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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 $a=35{\cdot}99$ (1), $b=6{\cdot}005$ (2), $c=9{\cdot}679$ (5) Å, $\beta=109{\cdot}12$ (5)° and $a=35{\cdot}91$ (1), $b=5{\cdot}838$ (2), $c=9{\cdot}679$ (8) Å, $\beta=93{\cdot}59$ (5)° respectively. There are four molecules in the unit cell with $D_m=1{\cdot}297$ g.cm^{-3} for the tosylate and $1{\cdot}498$ 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 $K\alpha$ 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 Cβ(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 (pseudo-isomorphous) 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 *p*-bromobenzenesulfonic 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 $0{\cdot}04\times 0{\cdot}4\times 0{\cdot}2$ 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 $0{\cdot}02\times 0{\cdot}5\times 0{\cdot}09$ 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 $K\alpha$ ($\lambda=1{\cdot}5418$ Å) radiation was used. A 30 sec count was employed at the peak position with background counted for 15 sec at $2\theta\pm\{1{\cdot}8(1{\cdot}0+0{\cdot}48\tan\theta)\}$. 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 2σ ($\sigma=\sqrt{I_{peak}+I_{back}}$). An empirical (Alexander & Smith, 1962) peak-height to intensity conversion curve was used to transform measured peak-heights 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 ($\mu=17{\cdot}3$ cm^{-1}) and 17% for the smaller brosylate crystal ($\mu=42{\cdot}0$ 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 $0{\cdot}04\times 1{\cdot}0\times 1{\cdot}0$ mm in size lying on (100) bounded by {001} and by $(0\bar{1}0)$ and {011} at opposite ends; they show perfect cleavage parallel to the (100) face, and are highly birefringent (+) with $\beta\|\mathbf{b}$ 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 $(0\bar{1}0)$ $(00\bar{1})$, (101), $(10\bar{1})$, and {041}. The crystals show perfect cleavage on the (100) face with $\gamma\|\mathbf{b}$. The space group is $P2_1$ (systematic absences $0k0$, $k=2n+1$ absent).

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

Table 1. *Physical data*

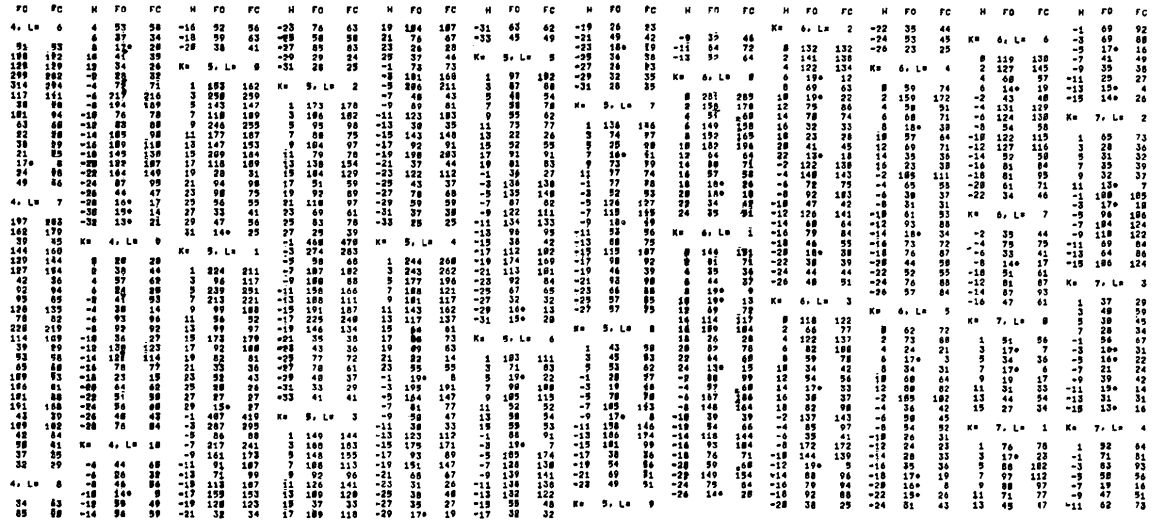
	Gly-L-phe TsOH	Gly-L-phe BsOH	Gly-L-phe
Mol. formula	$C_{18}H_{22}N_2O_6S$	$C_{17}H_{19}N_2O_6SBr$	$C_{11}H_{14}N_2O_3$
M.W.	394·44	459·31	222·24
Space group	$C2$	$C2$	$P2_1$
a*	35·99 ± 0·01 Å	35·91 ± 0·01 Å	16·74 ± 0·02 Å
b	6·005 ± 0·002	5·838 ± 0·002	5·505 ± 0·005
c	9·679 ± 0·005	9·679 ± 0·008	6·465 ± 0·005
β	109·12 ± 0·05°	93·59 ± 0·05°	97·76 ± 0·05°
V	1976·67 Å^3	2025·15 Å^3	
ϱ_m	1·297 g.cm^{-3}†	1·498 g.cm^{-3}‡	—
M.W. measured	386·0	446·8	—
Radiation	Cu $K\alpha$, 1·5418 Å		
No. of independent reflections	2237	2294	1349
No. of observed reflections	2073	1684	885
Z	4	4	2
d_{min}	0·80 Å	0·80 Å	0·80 Å

