18	-21 221 -23 180 -25 182 -27 151 -29 42	12 120 182 56	-25 94 -27 25 -29 94	122 99 38 113	-38 184 -32 79 -34 44 -36 19 -38 43	98 77 48 8 41	-32 B1 -34 3A -36 7A -36 76 -48 43	24 63 69 36	-9 217 -11 183 -13 215 -15 374 -17 361	228 164 212 351 312	-5 18 -7 12 -9 28 -11 26	157 119 174 231 211	-19 28 -21 87 -23 145 -25 58 -27 37	22 87 139 62 36	4 11 6 13 8 13 19 19	8 186 3 118 2 149 7 218 7 128
16 14• 18 275 28 63 22 168 24 72	1 -4 288 -4 164 K-	8 5A 2 38 8. Lu	58 31 6	-8 29 -18 182 -12 232 -14 278	9 287 248	K# 1, L#	3 583	-31 78 -33 52 -35 26 -37 19*	81 44 31 18	Ka 1, -13 56 -15 31	L= 12 65 33	-48 39 -42 19 K. 2. (31	K= 2,	228	-19 52 -21 261 -23 194 -25 197	48 246 178 151	-15 4 -17 18 -19 21 -21 42	48 171 198 483	-29 36 K• 3, 1	50	14 3 16 19 18 15 28 14	3 58 4 189 8 143 6 134
26 162 28 133 38 38 32 19•	148 132 35 25	8 434 2 471 4 255 6 264	417 459 214 272	-18 46 -28 68 -22 139 -24 165	35 53 134 161	5 734 7 346 9 162 11 294	734 314 153 276	-41 48 K= 1, L	48 • • •	K 2,	L. B	8 313 2 294 4 358 6 244	261 338 336 228	4 84 6 67 8 181 19 121	65 79 189 129	-29 79 -31 185 -33 24 -35 44	81 182 26 38	-25 83 -27 9 -29 114 -31 31	88 117 113 35	-11 78 -13 63 -15 58 -17 49	73 62 52 53	24 8 26 2 28 2 -2 10	2 88 5 24 2 35 2 152
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X× 8, L+ 8 216	3 -3 -3 178 -3	100 100 2 27 4 24	15 28 33	-26 79 -28 23 -38 79	92 22 96	-23 252 -25 251 -27 98 -29 18+	298 294 188 17	-23 185 -25 182 -27 158 -29 86	99 189 175 189	2 181 4 432 6 387 8 324	889 321 482 299	-24 228 -26 317 -28 191 -38 94	248 355 249 94	-30 30 X+ 2,1	.••• ••	-3 374 -5 64 -7 416 -9 249	267 72 333 209	-9 80 -11 219 -13 120 -19 220	71 176 185 217	K* 4, (8 453 2 248	• 1 429 233	6 9 8 17 18 18 12 19	9 118 1 198 8 219 3 215
4 785 6 291 8 373 18 652	883 -3 836 -3 358 -4 352 -4 637	8 24 8 18* 2 55	22 1 52	-10 183 -12 184 -14 86	32 224 121 98	-31 115 -33 143 -35 48 -37 19+ -39 42	132 146 48 7 33	-31 100 -33 100 -35 73 -37 37 -39 25	41 67 43 23	12 468 14 199 16 148 18 129	406 195 151	-37 189 -34 189 -38 31 -38 52 -48 72	183 183 34 33	2 51 4 39 6 87 8 187 18 38	52 41 84 198 28	-11 187 -13 217 -15 252 -17 149 -19 198	112 160 230 145 187	-17 40 -19 278 -21 144 -23 10 -25 180	29 232 148 28 199	4 231 6 212 8 228 10 69 12 139	231 287 228 62 155	14 4 16 9 18 18 28 9 22 2	2 59 1 97 5 95 9 95 6 21
12 338 14 126 16 208 18 353 28 112	381 K- 149 217 356	8. L* 8 67 2 18*	76 19	-16 123 -18 89 -25 37	131 86 36	-41 37 K+ 1, L+	36 4	-41 48 K= 1, L	42 • 8 • 147	28 9 22 170 24 170 26 147	68 164 166 136	-42 51 K= 2.L	40 . 5	12 66 14 69 -2 135 -4 183	62 51 128 97	-21 199 -23 274 -25 198 -27 68	183 239 183 69	-27 112 -29 184 -31 43 -33 66	112 183 41 62	14 98 16 124 18 178 28 142	95 131 153 135	24 9 -2 19 -4 22 -6 23	58 97 281 229
22 81 24 125 26 112 28 67	99 142 113 1 67 1	6 69 33 27 2 23	67 38 23 29	1 1134 3 1245 5 759	1221 1337 736	3 829 5 282 7 113 9 347	701 248 186 356	3 100 5 30 7 30 9 39	183 41 29 43	38 128 32 19 34 69 36 98	123 18 68 41	2 267 4 161 6 34 8 164	284 147 62 147	-6 163 -18 157 -12 71 -14 158	148 135 68 136	-31 62 -33 88 -35 18 -37 41	91 71 21 32	-37 51 -39 22 K• 3,	42 17 L= 7	24 67 26 78 28 43 39 32	54 63 37 32	-18 8 -12 17 -14 8 -16 18	81 171 92 17
32 19• 34 33 36 62 -2 1651	11 1 76 1 98 2 613 2	4 19• 4 19• 5 18• 2 56	28 18 3 56	9 485 11 566 13 187 15 593	417 522 127 557	11 333 13 115 15 176 17 242 19 137	127 178 256 141	13 19• 15 72 17 62 19 187	73 76 80	-2 400 -4 199 -8 914 -8 1985	441 184 832 944	12 428 14 293 16 27 18 95	486 371 71 94	-16 212 -18 28A -28 84 -22 282 -24 199	194 178 188	-3V 43 K= 3.L 1 493	• 3 • 29	1 221 3 194 9 54 7 33	229 166 54	32 164 34 32 -2 488 -4 89 -6 249	21 33 422 87 234	-10 14 -20 18 -22 3 -24 21 -26 13	135 1 98 1 26 6 288 5 138
-4 391 -6 9• -8 15 -18 214 -12 37	472 2 28 2 9 - 325 - 75 -	4 75 6 44 2 95 4 347 4 351	66 48 188 343 323	17 313 19 165 21 75 23 239 25 26	284 168 84 221 28	21 196 23 138 25 123 27 188 29 79	193 138 112 98 74	21 77 -1 218 -3 86 -5 325 -7 381	78 288 81 382 267	-18 300 -12 239 -14 218 -16 155	306 204 191 157 127	20 67 22 65 24 20 26 51 28 41	71 63 15 61	-26 89 -28 77 -38 128 -32 88 -34 81	87 88 129 82	3 143 9 187 7 332 9 234	172 193 316 253	9 71 11 174 13 99 19 33	81 284 186 41	-8 361 -19 205 -12 234 -14 98	301 298 263 94	-78 4	57 3 48 71 7 88
-14 192 -16 89 -18 582 -28 182	739 - 84 -1 685 -1 85 -1	8 316 9 219 2 429 4 203	385 192 485 222	27 57 29 86 31 31 33 92	78 92 24 182	31 33 33 24 -1 763 -3 333	33 28 679 323	-9 187 -11 369 -13 451 -15 299	182 330 431 297	-28 219 -22 27 -24 23 -26 11	186 259 238 95	39 15 -2 341 -4 547 -6 384	9 307 484 348	-36 144	20 .* 10	18 185 15 213 17 245 19 162	198 244 248 147	19 32 21 24 -1 183 -3 156	33 22 170 136	-18 386 -28 124 -22 88 -24 64	272 187 02 91		Li 4 33
-24 195 -26 69 -28 51 -38 98	30 -1 956 -1 71 -2 88 -7 79 -2	a 153 a 238 2 185 4 86	14# 262 121 91	37 33 39 18• 41 19	27 5 23	-7 618 -7 618 -9 575 -11 348 -13 298	326 578 583 296 292	-17 298 -19 245 -21 229 -23 195 -25 37	243 238 177 58	-26 287 -38 53 -32 18 -34 46 -36 7	195 53 92 52 71	-5 182 -18 431 -12 331 -14 64 -16 158	173 391 347 42 182	47 2 174 4 70 4 94 8 47	42 11 77 99	21 54 23 73 25 81 27 68 29 87	53 72 75 63 79	-7 444 -7 379 -9 244 -11 143 -13 341	413 344 233 138 326	-26 74 -28 199 -38 82 -32 59 -34 43	73 28 26 47 41	2 7 4 15 4 11 7	73 179 128 44 49
-32 118 -34 88 -36 19• -36 31 -48 69	131 -2 79 -2 18 -3 38 -3 67 -3	6 4R 6 39 8 63 2 4A 4 27	68 43 58 25	K# 1, L# 1 868 3 141 \$ 1371	1 817 133 1362	-15 235 -17 134 -19 145 -71 189 -23 240	199 133 142 119 287	-27 132 -29 68 -31 72 -33 24 -35 27	139 69 76 42 28	-38 45 -48 10 -42 20 Ka 2-	42 17 28	-18 213 -28 68 -22 114 -24 239 -26 274	189 69 118 256 389	-8 139 -4 178 -6 18 -8 116 -18	30 30 119	31 25 33 140 -1 521 -3 71 -5 385	28 16 448 69 341	-19 271 -17 126 -19 67 -21 110	235 138 71 181	-36 150 x0 4, 1	13 14 14 14 14 14	12 4	7 58 39 • 15 7• 12
-42 17. X. Ø. L.	24 -3	a 10* a 3> a 57	48	7 918 9 533 11 198	1929 588 235	-25 66 -27 172 -29 67	87 215 75	-37 28 -39 35 -41 10	24 26 28	8 201 8 201	333 199	-28 99 -38 72 -32 22	188 78 29	-12 78 •14 127 -16 87	76 118 82	-7 789 -9 777 -11 227	487 482 288	-25 93 -27 85 -29 23	63 87 18	2 274 4 333 4 387	275 323 385		146 145 259

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¥•	4. • •	, L. 34	8 63	-18	44 14+ 99	14 9 49	-13 -17 -17	113 159 178	187 153 123	11 13 19	126 189 37	141 120 33	-23	31 38 35	26 48 27	-11	134 132 55	138	-23 K+	49 5. La	91 •	-24 -26	75	28	-16	70 92 38	94 88 25	-25	16.	26	11	88 71	97	-7	19	16 51 73



Fig. 1. (a) Labeling, bond distances and angles for peptide portion of gly-L-phe-TsOH. For clarity, the part of the atom symbol referring to the residue has been omitted. Thus α in residue 1 refers to C α (1), C' in residue 2 refers to C'(2) etc. (b) Labeling, bond distances and angles in tosylate portion of gly-L-phe tosylate.

in the intensity distributions. The solution of the brosylate salt was, therefore, undertaken first in the expectation that it would lead to the determination of the tosylate salt structure by analogy. The E^2-1 vector map of the brosylate salt could not be unambiguously interpreted as the Harker section contained three potential Br-Br vectors of nearly equal magnitude. A choice between possible bromine

3552 GLYCYL-L-PHENYLALANINE p-TOLUENE- AND p-BROMOBENZENESULFONATE

 Table 3. Observed and calculated structure factors for glycyl-L-phenylalanine brosylate

The columns are h, $10F_o$, $10F_c$, and α . Unobserved reflections are marked with an asterisk (*).

N FO PC	N FO FC	H FO FC	H FO FC	H FO FC	H FO F	C H FO FC	N FO FI	: н Fa	FC H	F0 F	с н	FO FC	H FO	٢c
K= 0, L= 0 2 376 383	-38 44• 186 -32 151 138 -32 189 138	28 58 29 38 144 137 32 38• 38	5 1277 1420 7 848 876 9 653 721	-39 420 31 -41 390 21 -43 330 38	-7 379 36 -9 254 23 -11 118 18	3 38 261 283 8 32 44+ 18 9 34 196 82	18 128 17 28 258 29 .22 142 15	3 6 159 3 6 199 8 18 211	154 -21 174 -21 211 -25	73 6 168 16 44• 3	6 -1 7 -3 6 -5	193 164 69 45 299 276	9 374 11 38 13 47	78 12 62
4 213 333 6 972 1371 8 652 832	-34 188 147 -36 44• 37 -38 189 133	34 33• 1 -2 162 152 -4 178 155	11 1066 1166 13 313 373 15 617 571	K# 1, L# 4	-13 158 13 -15 121 9 -17 298 17	4 34 117 92 9 36 43• 13 3 38 42• 58	24 167 18 26 91 8 28 99 7 38 84 7	12 66 14 44+ 16 162	68 -31 23 -33 161 -35	88 6 44• 6 47• 3	3 -7 6 -9 9 -11	198 138 232 282 216 221	15 384 -1 66 -3 414	36 58 48
17 183 124 14 25• 187 16 695 713	-42 37* 7 -44 51 58	-8 184 97 -18 48• 22 -12 486 468	19 262 277 21 368 349 23 444 388	3 1331 1207 5 994 958 7 427 388	21 91 8 -23 145 17 -25 444 5	7 42 340 23 7 6 Km 2, LM 1	32 84 7 34 47• 6 36 48• 1	20 114 22 42• 24 71	133 -39 25 -41 63	36• 3 38• 1	8 -15 5 -17 -19	344 331 266 289 53 67	-7 59 -9 484 -11 63	25 69 73
18 438 448 28 77 94 22 276 268	K. A. L. 4 B 314 296	-14 131 121 -16 174 152 -18 74 48	25 325 382 27 181 168 29 221 188	9 836 824 11 488 426 13 284 288	-27 440 2 -29 98 8 -31 420	7 9 8 763 644 6 2 1348 966	38 34 3 -2 618 54 -4 683 53	26 56 28 34• -2 163	57 Ke 42 69 1	3.L= 207 15	2 -21 -23 9 -25	166 185 117 165 44• 33	-13 67 -15 36 -17 34	96 39 48
24 261 109 26 285 134 28 119 58 38 164 127	2 161 101 4 640 615 6 274 88 8 178 173	-28 84 77 -22 44• 53 -24 44• 58 -26 62 72	31 172 112 33 178 114 35 44• 49	15 583 550 17 53 55 19 183 185 21 275 293	-33 -10 2 -35 78 5 -37 32• 2	4 4 1109 883 9 6 228 188 8 8 192 238 18 189 128	-6 447 30 -8 348 37 -18 282 26 -19 382 30		248 275 123	567 48 57 5 371 31	-27 -29 -31	440 27 78 77 420 47	-19 314 Ke 3, L	• 51 .• 11
32 251 152 34 146 64 36 257 285	18 252 262 12 521 564 14 62 26	-28 66 12 -39 43• 14 -32 42• 51	39 42• 22 41 58 39 43 51 29	23 183 97 25 148 135 27 114 182	K= 1, L= 1 486 35	8 12 764 877 14 314 342 4 16 285 333	-14 294 29 -16 407 41 -18 185 11	-12 44• -14 159 -16 137	174 11 186 13 131 1	130 13 125 13 87 8	a -35 a -37	60 42 32• 25	1 56 -1 38 -3 37	61 47 34
38 43 73 48 75 52 42 186 86	16 454 511 18 36• 29 29 138 155	-32 42• 51 -34 48• 28 -36 36• 19	K= 1.L= 1	20 166 124 31 177 163 33 98 71	3 231 19 5 98 11 7 197 16	3 18 478 545 3 28 129 171 8 22 299 299	-28 254 27 -22 292 35 -24 255 32	-18 65 -28 88 -22 79	58 17 79 19 84 21	179 21 41• 4 5% 6	зк. 3 5 1	3. L= 6	-5 394 Ko 4, L	· 49
K* #+ L* 1	24 226 267 26 485 382 28 283 196	K. 8, L. 8	3 996 817 5 786 685 7 2038 2892	37 410 48 39 360 37 41 390 6	11 132 11 13 69 6 15 44• 4	6 26 254 216 9 28 275 217 3 38 148 177	-28 139 16 -38 128 18 -32 444 1	-26 420 -28 410 -38 370	26 25 34 25 31 25		3 3 8 7 8 7	165 153 267 218 453 429	8 434 2 489 4 54	488 472 59
8 583 693 2 132 194 4 216 186	30 53 43 32 161 121 34 444 40 34 444 40	8 132 123 2 132 117 4 43* 91	9 787 817 11 481 612 13 482 688	-1 544 576 -3 591 537 -5 626 525	17 44+ 5 19 44+ 5 21 44+ 6	8 32 114 95 1 34 68 87 2 36 96 92	-34 67 4 -36 118 8 -38 64 5	3• 2· L=	24 31 9 3	103 9 83 6 65 3	7 11 4 13 9 15	142 136 179 192 273 289	6 121 8 285 18 86	184 212 82
8 187 128 18 21• 158 12 121 142	38 98 67 48 35• 19 -2 972 913	B 148 116 18 99 87 12 181 185	17 576 559 19 345 331 21 152 156	-9 362 332 -11 263 239 -13 327 294	25 93 18 27 66 6 29 69 5	7 48 39• 86 8 42 55 88 3 -2 263 -241		5 5 122 5 2 298	116 30 167 -1	33• 2 621 51	1/ 19 2 21 23	151 181 158 186 69 52	12 1/ 14 288 16 141	1/8 281 153
14 375 488 16 73 98 18 864 898	-4 71 116 -6 1647 944 -8 331 336	14 131 113 16 44* 1 18 68 71	23 124 148 25 85 78 27 155 131	-15 232 189 -17 141 148 -19 365 378	31 79 6 -1 121 13 -3 283 27	4 -4 1225 1889 6 -6 1818 968 8 -8 1013 1888	8 467 42 2 596 51 4 128 12	6 44• 8 188 7 1 9 59	43 - 201 - 51 -	227 21 324 28 227 28	9 25 5 27 4 29	168 168 54 38 39+ 6	28 92 22 289 24 119	284 187
28 649 659 22 76 63 24 789 656	-18 716 788 -12 216 154 -14 898 795	28 57 58 22 43• 22 24 134 149 26 414 14	29 218 173 31 91 76 33 89 77	-21 255 258 -23 132 144 -25 173 188 -27 100 322	-5 500 48 -7 127 14 -9 265 25	3 -10 437 565 6 -12 29• 147 7 -12 79 147	6 261 22 8 319 32 18 168 16	12 43 • 14 66 16 78	25 -11 76 -13 71 -1	235 22 274 38 86 8		51 37 38• 25 326 382	26 444 28 444 38 434	53 56 52
28 175 156 38 259 297 32 44• 21	-18 69 60 -28 314 326 -22 166 176	28 39+ 22 38 35+ 22 -2 187 98	37 143 118 39 420 22 41 480 26	-29 74 81 -31 192 172 -33 139 96	-13 212 20 -15 199 18 -17 89 9	-16 307 449 5 -18 174 109 4 -28 276 281	14 141 15 16 342 39 18 466 53		38 -19 44 -21 48 -21	74 6 178 18 181 19	-5	296 258 138 111 208 198	34 39 36 35	73 33
34 181 75 36 44• 16 38 43• 61	-24 99 123 -26 182 111 -28 116 111	-4 112 188 -6 146 139 -8 69 64	43 58 52 -1 875 782 -3 1837 911	-35 44• 49 -37 132 92 -39 41• 13	-19 109 12 -21 61 4 -23 44• 4	0 -22 193 182 2 -24 261 298 4 726 163 284	28 169 28 22 121 15 24 98 8	-2 52 -4 93 -6 235	43 -2 89 -27 213 -25	145 17 67 7 62 5	-11 -13 7 -15	118 76 165 141 224 229	K+ 4, L 8 549	• 1 384
48 75 46 42 94 48 44 324 {9 •7 884 777	-38 64 81 -32 82 66 -34 444 18 -36 439 36	-10 223 210 -12 123 105 -14 137 139 -16 245 255	-9 11V3 1186 -7 178 196 -9 581 593	x= 1, L= 5	-25 02 3 -27 43• 4 -29 63 7 -31 39• 2	3 -38 148 139 2 -32 69 74	28 175 14 28 59 51 39 56 4 39 112 01		167 -33 188 -3	125 11 43• 3 42•	7 -17 6 -19 8 -21	144 142 65 75 134 138	2 508	435 375 323
-4 425 496 -6 1084 1275 -8 108 238	-38 126 63 -48 48* 12 -42 52 41	-18 138 137 -28 115 117 -22 99 118	-13 118 96 -15 366 364 -17 679 716	1 725 653 3 584 427 5 769 716	-33 51 2 -35 38• 2	8 •36 43• 33 7 •38 97 81 •48 66 27	34 48• 11 36 36• 21 -2 164 14	-16 129 -18 43+ -28 87	128 -39 25 94 K	35• 1 3. L9	9 -25 -27 3 -29	66 69 79 81 42• 37	12 151 14 78 16 158	178 49 166
-18 1318 1546 -12 886 1876 -14 183 158	K= 8, L= 5	-24 44• 11 -26 43• 58 -28 127 119	-10 166 145 -21 428 425 -23 385 311	7 201 169 9 283 384 11 77 92	K= 1.L=	9 -42 340 2 5 8 Km 2.Lm 2	-4 258 22 -6 413 37 -8 274 24	-22 71 -24 40 -26 37	183 53 1	294 28 772 59	-31 -33 1 -35	41+ 37 37+ 35 71 48	18 132 28 119 22 210	115 118 226
-18 333 343 -28 32• 38 -22 546 596	2 144 136 4 72 95 4 1887 968	-32 39• 28 -34 34• 18	-27 265 268 -27 265 268 -29 195 285 -31 115 128	13 146 133 15 228 229 17 148 169 19 117 132	3 12 V 5 44 4 7 112 7 0 59 7	6 8 1182 993 6 2 818 786 1 4 798 561	-10 107 18 -12 266 24 -14 131 14 -16 218 21	-28 330 5 X= 2.L.	10 1	272 24 352 35 287 38	\$ x•	3. LE 7	24 74 26 444 28 444	14 31 31
-24 68 32 -26 128 98 -28 92 188	8 64 49 18 535 588 12 414 465	K= 8, L= 9	-33 166 128 -35 145 117 -37 79 67	21 179 224 23 258 262 25 137 147	11 440 4 15 51 6 17 430 5	7 6 338 264 9 8 245 249 4 18 653 681	-18 266 26 -28 319 33 -22 176 23	8 59 2 181 4 42•	48 13 87 15 69 17	388 31 83 7 238 28	2 3	376 351 44• 82 229 285	32 72 34 38 36 33	43 41 25
-38 103 103 -32 74 69 -34 440 61 -36 440 76	16 311 358 18 84 97 28 41• 56	2 357 324 4 198 181 6 185 118 8 125 117	-41 41• 49 -43 35• 28	29 139 113 31 44• 49 33 96 81	21 53 4 23 55 5 25 68 7	9 16 244 285 5 18 285 389 9 28 285 347	-24 114 12 -26 77 6 -28 44• 6 -38 184 9	0 124 0 161 18 181 12 4	114 11 152 21 185 23	264 29 132 14 192 18		262 288 448 22 79 89	-2 304 -4 313 -6 329	286 282 291
-38 115 67 -49 420 38 -42 390 13	22 26 ⁵ 388 24 43* 48 26 44* 13	18 92 86 12 64 79 14 51 63	K= 1, L= 2 1 2692 2362	35 410 6 37 370 15 39 74 59	27 82 7 -1 81 18 -3 63 9	4 22 67 46 8 24 194 171 1 26 186 88	-32 430 5 -34 470 2 -36 87 5	14 61 16 48 18 47	71 27 58 29 69 31	44• 5 149 18 184 11	7 17 7 19 4 21	84 96 145 164 54 62	-18 312 -12 144 -14 170	342 178 197
-44 330 10 X: D:L. 2	28 100 138 38 44+ 65 32 86 94 34 42+ 54	10 440 11 18 430 2 28 420 8 22 410 44	5 1298 1868 7 797 748 9 36 46	-3 457 457 -3 467 457 -5 188 69 -7 561 495	-7 112 12 -9 213 21 -11 218 21	8 28 71 81 2 38 188 71 5 32 83 64 1 34 78 108	-48 38 4 Xe 7, Le 4	-2 56 -4 111 -6 86 -8 43	62 33 111 35 85 37 37 -1		1 23 8 25 2 27 8 29	96 184 48• 38 37• 26 33• 5	-16 216 -18 386 -28 444	223 333 25
Ø 1185 1160 2 1487 1585 4 2652 2561 4 266 744	36 48• 18 38 34• 22 -2 192 131	24 38+ 15 26 35+ 52 28 38+ 2	11 361 382 13 238 295 15 86 183	-9 511 584 -11 123 184 -13 519 588	-13 193 21 -15 158 18 -17 57 4	0 36 43• 59 3 38 41• 22 9 48 37• 84	523 414 2 799 68	-18 42• -12 97 -14 73	29 -3 89 -5 78 -1	741 59 678 56 686 63	-1	279 275 168 167 248 216	-24 115 -26 60 -28 44	123 71 92