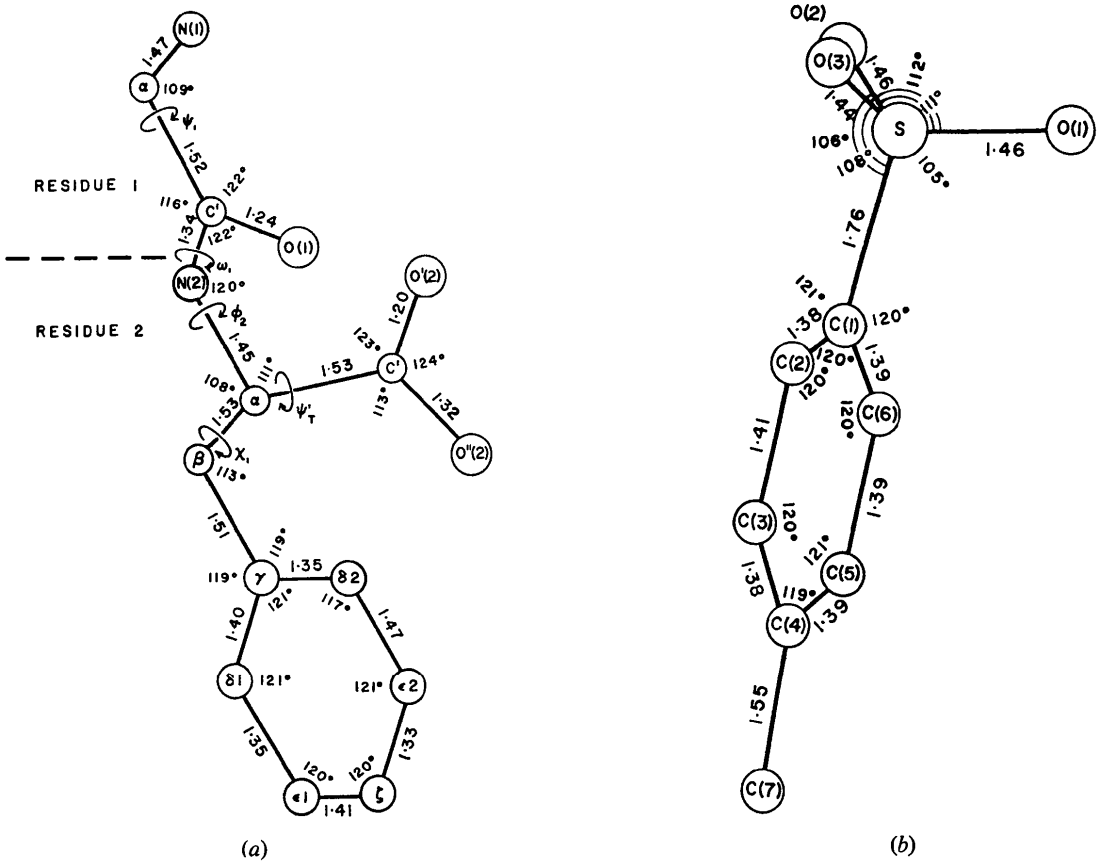
* The limits of error cited for the unit-cell dimensions are mean-square deviations from the mean.
† Gradient column of water saturated bromobenzene/*o*-xylene.
‡ Gradient column of water saturated bromobenzene/*o*-xylene/carbon tetrachloride.

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 (*).

Table 2 (*cont.*)





(*a*) (*b*)

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 Cα(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

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 (*).

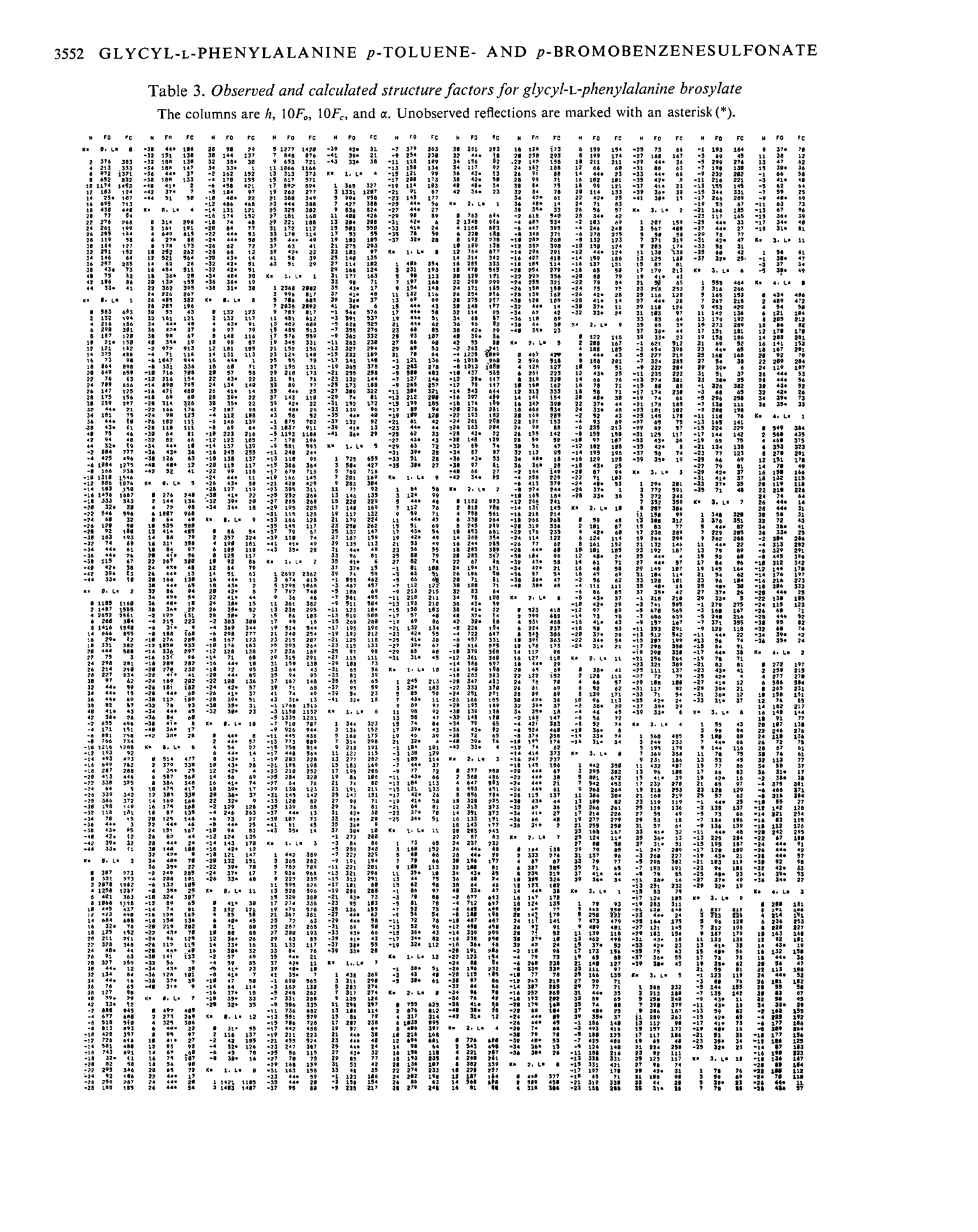
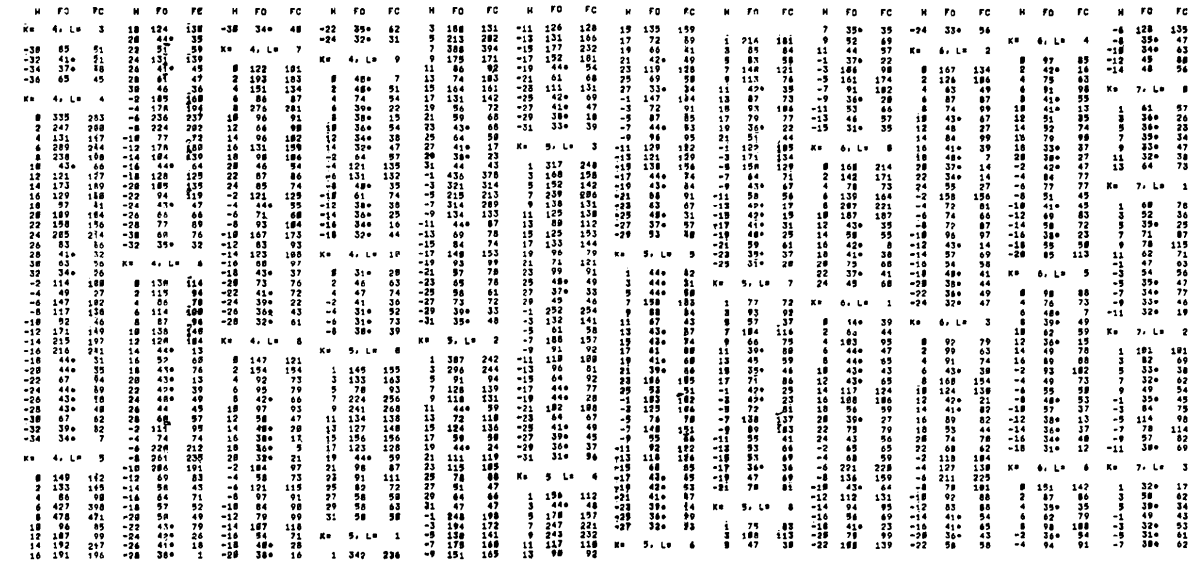