8 1416 1548 14 666 855 16 29• 42	-6 310 9 -8 188 168 -18 274 285	-4 369 344 -6 298 277 -8 167 173	19 514 544 21 246 254 23 215 287	-17 195 196 -19 192 212 -21 125 118	-21 132 13 -23 42• 5 -25 41• 3	4 -2 226 194 5 -4 722 647 8 -6 457 331	6 224 23 8 345 30 18 391 36	-18 58 -28 37- 5 -22 34-	53 -11 26 -13 54 -11	157 10 353 29 512 54 287 19		122 118 44• 22 56 74	-32 48 -34 394 -36 35	74 42 24
18 331 382 28 444 588 22 75 3 24 298 281	-12 1858 933 -14 336 297 -16 131 96 -18 289 282	-18 176 183 -12 128 138 -14 71 68 -16 449 19	25 293 264 27 236 189 29 315 291 31 159 138	-23 115 133 -25 97 98 -27 115 111 -29 10a 73	-27 390 6 -29 65 8 -31 310 4	7 -8 616 595 8 -18 379 348 5 -12 361 368 -14 586 597	12 178 17 14 117 90 16 127 110	-24 31+ K# 2.L#	21 -17 -19 11 -21	298 35 298 33 256 26	-15 -17 -19	84 91 44• 38 78 71	K= 4, L	• 2
26 214 248 28 227 234 38 97 62	-28 278 232 -22 41 41 -24 169 282	-18 72 05 -20 44- 85 -22 108 136	33 64 43 35 94 95 37 167 148	-31 65 56 -33 83 39 -35 65 65	X. 1. L. 1 1 245 21	8 -16 148 108 -18 283 383 3 +28 347 433	28 67 6 22 122 15 24 76 76	8 38• 2 128 4 66	41 -2 116 -27 57 -29	111 13 72 7 188 18	-23	43• 41 42• 4 41• 12	2 259 4 277 6 586	215 278 564
32 440 59 34 440 15 36 440 69 38 82 87	-26 181 182 -26 44+ 68 -38 112 189 -32 78 93	-24 42• 57 -26 41• 37 -28 30• 51 -38 35• 31	39 71 68 41 74 49 43 31 13 -1 1700 1513	-37 95 59 -39 54 23 -41 32• 18	3 22* 18 5 85 5 7 43* 1 9 89 9	3 -22 333 378 9 -24 251 271 1 -26 166 185 7 -28 195 189	26 81 8 28 89 8 38 47• 30 32 39• 3	6 52 8 139 10 96	62 -31 171 -33 113 -35	117 9 71 5 420 2	-29 -31 -33	300 21 360 12 310 37	8 265 18 158 12 76	231 151 85
48 41+ 43 42 36+ 26 -2 655 496	-34 444 45 -36 84 68 -38 410 8	-32 38+ 23 X+ 8.L= 18	-3 1150 1132 -5 1335 1281 -7 710 707	K* 1, L* 6	11 98 9 13 55 4 15 74 8	2 +38 139 138 7 -32 148 188 4 -34 79 65	34 39• 1 -2 169 14 -4 421 38	-4 46 -6 56 -8 52	45 -35 72 74 Ke	3	і к. • 1	3. L* 8 55 43	16 148 18 91 28 187	144 77 13
-4 1/1 171 -6 881 758 -8 766 734 -18 1216 1288	-42 JA- 28	8 44+ 8 2 44+ 57 4 54 27	-11 445 436 -13 773 889 -15 758 814	5 168 175 7 314 298 9 218 191	17 45 3 21 32 -1 184 18	3 -36 -30 -22 9 -38 72 65 4 -48 390 16 1 -42 330 4	-8 374 35 -18 197 17 -12 74 6	-14 33• -14 33• -16 31•	74 1 34 3	568 48 249 23	5 5 3 7	99 94 186 89 44- 66 144 116	22 240 24 118 26 72 28 67	276 136 75
-12 193 92 -14 493 473 -16 699 752	0 514 477 2 379 330	6 44• 14 8 43• 1 18 43• 28	-17 448 564 -19 203 228 -21 195 198	11 122 115 13 277 282 15 183 169	-3 138 12 -5 105 11 -7 44* 3	4 Ke 2, Le 3	-14 414 37 -16 247 23 -18 145 15	K= 3.L=	8 7 358 11	360 35 231 18 432 48	11 13 7 15	78 75 53 45 77 86	38 76 32 113 34 58	61 77 37
-20 413 446 -22 338 375 -24 64 5	6 587 568 8 384 348 18 475 417	14 56 69 16 41• 74 18 30• 17	-25 284 328 -27 64 76 -29 138 123	19 86 186 21 74 80 23 191 211	-11 43• 6 -13 184 11 -15 121 13	6 2 568 486 3 4 647 593 3 6 493 451	-27 444 31 -24 444 21 -26 444 61	5 881 7 542 9 268	672 15 453 17 264 15	41+ 3 232 27 218 25	19	42+ 16 85 97 128 129	-2 384 -4 375 -4 466	38 381 371
-28 339 342 -28 366 372 -38 198 149 -12 118 181	12 383 338 14 169 166 16 175 168 18 87 135	20 36+ 37 22 32+ 9 -2 129 128	-31 145 142 -33 128 82 -35 139 88	25 147 151 27 99 71 29 76 81 31 478 38	-17 42* 2 -19 41* 5 -21 64 8 -23 37* 7	6 8 656 784 8 18 328 275 1 12 313 373 8 14 351 373	-28 115 13 -38 43• 44 -32 62 30	11 386 13 189 15 266	384 21 82 23 261 25	169 21 119 11 119 13	-1	57 62 44• 25 135 137	-8 316 -18 55 -12 142	394 27 128
-34 78 15 -36 44• 3 -38 43• 55	28 125 146 22 440 46 24 151 167	-6 73 27 -8 44+ 25 -18 94 83	-39 167 73 -41 61 45 -43 35+ 14	33 41• 28 35 36• 9 37 38• 19	-25 340 5 Ka 1, La 1	1 16 133 171 18 143 177 1 28 283 243	-36 66 41 -38 310	19 277 21 255 23 168	279 29 258 31 167 33	53 1 57 6 41• 3	-7 -9 -11	184 195 136 139 44• 48	-16 83 -18 112 -28 242	115 126 295
-40 420 12 -42 390 32 -44 330 11	28 44 24 38 148 188 32 47 9	-12 124 135 -14 143 178 -16 420 12 -18 121 147	K= 1,L= 3 1 442 389	-1 272 280 -3 84 86 -5 250 243 -7 222 225	1 73 6 3 169 15 5 69 6	22 87 83 5 24 237 232 2 26 44• 48 6 28 44• 79	K= 2, L0 1 8 164 131 2 333 270	23 124 27 80 29 70 31 137	114 35 58 37 85 -1	36* 1 31* 5 247 28 268 22	-13	225 284 195 187 128 189	-22 67 -24 446 -26 446	188 91 42 57
K. B. L. 3 B 307 273	34 40 78 36 35 22 -2 240 285	-28 132 151 -22 39* 78 -24 37* 17	3 365 282 5 782 789 7 934 968	-9 191 194 -11 221 281 -13 321 296	7 78 6 9 188 11 11 35• 1	6 30 196 177 3 32 100 81 8 34 43• 85	4 87 81 6 387 385 8 235 215	33 79 35 71 37 41•	77 -9 65 -7 44 -9	298 38 193 19 79 8	-21 -23 -25	183 119 94 186 480 23	-30 92 -32 42 -34 39	98 33 53
2 2878 1982 4 1258 1287 6 401 363	-6 132 185 -8 35 25 -18 324 387	x= 8. L= 11	11 595 626 13 528 596 15 329 380	-17 181 80 -19 289 288 -21 43• 73	13 62 9 -1 86 9 -3 78 8	9 38 64 46 7 48 33 47 8 -2 677 613	10 307 320 12 123 16 14 449 30 16 147 173	X. 3. L.	1 -13	251 23 83 7	-27	320 19 321 19	-36 340 Xo 4, L	• 3
8 1866 1118 18 445 437 12 473 448	-12 80 65 -14 74 81 -16 155 165	8 41• 38 2 152 121 4 85 58	17 274 338 19 479 578 21 367 381	-23 95 183 -25 136 155 -27 440 62	-5 81 7 -7 52 7 -6 54 5	6 -4 712 617 3 -4 665 405 4 -8 188 198	16 124 13 28 147 17 28 147 17	1 79 3 443 5 250	93 -19 556 -21 222 -23	283 311 138 14 44• 2	7	237 211 223 223	214	181
16 32• 76 18 125 192 20 211 211	-28 219 282 -22 434 78 -24 96 125	8 71 80 10 88 88 12 36+ 26	25 287 268 27 298 193 29 63 85	-31 60 58 -33 43* 66 -35 41* 43	-13 52 9 -15 36+ 4 -17 34+ 8	6 +12 458 458 3 +14 339 209 2 -16 238 258	26 97 9 28 71 5 38 37• 1	9 489 11 139 13 462	481 -27 118 -29 496 -31	121 14 183 15 43- 1	11	212 198 187 179 133 138	8 228 18 163 12 92	227 168 191
22 328 348 24 488 44 26 91 63 28 327 269	-26 112 115 -28 440 40 -38 141 133 -32 54 7	14 33* 16 16 38* 32 -2 57 49 -4 50 85	31 133 117 33 84 76 35 440 21	-37 380 55 -39 330 28	-19 320 11 Ke 1, Le 1	2 -18 360 48 -28 191 286 2 -27 123 154 -24 A8 84	32 47 24 -2 118 96 -4 79 73	15 37• 17 173 19 69	52 -33 196 -35 88 -37	42• 2 75 4 36• 5	13	410 38 480 56 73 78	14 43. 16 132 18 44.	19 158 38
30 44• 12 32 134 84 34 44• 16	-34 43* 38 -36 12A 181 -38 37* 39	-6 41+ 23 -8 41+ 7 -18 47 58	39 48+ 18 41 35+ 7 -1 698 565	1 438 369	-1 38+ 5 -3 43 4 -5 38+ 6	1 -26 196 232 9 -28 115 185 1 -38 97 86	-8 339 33 -18 77 78 -19 243 219	23 111 25 166 27 59	135 K. 71	3, L+	21 -1 -3	55 51 123 119 86 76	22 113 24 44• 26 181	188 52 182
J0 /6 65 J8 127 08 48 39+ 29 42 33+ 42	-48 314 9 K= 8,L= 7	-14 64 114 -16 37• 18 -18 33• 33 -28 32• 34	-3 167 138 -9 248 262 -7 331 288 -9 384 334	5 283 274 7 317 274 9 135 126 11 206 207	K= 2. L=	-32 64 66 # -34 96 78 -36 76 42 5 -38 416 9A	-14 307 285 -16 252 265 -18 193 203 -20 170 44	27 77 31 44• 33 89 35 74	71 1 35 3 65 5	268 23 213 18 258 240	-7	144 155 135 142 430 11	28 55 38 83 32 58 34 33-	18 67 45
-2 888 945 -4 677 688 -6 518 519	8 492 483 2 273 269 4 325 386	X= 0. L= 12	-11 736 682 -13 581 979 -15 786 728	13 189 114 15 86 79 17 287 238	2 876 81 4 317 31 6 1835 99	2 -48 380 28 4 -42 310 12	-29 60 10 -24 44 81 -26 44 41	37 48+ 39 35+ -1 186	25 37 11 148 13	286 18 289 26 112 9	-13 -15 -17	59 82 42• 45 41• 73	-2 162 -4 223 -4 177	195 192 186
-6 813 893 -18 428 357 -12 726 616 -14 591 488	8 95 97 18 41 27 19 93 09	2 116 137 -2 42 185 -4 320 124	-1/ 442 488 -19 211 223 -21 455 524 -23 247 307	21 440 38 23 440 48 25 440 24	5 480 39 18 216 16 12 694 68 14 98 4	, 2, L. 4 8 1 8 726 628 4 2 543 498	-38 74 84 -38 79 74 -39 48• 53 -34 36• 53	-3 493 -5 180 -7 435 -9 124	+16 15 125 17 486 19	177 173 117 180 69 40	-19 -21 -23	48• 16 53 36 35• 34 32• 9 ¹	-18 177 -18 177 -12 126 -14 87	264 156 125 183
-16 743 691 -18 32- 41 -28 82 58	14 67 68 16 75 187 18 56 98	-6 45 78 -8 38• 16	-25 86 115 -27 78 75 -29 168 159	27 43• 32 29 65 77 31 53 42	16 156 11 18 193 23 28 136 19	4 221 287 5 6 268 261 7 8 387 339	-36 38+ 21 K+ 2, L+ 6	-11 108 -13 338 -15 331	216 23 331 29 421 27	92 11 123 11 98 7	x•	3, 1. 18	-16 199 -18 136 -28 88	223 147 164
-24 92 186 -26 250 287 -28 188 185	22 44• 17 24 44• 28 26 44• 54	1 1471 1185 3 1483 1487	-33 44• 59 -35 44• 20 -37 95 80	-1 123 186 -3 156 154 -5 235 217	24 282 19 24 88 6 26 879 24	6 12 187 184 3 14 968 678 8 16 81 60	8 448 377 9 580 458 4 318 389	-19 65 -21 319 -23 188	71 51 336 33 266 35	100 94 44 20 31• 81	3	50 40 394 23 78 85	-24 78 -26 44 -28 43	110 11 57