Table 3 (*cont.*)



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.

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. 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

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

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

	x	y	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)
Cα(1)	137 (4)	6863 (24)	7477 (10)	13 (1)	270 (41)	79 (9)	−18 (38)	18 (38)	−1 (12)
C′(1)	432 (3)	6801 (22)	6377 (11)	9 (1)	189 (32)	94 (11)	−55 (36)	−9 (5)	−10 (10)
O(1)	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)
Cα(2)	948 (4)	4605 (23)	5479 (11)	11 (1)	243 (39)	88 (11)	41 (35)	0 (6)	7 (11)
C′(2)	732 (3)	4084 (23)	4064 (11)	10 (1)	292 (38)	75 (11)	15 (35)	2 (5)	21 (11)
O″(2)	912 (3)	5022 (21)	3039 (8)	11 (1)	399 (34)	99 (8)	−7 (33)	5 (4)	−22 (10)
O′(2)	451 (2)	3144 (20)	3907 (9)	10 (1)	379 (35)	122 (10)	−18 (33)	−1 (4)	−11 (9)
Cβ(2)	1165 (4)	2453 (26)	5950 (13)	13 (1)	263 (38)	99 (13)	61 (39)	4 (7)	29 (13)
Cγ(2)	1469 (3)	1850 (24)	4997 (12)	9 (1)	266 (40)	130 (13)	111 (42)	1 (6)	15 (11)
Cδ1(2)	1813 (5)	2821 (54)	5138 (18)	12 (2)	993 (141)	162 (21)	−153 (95)	−8 (9)	75 (27)
Cε1(2)	2108	2224 (71)	4297 (22)	13 (2)	1087 (194)	257 (27)	−4 (140)	32 (11)	38 (32)
Cζ(2)	2034 (7)	468 (55)	3334 (24)	23 (3)	901 (138)	171 (29)	197 (112)	15 (15)	181 (36)
Cε2(2)	1686 (6)	−508 (36)	3169 (21)	20 (2)	417 (68)	196 (25)	−36 (71)	8 (12)	56 (20)
Cδ2(1)	1396 (4)	82 (28)	3976 (16)	14 (2)	294 (43)	149 (17)	54 (53)	9 (8)	17 (15)
O(1)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)
S	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 $F_{min}=3{\cdot}6$ and $F_{max}=269{\cdot}7$ 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 ($R=0{\cdot}107$) and finally for two more cycles anisotropically with the weighting scheme as defined earlier ($R=0{\cdot}095$). 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 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).