Table 3 (cont.)

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	4. 10 85 5 1376 65 1378 65 1374 13 131 132 132 132 133 132 134 132 137 132 138 132 139 132 131 14 147 152 147 121 132 14 43 43 43 43 43 43 44 147 147 132 147 133 43 43 43 43 43 43 43 43 140 140	P 3 5724 4 338774886770844450463206887928669011594685846827 9 21010	H 8827448827468874688746887468874688746874687468746	F 124511. 5134848855547758448894767653 4 131561875884574348488174816698685	F 11359544438847788364835974686762 4 4448484386433944577742551354719	H & B24688121112222	F0 4 4. 122 151 158 127 158 127 158 127 167 167 167 167 167 167 167 16	F 4 7 8133471988745584733877722436 6 21447796037722436 11547378037722436 11547378037722436 11547379603772111018	H 24 . W2448882424488824448 . W2474468 . 1357913579	F0 33.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.	FC 423 0 711127772873377382314 1 283739739739 8 354395601111112772728			H 11355779118597901 K. 13577913522291-35779113517913852931 K. 13	126 131 137 137 147 131 14 133 9. 122 2338 132 132 133 126 133 133 134 135 136 137 138 139 131 132 131 132 132 133 134 135 136 137 138 139 139 130 131 132 134 135	F 286121914 681319 21914 1997 1997 1997 1997 1997 1997 1997	x 979135713579135791357013570 . 13579135791357913579135791357			H .1357911351921-1-1-1-1-1-2-2 K 135791351-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1	F 45378730517554384999* L0 7337460437389533467 L	FC 14551274537847724453491475555133756172 7 20374556484523315773146494854914	H 7911137791133 . S210658121468822 . S21658212468822277795882	F 0 52 52 52 52 52 52 52 52 52 52	F 367284286575 8 41341755588818 1 9457533546897965929411 1	F0 3.3+ 4.1 107 4.5 5.7 4.5 5.7 5.8 5.7 5.8 5.7 5.8 5.7 5.8 5.7 5.8 5.8 5.8 5.8 5.8 5.8 5.8 5.8	F 5 2 466979799974476687749814497 3 934841922884782488351888	H . B244698244068244098244688 . G*6882446284	F0 L	F 4 814345353449777744487251 5 8377995888238373782 4 2455	H 44824 K 1857913 K 135791135791 K 13579175791 K 135	FG 128 3344 48 7. L. 41 48 48 48 48 48 48 48 48 48 48	F 33-773686 8 7283477387 1 78328777459 2 1809382545780 11826 3 7024
10	149 133 66 427 478 96 187 192 191	142 145 98 398 471 85 99 217 196	-18 -12 -14 -14 -18 -29 -24 -24 -24 -24	286 58 64 57 58 42 9 41 9 38	191 83 45 75 49 26 18 1	-2 -4 -88 -112 -14 -14 -18 -18	184 58 121 97 84 79 167 54 48+ 38+	97 73 115 98 99 118 71 28 16	21 23 25 27 29 31 K=	98 91 1 82 58 58 58 58 5, L= 342 2	87 2 11 2 58 2 63 3 58 - 1 -	3 11 5 7 5 7 5 7 5 7 5 7 5 7 5 7 5 7	5 185 8 88 47 47 198 198 172 141 165	K. 1 3 5 7 9 11	5 L 196 440 178 247 243 117 98	112 48 157 221 232 110 92	-15 -17 -21 -23 -25 -27 K-	43. 43. 41. 37. 34. 32. 5. L	85 53 87 14 93 6	-17 -19 -21 Ke 1 3	36* 47 78 5, L9 75 188 47	34 81 81 113 113 38	-6 -19 -12 -14 -16 -29 -22	221 136 43. 112 94 56 41. 79 288	228 159 64 131 95 69 23 99 139	 127 211 78 92 83 41• 41• 36• 58	138 225 191 88 88 54 43 58	X* 2 4 6 -2 -4	<pre> •, L= 151 87 35• 62 98 36• 94 </pre>	6 35 79 188 54 91	K. 35 -1 -3 -5 -7	7. Le 32. 58 39. 49 32. 31. 38.	3 17 62 34 43 53 61 62

positions was made both by analysis of the variation in reciprocal space of $|\Delta F_{h00}|$ between brosylate and tosylate according to the procedure described by Bragg (1958) and by use of the single-atom superposition technique. Five block-diagonal least-squares refinement cycles (isotropic) using all the data reduced $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ to 0.20. Five further cycles of anisotropic refinement using a weighting scheme (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961) of the form

In a three-dimensional Fourier synthesis calculated with phases based on the bromine position (fixed arbitrarily at y=0), the nonhydrogen atom positions, together with their mirror images, appeared clearly.

 $W = \frac{1}{2F_{\min} + |F_o| + \frac{2}{F_{\max}} |F_o|^2}$

Table 4. Fractional coordinates ($\times 10^4$) and thermal parameters ($\times 10^4$) for glycyl-L-phenylalanine brosylate

The numbers in parentheses are the estimated standard deviations of the positional and thermal parameters.

The thermal parameters are expressed in the form $T = \exp\left[-\left(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl\right) \times 10^{-4}\right]$.

	x	у	Z	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
N(1)	-82(3)	8980 (20)	7211 (10)	11(1)	267 (32)	102 (10)	-62(32)	-4 (5)	17 (10)
$C\alpha(1)$	137 (4)	6863 (24)	7477 (10)	13 (1)	270 (41)	79 (9)	-18(38)	18 (38)	-1(12)
$\mathbf{C}'(\mathbf{i})$	432 (3)	6801 (22)	6377 (11)	9 (1)	189 (32)	94 (11)	- 55 (36)	-9(5)	-10(10)
ŌÌÌ	444 (3)	8191 (16)	5463 (8)	14 (1)	209 (24)	99 (8)	71 (25)	6 (4)	4 (8)
N(2)	662 (3)	4969 (20)	6528 (9)	12(1)	270 (30)	82 (10)	45 (32)	5 (5)	13 (10)
$C\alpha(2)$	948 (4)	4605 (23)	5479 (11)	11 (1)	243 (39)	88 (11)	41 (35)	0 (6)	7 (11)
$\tilde{C}(2)$	732 (3)	4084 (23)	4064 (11)	10 (1)	292 (38)	75 (11)	15 (35)	2 (5)	21 (11)
$\tilde{O}(2)$	912 (3)	5022 (21)	3039 (8)	11 (1)	399 (34)	99 (8)	-7(33)	5 (4)	-22(10)
$\tilde{O}'(\tilde{2})$	451 (2)	3144(20)	3907 (9)	10 (1)	379 (35)	122 (10)	-18(33)	-1(4)	-11(9)
$\widetilde{CB(2)}$	1165 (4)	2453 (26)	5950 (13)	13 (1)	263 (38)	99 (13)	61 (39)	4 (7)	29 (13)
$\tilde{C}_{\nu}(2)$	1469 (3)	1850 (24)	4997 (12)	9 (1)	266 (40)	130 (13)	111 (42)	1 (6)	15 (11)
$\tilde{C}\delta \tilde{l}(2)$	1813 (5)	2821 (54)	5138 (18)	12 (2)	993 (141)	162 (21)	-153 (95)	-8(9)	75 (27)
$C\epsilon_1(2)$	2108	2224 (71)	4297 (22)	13 (2)	1087 (194)	257 (27)	-4 (140)	32 (11)	38 (32)
$\tilde{C}(2)$	2034 (7)	468 (55)	3334 (24)	23 (3)	901 (138)	171 (29)	197 (112)	15 (15)	181 (36)
$\tilde{C}\epsilon^2(2)$	1686 (6)	- 508 (36)	3169 (21)	20 (2)	417 (68)	196 (25)	- 36 (71)	8 (12)	56 (20)
$C\delta 2(1)$	1396 (4)	82 (28)	3976 (16)	14 (2)	294 (43)	149 (17)	54 (53)	9 (8)	17 (15)
$O(1)\hat{S}$	488 (3)	1618 (22)	-1521(8)	16(1)	365 (30)	77 (7)	- 34 (35)	-2(4)	-23 (11)
O(2)S	545 (3)	-441 (17)	638 (10)	20 (1)	292 (31)	138 (11)	191 (32)	38 (6)	-14 (10)
O(3)S	650 (3)	3734 (20)	565 (11)	16 (1)	387 (38)	142 (12)	- 144 (39)	-12 (6)	23 (11)
SÌ	668 (1)	1551 (7)	-123(3)	13 (0)	226 (7)	75 (2)	38 (9)	1 (1)	-11 (3)
C(1)	1144 (5)	1068 (21)	- 364 (14)	19 (2)	208 (40)	81 (11)	111 (39)	-23 (7)	- 39 (12)
C(2)	1409 (5)	2691 (33)	-82(16)	19 (2)	369 (55)	125 (17)	-9 (54)	0 (9)	-22 (18)
C(3)	1764 (5)	2369 (40)	- 390 (18)	15 (2)	553 (81)	156 (22)	135 (71)	-5 (10)	-22 (20)
C(4)	1883 (5)	328 (38)	-1032 (18)	17 (2)	407 (63)	176 (20)	117 (67)	-6 (9)	36 (20)
C(5)	1621 (6)	-1326 (33)	- 1359 (18)	17 (2)	377 (64)	204 (22)	139 (66)	1 (11)	51 (19)
C(6)	1234 (5)	-1008 (28)	- 992 (17)	15 (2)	271 (44)	208 (20)	90 (53)	- 16 (10)	4 (15)
Br	2356 (1)	0 (0)	-1605 (3)	18 (0)	1256 (22)	329 (5)	346 (21)	15 (2)	72 (4)

with $F_{\min} = 3.6$ and $F_{\max} = 269.7$ reduced R to 0.12. This weighting scheme was chosen to give a minimum variation of R as a function of 2θ . Final observed and calculated structure factors are listed in Table 2.

Glycyl-L-phenylalanine tosylate

In the $E^2 - 1$ vector map of the tosylate the sulphur atom was readily located, and it proved unnecessary to refer to the brosylate structure. A three-dimensional Fourier map was calculated using the phases of the sulfur atom alone. The first electron-density map showed the positions of six atoms and their mirror images. After four further structure factor-Fourier iterations all 27 nonhydrogen atoms were located. As their positional and isotropic temperature parameters were further refined by block-diagonal least-squares calculations R decreased to 0.18. At this point the nonhydrogen atom positions were refined anisotropically for three cycles (R=0.107) and finally for two more cycles anisotropically with the weighting scheme as defined earlier (R=0.095). The final observed and calculated structure factors are listed in Table 3.

A difference map had no well defined peaks within bonding distance of carbon, nitrogen, and oxygen although there were broad plateaus with an average electron density of 0.2 where hydrogen atoms would have been expected.

Scattering factors for carbon, nitrogen, oxygen, sulfur, and bromine were taken from *International Tables for X-ray Crystallography* (1962). Anomalous dispersion corrections were not made for sulfur or



Fig. 2. (a) Intermolecular packing diagram showing peptide and tosylate regions, hydrophilic and hydrophobic regions, and thermal motion. Insert (b), intermolecular packing of peptide and brosylate for comparison.

bromine. The maximum error in y for these atoms was estimated to be 0.01 Å (Cruickshank & McDonald, 1967). Initial calculations were carried out on an IBM 360-91 computer using the set of X-ray 67 programs (Stewart, 1967) and completed using a PDP-10 computer and the National Research Council of Canada programs (Ahmed, Hall, Pippy & Saunderson, 1966).

Table 5. Fractional coordinates ($\times 10^4$) and thermal parameters ($\times 10^4$) for glycyl-L-phenylalanine tosylate

The numbers in parentheses are the estimated standard deviations of the positional and thermal parameters.

The thermal parameters are expressed in the form $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \times 10^{-4}].$

	x	у	z	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
N(1)	-97(2)	8879 (9)	7175 (5)	13(1)	210 (13)	104 (5)	-25(14)	28 (3)	20 (4)
$C\alpha(1)$	140(2)	6867 (11)	7686 (5)	12(1)	243 (18)	85 (18)	-21(17)	27 (3)	0 (5)
$\mathbf{C}'(\mathbf{i})$	436 (1)	6653 (12)	6874 (5)	11 (0)	210 (14)	86 (5)	- 29 (17)	23 (2)	-4(5)
õm	453 (1)	8027 (8)	5949 (4)	15 (0)	204 (11)	108 (4)	73 (12)	35 (2)	13 (4)
N(2)	679 (2)	4906 (9)	7238 (5)	13 (1)	229 (14)	102 (5)	77 (15)	31 (3)	19 (5)
$C\alpha(2)$	947 (2)	4444 (11)	6441 (5)	12 (5)	231 (16)	85 (5)	33 (17)	25 (3)	3 (5)
C'(2)	720 (2)	4000 (10)	4829 (5)	12 (1)	187 (15)	89 (5)	-4 (16)	25 (3)	9 (5)
$\tilde{O}(2)$	886 (1)	4904 (10)	3938 (4)	15 (1)	339 (17)	98 (5)	-31 (17)	34 (2)	-24 (5)
$\tilde{O}(\tilde{2})$	417(1)	2964 (10)	4425 (5)	14 (1)	301 (16)	131 (1)	- 37 (16)	23 (3)	- 29 (5)
CB(2)	1186 (2)	2369 (14)	7109 (6)	14 (l)	286 (19)	135 (7)	116 (21)	33 (4)	31 (6)
$C_{\nu}(2)$	1482 (2)	1722 (13)	6380 (6)	12(1)	312 (18)	109 (6)	52 (21)	24 (3)	26 (6)
$C\delta^{1}(2)$	1825 (3)	2848 (24)	6710 (11)	13 (1)	666 (50)	258 (15)	- 192 (50)	44 (5)	-15(11)
$C\epsilon l(2)$	2100 (3)	2182 (35)	5953 (15)	19 (1)	835 (75)	426 (28)	272 (89)	99 (10)	52 (17)
C(2)	2011 (4)	533 (28)	4982 (12)	28 (2)	652 (60)	257 (17)	166 (57)	108 (9)	126 (19)
$\tilde{C}\epsilon^2(2)$	1655 (4)	-640(22)	4708 (10)	33 (2)	579 (45)	184 (12)	56 (40)	64 (8)	138 (17)
$C\delta 2(2)$	1398 (3)	-47 (16)	5387 (8)	21 (1)	319 (24)	159 (9)	-6 (28)	53 (5)	37 (9)
O(1)S	505 (1)	1543 (11)	- 1003 (4)	19 (1)	347 (15)	79 (4)	- 32 (16)	35 (2)	- 58 (6)
$O(2)\tilde{S}$	613 (2)	- 558 (10)	1201 (5)	20 (1)	400 (19)	165 (7)	155 (19)	59 (4)	-45 (6)
O(3)S	565 (2)	3471 (11)	1228 (5)	16 (1)	426 (20)	128 (5)	- 130 (20)	23 (3)	19 (6)
S	680 (1)	1551 (0)	584 (1)	16 (0)	249 (4)	76 (1)	8 (4)	33 (1)	-20 (2)
$\tilde{\mathbf{C}}(1)$	1189 (2)	1714 (13)	898 (6)	16 (1)	214 (17)	96 (5)	29 (21)	30 (3)	2 (7)
$\tilde{C}(2)$	1388 (2)	3685 (14)	1430 (8)	15 (1)	302 (23)	162 (8)	0 (25)	37 (4)	- 26 (7)
ČĠ	1784 (3)	3870 (18)	1607 (9)	16 (1)	411 (29)	196 (11)	- 57 (33)	34 (5)	- 19 (9)
C(4)	1984 (2)	2131 (19)	1209 (8)	15 (8)	422 (37)	183 (10)	183 (33)	27 (5)	21 (9)
$\tilde{C}(\tilde{5})$	1790 (3)	160 (17)	717 (9)	18 (1)	391 (29)	174 (11)	154 (32)	36 (5)	46 (8)
Č(6)	1388 (3)	-46 (14)	555 (8)	21 (l)	243 (21)	132 (8)	78 (25)	38 (5)	26 (8)
$\vec{C}(\vec{7})$	2423 (3)	2411 (31)	1332 (13)	15 (1)	700 (62)	297 (17)	150 (66)	43 (6)	26 (14)

Table 6. Intramolecular bond lengths in Å

The number in parentheses is the e.s.d. $\times 10^3$.

	Tanulata	Desculate
	Tosylate	Brosylate
$N(1)-C\alpha(1)$	1.469 (8)	1.477 (18)
$C\alpha(1)-C'(1)$	1.519 (8)	1.549 (16)
C'(1) -O(1)	1.235 (7)	1.203 (14)
C'(1) - N(2)	1.337 (8)	1.352(17)
$N(2) - C\alpha(2)$	1.446 (8)	1.505 (16)
$C\alpha(2)-C'(2)$	1.529 (7)	1.562 (16)
C'(2) - O''(2)	1.316 (8)	1.335 (15)
C'(2) - O'(2)	1·204 (8)	1.148 (16)
$C\alpha(2) - C\beta(2)$	1.531 (10)	1.532 (20)
$C\beta(2) - C\gamma(2)$	1.510 (10)	1.514(19)
$C_{\gamma}(2) - C\delta^{2}(2)$	1.349 (13)	1.358(24)
$C\delta 2(2) - C\epsilon 2(2)$	1.468 (17)	1.419 (29)
$C\varepsilon^{2}(2) - C\zeta^{2}(2)$	1.330 (23)	1.399 (44)
$C\zeta(2) - C\varepsilon I(2)$	1.411 (21)	1.374 (34)
$C\varepsilon 1(2) - C\delta 1(2)$	1.346 (17)	1.386 (26)
$C\delta 1(2) - C\gamma(2)$	1.397 (11)	1.442 (21)
SO(1)S	1.458 (3)	1.464 (8)
SO(2)S	1.454 (6)	1.442(12)
SO(3)S	1.436 (6)	1.443 (12)
S C(1)	1.756 (7)	1.761 (17)
C(1)C(6)	1.392 (11)	1.360 (24)
C(6) - C(5)	1.386 (13)	1.340 (25)
C(5)C(4)	1.391 (15)	1.422(30)
C(4) - C(3)	1·378 (15)	1.371 (28)
C(3)C(2)	1.408 (14)	1.467 (27)
C(2) - C(1)	1.377 (12)	1.402(21)
C(4) - C(7)	1.553 (14)	()
BrC(4)	· ·	1.828 (18)

Table 7. Bond angles (°)

The number in parentheses is the estimated standard deviation.

	Tosylate	Brosylate
$N(1) - C\alpha(1) - C'(1)$	108.9 (0.5)	106.2(1.0)
$C\alpha(1) - C'(1) - O(1)$	122.0 (0.5)	$123 \cdot 1 (1 \cdot 1)$
$C\alpha(1) - C'(1) - N(2)$	116.0 (0.5)	112.5(1.0)
O(1) - C'(1) - N(2)	122.1(0.5)	124.3 (1.1)
$C'(1) - N(2) - C\alpha(2)$	120.2 (0.5)	118.5 (1.0)
$N(2) - C\alpha(2) - C'(2)$	110.6 (0.5)	107.2(1.0)
$N(2) - C\alpha(2) - C\beta(2)$	108.2 (0.5)	105.8 (1.0)
$C\alpha(2) - C'(2) - O''(2)$	113.0 (0.5)	109.5 (1.0)
$C\alpha(2) - C'(2) - O'(2)$	123.0 (0.5)	126.3 (1.1)
O''(2) - C'(2) - O'(2)	123.9 (0.6)	124.0 (1.2)
$C\alpha(2) - C\beta(2) - C\gamma(2)$	113.4 (0.6)	112.4 (1.1)
$C\beta(2) - C\gamma(2) - C\delta 2(2)$	119.4 (0.7)	121.8 (1.9)
$C\beta(2) - C\gamma(2) - C\delta I(2)$	119.3 (0.7)	118.4 (1.2)
$C\gamma(2)$ — $C\delta 2(2)$ — $C\varepsilon 2(2)$	117.3 (1.0)	123.1 (2.1)
$C\delta^{2}(2)-C\varepsilon^{2}(2)-C\gamma^{2}(2)$	120.8 (1.4)	116.5 (2.5)
$C\varepsilon^{2}(2) - C\zeta^{2}(2) - C\varepsilon^{1}(2)$	119.8 (1.3)	120.9 (2.4)
$C\zeta(2)$ C ε 1(2) -C δ 1(2)	120.3 (1.2)	122.9 (2.0)
$C\varepsilon 1(2) - C\delta 1(2) - C\gamma(2)$	120.5 (0.9)	116.9 (1.5)
$C\delta 1(2) - C\gamma(2) - C\gamma(2)$	121.3 (0.8)	119.6 (1.5)
O(1)S - S - O(2)S	110.9 (0.3)	110.9 (0.6)
O(1)S - S - O(3)S	111.9 (0.3)	111.9 (0.6)
O(1)S - S - C(1)	104.5 (0.3)	105.0 (0.6)
O(2)S = S = O(3)S	114.2 (0.3)	116.6 (0.6)
O(2)S - S - C(1)	106.4 (0.3)	105.4 (0.6)
O(3)S - S - C(1)	108-3 (0-3)	106.0 (0.6)
S C(1) - C(6)	119.5 (0.5)	122.4 (1.1)
C(1) - C(6) - C(5)	119.9 (0.8)	121.5 (1.7)
C(6) - C(5) - C(4)	120.7 (0.9)	122.0 (1.8)
C(5) - C(4) - Br [or C(7)]	120.1 (0.9)	122.0 (1.4)
C(3) - C(4) - Br [or C(7)]	120.5 (0.9)	119.6 (1.4)
C(5) - C(4) - C(3)	119.4 (0.9)	118.1 (1.8)
C(4) - C(3) - C(2)	120.0 (0.8)	120.1 (1.7)
C(3) - C(2) - C(1)	119.8 (0.7)	117.5 (1.5)
C(3) - C(2) - S	120.7 (0.6)	116.6 (1.1)

Results and discussion

Final coordinates and thermal parameters for all nonhydrogen atoms in glycyl-L-phenylalanine brosylate and in glycyl-L-phenylalanine tosylate are given in Tables 4 and 5 respectively. Fig. 1(a) and (b) and Tables 6 and 7 show bond distances and bond angles in the tosylate and brosylate structures. The numbering scheme and all other abbreviations and symbols employed in the description of the conformation of the peptide chain are those proposed by the IUPAC-IUB Commission on Biochemical Nomenclature (1970) Report.

The tosylate provides the more reliable determination of bond lengths and angles because of the large bromine contribution to the structure factors. The estimated standard deviations of the brosylate parameters are approximately twice those of the tosylate. We shall therefore discuss in greatest detail the more accurately determined tosylate structure.

As Tables 4 and 5 show, the x and y coordinates of the peptide in the two structures are virtually identical. Furthermore, the apparent differences in z coordinates reflect the different β angles. When the z coordinates of a peptide in the tosylate structure are converted to the brosylate-structure lattice parameters, they coincide with the local peptide z coordinates. The overall packing differences which lead to different lattice parameters will be considered later. The intramolecular bond lengths and bond angles are very similar in the two structures both in the peptide and in the sulfonate ions. In both structures the estimated standard deviations of the two phenyl rings are almost twice those for the remaining backbone peptide chain and sulfonate group. The librations of the phenyl groups are clearly shown in Fig. 2.

Glycyl-L-phenylalanine tosylate

Bond distances and bond angles in the peptide (both side chain and peptide backbone residues) are not significantly different from the weighted average values reported from studies of three-dimensional crystal structures of di- and tri-peptides (Marsh & Donohue, 1967). In the salt the carboxyl group is protonated and exists with a formal carbonyl (C=O) and a single C-O bond. One feature of the peptide carboxyl group is common to both protonated and unprotonated forms, the angle C α (2)-C'(2)-O'(2), which involves the oxygen lying closer to the nitrogen atom, here as elsewhere is invariably larger [123·0 (0·5)°] than that which involves the oxygen opposite to the nitrogen atom [113·0 (0·5)°].

Within the phenyl ring of the peptide the average carbon-carbon bond distance is 1.38 Å, but variations are marked. The longest bond is 1.47 (2) and the shortest 1.33 (2) Å, a difference of eight e.s.d.'s. If the differences are real they are noteworthy. The structure as seen is not quinonoid but corresponds to the apparent stabilization of one principal canonical form. Similar large variations in glycylphenylalanylglycine (Marsh & Glusker, 1961) were observed, although the spread there was only 4.5 e.s.d.'s [1.35 (2)–1.44 (2) Å]. These differences may not be real since the authors pointed out that the quality of the data was poor and that anisotropic effects were not allowed for. In the tosylate group the aromatic C–C distances and angles differ very little. The average value of 1.39 (1) Å is unexceptional. The sulfonate group has a normal tetrahedral arrangement with an average S–O bond distance of 1.45 Å and an average O–S–O angle of 113° . These values are quite similar to those found in *p*-toluene-sulfonic acid and in other sulfonate structures.* (Dexter, 1972; see also Arora & Sundaralingam, 1971).

Mean planes were calculated for all putative planar groups including the phenyl rings, and the peptide carboxyl groups. The results are tabulated in Table 8. The phenyl ring in the tosylate is essentially planar $(\pm 0.01 \text{ Å})$. It is noteworthy that the substituents, the methyl carbon atom C(7) and sulfur atom, lie ± 0.08 and $\pm 0.12 \text{ Å}$ respectively out of the plane.[†] The sulfonate anion has a nearly eclipsed conformation with O(3)S rotated -10.0° out of the plane of the aromatic ring. In the other sulfonates the ArSO₃⁻ group is found in an eclipsed conformation (Huber, 1969) while the ArSO₃H group is found in a skew conformation (Dexter, 1972).

In the peptide molecule the six atoms of the phenyl ring and the C β (2) atom form a plane (±0.02 Å; χ^2 = 10.0).‡ For the five atoms [C α (1), C'(1), O(1), N(2), and

[†] This feature, a boat-shaped conformation, appeared in the structure of *p*-toluenesulfonic acid before anomalous dispersion effects were considered.

‡ See Stout & Jensen (1968) for a discussion of the χ^2 test.

 $C\alpha(2)$] of the peptide unit, which might be expected to be coplanar, deviations do occur (Table 8) with, for example, N(2) 0.049 Å below and $C\alpha(2)$ 0.037 Å above the mean plane. Both terminal N(1) and $C\beta(2)$ atoms lie in the mean plane of the amide group (deviation from planarity of ± 0.05 Å). The three atoms of the carboxyl group plus the adjacent $C\alpha(2)$ atom form a plane ($\chi^2 = 1.8$). The dihedral angles between the peptide plane and (a) the peptide phenyl ring and (b) the carboxyl group are 74.0 and 99.3° respectively. The angle between the planes of the phenyl and carboxyl groups is 48.0°.

The standard torsional angles (IUPAC-IUB, 1970) are given in Table 9; thus in the phenylalanine residue the chain has the appropriate angles for a right-handed α -helix ($\varphi = -57^{\circ}$, $\psi = -47^{\circ}$), while at the glycyl end it has an extended chain ($\varphi = 180$, $\psi = 180^{\circ}$) conformation.

 Table 9. A comparison of torsional angles in gly-L-phegly and gly-L-phe TsOH

$ \begin{array}{c} \psi_1 \\ \omega_1 \\ \varphi_2 \\ \psi_2 \text{ or } \psi_T \\ \omega_2 \\ \varphi_3 \\ \psi_2 \end{array} $	Rotation bond $C\alpha(1)-C'(1)$ C'(1) -N(2) $N(2)C\alpha(2)$ $C\alpha(2)-C'(2)$ C'(2) -N(3) $N(3)C\alpha(3)$ $C\alpha(3)-C'(3)$	Gly-L-phe TsOH - 179·0° - 174·5 - 60·8 - 40·2 	Gly-L-phe-gly 132·6° - 175·4 - 126·3 134·3 - 179·7 84·3 - 0.7
$\varphi_{3,}$ ψ_{T} χ_{1} χ_{2}	N(3)C α (3) C α (3)C'(3) C α (2)C β (2) C β (2)C γ (2)	35·9 78·5	84·3 -0·7 5·3 -77·5

The crystal structure shows extensive hydrogen bonding. Table 10 is a listing of all intermolecular hydrogen bonds with distances less than 3.0 Å. The overall packing can be described in terms of unimolecular sheets parallel to the (001) plane of peptides, alternating with tosylate. Within their respective sheets, peptide and tosylate molecules are 'extended' parallel

Table 8. Best planes through various groups of atoms

The equations of the plane are expressed in the form A(X') + B(Y') + C(Z') = D, where D is the origin-to-plane distance. X', Y', Z' are orthogonal coordinates in Å units, X' coincident with a, Z' in the ac plane || to c*, and Y' parallel to b*.

The numbers in parentheses are e.s.d.'s $\times 10^3$.

	Peptide	Carboxyl	group	Ph	e phenyl ring	Tosyla	te phenyl ring
Ator	ns Deviation	Atoms Dev	viation	Atoms	Deviation	Atoms	Deviation
$C\alpha(1)$ $C'(1)$ $O(1)$ $N(2)$ $C\alpha(2)$ $C\beta(2)$	$\begin{array}{l} 0.027 (6) \\ -0.005 (5) \\ -0.009 (4) \\ -0.049 (5) \\ 0.037 (6) \end{array}$	$\begin{array}{ccc} O''(2) & 0.0 \\ O'(2) & 0.0 \\ C'(2) & -0.0 \\ C\alpha(2) & 0.0 \end{array}$	02 (6) 03 (6) 07 (6) 02 (7)	$C\gamma(2)$ $C\delta(2)$ $C\varepsilon 1(2)$ $C\zeta(2)$ $C\varepsilon 2(2)$ $C\delta 2(2)$	$\begin{array}{c} 0.000 (7) \\ - 0.015 (12) \\ - 0.003 (17) \\ 0.021 (14) \\ - 0.007 (11) \end{array}$	C(1) C(2) C(3) C(4) C(5) C(6) S*	$\begin{array}{c} 0.019 \ (8) \\ - 0.007 \ (8) \\ - 0.007 \ (8) \\ 0.010 \ (6) \\ 0.002 \ (7) \\ - 0.017 \ (8) \\ 0.126 \ (1) \end{array}$
N(1)	-0.049(5)			$C\beta(2)$	0.014 (7)	Č(7)*	0.078 (13)
A B C D	-0.4737 -0.5258 -0.7069 -6.216	-0.540 0.840 -0.034 -1.245	3 8 1 7		0.0750 0.3471 -0.9348 -0.1093		0.0683 0.3468 -0.9354 -0.1713 14.5
χ²	168.	1.8			14.5		14.5

* These atoms were not used to determine the mean plane.

^{*} Dexter has prepared a tabular summary of the appropriate bond distances and bond angles in sulfonic acid groups in many different environments. The *p*-toluenesulfonic acid structure determination was undertaken as part of this laboratory's study of the usefulness of tosyl co-crystallization as well as our interest in the sulfonic acid group.

to the *a* axis. Each 'extended' peptide molecule, as seen in the h0l projection, has a nonpolar (benzene ring) and a polar end. Twofold axes in the peptide sheet lie between the polar ends of two hydrogenbonded molecules and thus provide maximum separation between the nonpolar ends of each molecular pair. Similarly, in the tosylate ion sheets, the twofold axis also lies between the polar ends (sulfonate) and thus provides maximum separation between the nonpolar ends of each molecular ends of the tosylate molecules. This arrangement establishes bimolecular layers of alternating pairs of peptide and tosylate molecules which lie parallel to c (Fig. 2).



Fig. 3. Hydrogen-bonding network viewed along b.



Fig.4. Hydrogen-bonding network viewed along a*. The phenyl rings in both peptide and tosylate have been omitted.

Table 10. Hydrogen bonds

Donor	Acceptor	Sym	metry op on accep	peration otor	Length Å
N(1)	O(1)S	х	1+y	1 + z	2.803 (7)
N(1)	O(3)S	-x	1 + y	1 - z	2.819 (8)
N(1)	O(1)	-x	y	1 - z	2.917 (6)
N(1)	O'(2)	-x	1 + y	1 - z	2.928 (7)
N(2)	O(1)S	x	y	1 + z	2.840 (7)
O''(2)	O(3)S	x	y	Z	2.641 (6)

Within one peptide sheet a pair of peptide molecules related by the twofold axis at $(0, y, \frac{1}{2})$ are held together by two hydrogen bonds between the terminal nitrogen, N(1), of the peptide and the carboxyl oxygen O(1) of the glycyl residue of the related peptide (Fig. 3). In addition each peptide molecule is hydrogen bonded between N(1) and the non-protonated carboxyl oxygen O'(2) of the peptide molecule related to it by unit translation along **b** and the twofold axis (Fig. 4 and Table 10).

Within the tosylate sheet, the pair of molecules related by the twofold axis at (0, y, 0) are not directly bonded. However, a sulfonate oxygen, O(1)S, in one tosylate ion is hydrogen bonded to the terminal N(1) of a peptide which is also hydrogen bonded to a second sulfonate oxygen, O(3)S, of another tosylate ion related to the first by the twofold axis. The bonding between tosylate ions is, therefore, mediated by an NH₃⁺ group. The hydrogen bonding between the terminal nitrogen and two sulfonate oxygen atoms together with N(2)-O(1)S and O(3)S-O''(2) hydrogen bonds serve to bind adjacent peptide and tosylate sheets.

In the nonpolar regions the benzene rings are related by screw axes at $(\frac{1}{4}, y, 0)$ and $(\frac{1}{4}, y, \frac{1}{2})$. This results in a hydrophobic region at $x = \frac{1}{4}$ and $x = \frac{3}{4}$ parallel to the *c* axis.

As shown in Fig. 5, there is no π overlap between aromatic rings of tosylate related by unit translation along b. The projection of a tosylate phenyl ring onto the plane of the phenyl ring located below it shows that the rings here are shifted 5.6 Å laterally with respect to each other. The vertical separation between the planes is 2.1 Å. The closest approach between tosylate groups is 3.34 Å between H(2) and H'(6). A projection of the peptide phenyl ring onto the plane of the phenyl ring below results in a lateral shift of 4.60 Å. The planes are separated by 3.86 Å vertically. There is a 4.5 Å separation of H δ 1(2) and H' ϵ 2(2). The phenyl rings of the tosylate and the adjacent phenylalanyl group form the 'herring bone' pattern typical of the packing of aromatic rings (Chiu, 1966; Craig, Mason, Pauling & Santry, 1965). The dihedral angle between adjacent rings is 25.9°. The H $\zeta(2)$ and H $\epsilon 2(2)$ atoms of the phenylalanine lie 3.24 and 3.41 Å from the plane of the tosylate respectively.

In summary, the hydrogen-bonding network consists of intermolecular bonds between the terminal NH_{3}^{+} of the peptide and the carboxyl and carbonyl oxygen atoms of a symmetry-related gly-phe ion. In

addition, hydrogen bonds are formed between this same NH⁺ group and one of the oxygen atoms in each of two tosylate ions lying in the adjacent sheet of tosylate ions. One of the tosylate oxygens is bound to both the NH of the peptide link and to the terminal NH_3^+ forming a connection between peptide and sulfonate sheets. One oxygen atom of the carboxyl group is bound to the terminal NH_3 + of a symmetry related peptide while the other carboxyl oxygen is hydrogen bonded to an oxygen atom of the tosylate group.

Glycyl-L-phenylalanine tosylate and brosylate comparison

In the tosylate and brosylate structures there are no appreciable differences in x and y coordinates for the peptide. The tosylate ion differs considerably from the brosylate ion in its y coordinate. The methyl group lies 1.44 Å along **b** above the corresponding Br position in the brosylate. The atoms of the sulfonic acid group (which is extensively hydrogen bonded to other atoms) are in essentially the same location in both structures, but the rest of the tosylate ion is swung upward while the brosylate ion plane is swung downward with respect to the (010) plane. If one converts the fractional zcoordinates for the tosylate to the value they have in the brosylate lattice there is virtually no difference in position of the peptide (see Table 11). The methyl group of the tosylate is displaced 0.06 Å from the bromine position in the brosylate; the sulfur atoms have virtually the same z coordinates. The really striking difference between the tosylate and brosylate structures, which leads to such different β angles, lies in the different positions of the screw axis at $x = \frac{1}{4}$ (see insert Fig. 2). The positions of the counter-ions in both structures differ, therefore, markedly from each other without greatly affecting the peptide conformation. In spite of the differences in detailed packing between the brosylate and tosylate structures the pair of salts were closely enough related to permit some phasing by analogy. Furthermore the peptide conformation remained identical.

The two sulfonate ions may have broad general usefulness in the crystallization and subsequent comparative structure determination of peptides and other cationic groups.

References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & SAUNDERSON, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. Division of Pure Physics and Pure Chemistry, National Research Council, Ottawa, Canada.
- ALEXANDER, L. E. & SMITH, G. S. (1962). Acta Cryst. 15, 983.
- ARORA, S. K. & SUNDARALINGAM, M. (1971). Acta Cryst. B27, 1293.
- BRAGG, W. L. (1958). Acta Cryst. 11, 70.



Fig. 5. Packing of phenyl rings as viewed along a^* axis. The hydrogen positions are shown for purposes of packing. They were not established experimentally.

Table 11. Comparison of fractional z coordinates for tosylate and brosylate

	z (tos.)	z' (tos.)*	z (bros.)
N(1)	0.718	0.727	0.721
$C\alpha(1)$	0.769	0.755	0.748
C'(1)	0.687	0.645	0.638
OÌÌ	0.595	0.551	0.546
N(2)	0.724	0.658	0.653
$C\alpha(2)$	0.644	0.552	0.548
C'(2)	0.483	0.413	0.406
O''(2)	0·394	0.308	0.304
O'(2)	0.443	0.402	0.391
$C\beta(2)$	0.711	0.596	0.595
$C_{\gamma}(2)$	0.638	0.495	0.500
Cδ1(2)	0.671	0.494	0.514
Ce1(2)	0.595	0.391	0.430
Cζ(2)	0·498	0.303	0.333
Ce2(2)	0.471	0.305	0.317
Cδ2(2)	0.539	0.403	0.398
O(1)S	-0.100	-0.149	-0.152
O(2)S	0.120	0.060	0.064
O(3)S	0.123	0.068	0.057
S	0.028	-0.008	-0.012
C(1)	0.090	-0.025	-0.036
C(2)	0.143	0.008	-0.008
C(3)	0.161	-0.012	-0.039
C(4)	0.121	-0.071	-0.103
C(5)	0.072	-0.102	-0.136
C(6)	0.056	-0.079	-0.099
C(7)	0.133	-0·102	—0·161 (Br)

^{*} Converted to the corresponding position in the brosylate lattice, $z' = z - \frac{\chi_{tos}(35.99) (\sin 19.12 - \sin 3.8)}{z + 10.12}$

9.679

CHIU, C. C. (1966). Ph. D. Thesis, Department of Biochemistry, Columbia University.

CRAIG, D. P., MASON, R., PAULING, P. & SANTRY, D. P. (1965). Proc. Roy. Soc. A286, 98.

CROSBY, B. L. & KIRK, P. L. (1935). Mikrochemie, 18, 137.

- CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). Computing Methods and the Phase Problem in X-ray Crystal Analysis. Edited by R. PEPINSKY, J. M. ROBERTSON & J. C. SPEAK-MAN. p. 32. New York: Pergamon Press.
- CRUICKSHANK, D. W. J. & MCDONALD, W. S. (1967). Acta Cryst. 23, 9.
- DEXTER, D. D. (1972). Z. Kristallogr. In the press.
- HUBER, C. S. (1969). Acta Cryst. B25, 1140.
- International Tables for X-ray Crystallography (1952). Vol. III. Birmingham: Kynoch Press.
- IUPAC-IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). J. Mol. Biol. 52, 1.

- Low, B. W. & RICHARDS, F. M. (1952). J. Amer. Chem. Soc. 74, 1660.
- MARSH, R. E. & DONOHUE, J. (1967). Chapter in Advanc. Protein. Chem. p. 22. New York: Academic Press.
- MARSH, R. E. & GLUSKER, J. P. (1961). Acta Cryst. 14, 1110.
- STEIN, W. H., MOORE, S. & BERGMAN, M. (1944). J. Biol. Chem. 154, 191.
- STEWART, J. M. (1970). Crystallographic Computing. Edited by F. R. AHMED, p. 71. Copenhagen: Munksgaard.
- STEWART, J. M. (1967). X-ray 67 Program System for X-ray Crystallography, Technical Report 67–58, Computer Center, Univ. of Maryland.
- STOUT, G. H. & JENSEN, L. H. (1968). X-ray Structure Determination. p.422. New York: Macmillan.

Acta Cryst. (1972). B28, 3559

The Crystal Structure of Sborgite, NaB₅O₆(OH)₄.3H₂O

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The crystal structure of sborgite (space group C2/c, cell parameters $a=11\cdot119$, $b=16\cdot474$, $c=13\cdot576$ Å, $\beta=112^{\circ}50'$) was determined by the symbolic addition method and refined by the least-squares method (with anisotropic thermal parameters for non-hydrogen atoms) to a final *R* value of 0.062. The structure contains the pentaborate ion $[B_3O_6(OH)_4]^-$ characterized by the double ring built up from one BO₄ tetrahedron and three BO₃ triangles. The two sodium ions in the asymmetric unit are in special positions along a binary axis: one is octahedrally coordinated by four water molecules and two hydroxyl ions, the other is tetrahedrally coordinated by two water molecules and two hydroxyl ions, with two more distant contacts at nearly 3 Å. A complex system of hydrogen bonds connects the pentaborate ions and the sodium coordination polyhedra.

Introduction

Sborgite was reported as a new mineral phase by Cipriani (1957) who found it associated with borax and thenardite among the compounds incrusting the training pipes of some 'soffioni' in the boriferous area of Larderello. Cipriani identified it, on the basis of its powder diffraction pattern, optical data and density, with the compound NaB₅O₈.5H₂O, synthesized and studied by Sborgi in his researches on the ternary system Na₂O-B₂O₃-H₂O. The cell data and space group were determined by Sabelli (1962).

Christ (1960), in his study on the crystal chemistry of hydrated borates, advanced the hypothesis that sborgite must contain the pentaborate ion $[B_5O_6(OH)_4]^-$, known to exist, to that date, in the compound

 $NH_4B_5O_6(OH)_4.2H_2O$ and in its potassium analogue $KB_5O_6(OH)_4.2H_2O$ (Zachariasen, 1937). Recently we found this same group isolated, or variously polymerized, in some minerals and artificial products (Merlino, 1969; Merlino & Sartori, 1969, 1971). We were thus strongly motivated to undertake the structural study of sborgite in order to define its position in the crystal-chemical classification of borates and its relations with the other compounds containing the pentaborate group.

Experimental

Synthetic crystals of sborgite, suitable for X-ray singlecrystal investigations, were obtained following the suggestions of Cipriani (1957). Unit-cell constants were determined from the least-squares refinement of powder data.

Sborgite, NaB₅O₈. 5H₂O M.W. 295·17 Monoclinic, space group C2/c or Cc (C2/c established by intensity statistics)

a=11·119 (8) Å
b = 16.474(14)
c = 13.576(9)
$\beta = 112^{\circ} 50 (2)'$

Unit-cell volume, $V = 2291.9 \text{ Å}^3$ Z = 8 $D_m = 1.713 \text{ g.cm}^{-3}$, as determined by Sabelli, $D_c = 1.711 \text{ g.cm}^{-3}$, F(000) = 1200, $\mu = 17.0 \text{ cm}^{-1}$ (Cu Ka).

The intensity data were recorded with nickel-filtered Cu K α radiation ($\lambda = 1.5418$ Å), by means of Weissenberg photographs, with the multiple-film technique and integration process. A fragment elongated in the **a** direction was cut from a large crystal and reduced to cylindrical shape with cross sectional radius of 0.025 cm ($\mu R = 0.382$ for Cu K α radiation). Eleven layers with *a* as rotation axis (h = 0 through 10) were recorded