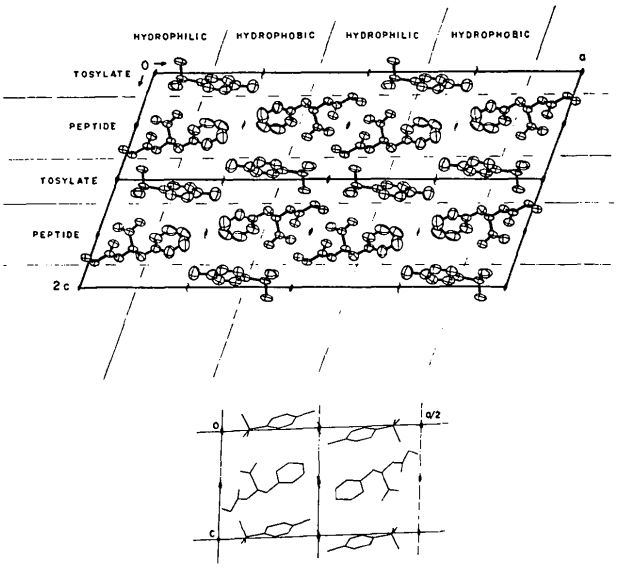


Fig. 2. (*a*) Intermolecular packing diagram showing peptide and tosylate regions, hydrophilic and hydrophobic regions, and thermal motion. Insert (*b*), intermolecular packing of peptide and brosylate for comparison.

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	y	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)
Cα(1)	140 (2)	6867 (11)	7686 (5)	12 (1)	243 (18)	85 (18)	−21 (17)	27 (3)	0 (5)
C′(1)	436 (1)	6653 (12)	6874 (5)	11 (0)	210 (14)	86 (5)	−29 (17)	23 (2)	−4 (5)
O(1)	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)
Cα(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)
O″(2)	886 (1)	4904 (10)	3938 (4)	15 (1)	339 (17)	98 (5)	−31 (17)	34 (2)	−24 (5)
O′(2)	417 (1)	2964 (10)	4425 (5)	14 (1)	301 (16)	131 (1)	−37 (16)	23 (3)	−29 (5)
Cβ(2)	1186 (2)	2369 (14)	7109 (6)	14 (1)	286 (19)	135 (7)	116 (21)	33 (4)	31 (6)
Cγ(2)	1482 (2)	1722 (13)	6380 (6)	12 (1)	312 (18)	109 (6)	52 (21)	24 (3)	26 (6)
Cδ1(2)	1825 (3)	2848 (24)	6710 (11)	13 (1)	666 (50)	258 (15)	−192 (50)	44 (5)	−15 (11)
Cε1(2)	2100 (3)	2182 (35)	5953 (15)	19 (1)	835 (75)	426 (28)	272 (89)	99 (10)	52 (17)
Cζ(2)	2011 (4)	533 (28)	4982 (12)	28 (2)	652 (60)	257 (17)	166 (57)	108 (9)	126 (19)
Cε2(2)	1655 (4)	−640 (22)	4708 (10)	33 (2)	579 (45)	184 (12)	56 (40)	64 (8)	138 (17)
Cδ2(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)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)
C(1)	1189 (2)	1714 (13)	898 (6)	16 (1)	214 (17)	96 (5)	29 (21)	30 (3)	2 (7)
C(2)	1388 (2)	3685 (14)	1430 (8)	15 (1)	302 (23)	162 (8)	0 (25)	37 (4)	−26 (7)
C(3)	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)
C(5)	1790 (3)	160 (17)	717 (9)	18 (1)	391 (29)	174 (11)	154 (32)	36 (5)	46 (8)
C(6)	1388 (3)	−46 (14)	555 (8)	21 (1)	243 (21)	132 (8)	78 (25)	38 (5)	26 (8)
C(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. × 10^3.

	Tosylate	Brosylate
N(1)—Cα(1)	1·469 (8)	1·477 (18)
Cα(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)—Cα(2)	1·446 (8)	1·505 (16)
Cα(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)
Cα(2)–Cβ(2)	1·531 (10)	1·532 (20)
Cβ(2)–Cγ(2)	1·510 (10)	1·514 (19)
Cγ(2)–Cδ2(2)	1·349 (13)	1·358 (24)
Cδ2(2)–Cε2(2)	1·468 (17)	1·419 (29)
Cε2(2) –Cζ(2)	1·330 (23)	1·399 (44)
Cζ(2)—Cε1(2)	1·411 (21)	1·374 (34)
Cε1(2) –Cδ1(2)	1·346 (17)	1·386 (26)
Cδ1(2)–Cγ(2)	1·397 (11)	1·442 (21)
S———O(1)S	1·458 (3)	1·464 (8)
S———O(2)S	1·454 (6)	1·442 (12)
S———O(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)	
Br———C(4)		1·828 (18)

Table 7. *Bond angles* (°)

The number in parentheses is the estimated standard deviation.

	Tosylate	Brosylate
N(1)——Cα(1)—C′(1)	108·9 (0·5)	106·2 (1·0)
Cα(1)—C′(1)—O(1)	122·0 (0·5)	123·1 (1·1)
Cα(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)—Cα(2)	120·2 (0·5)	118·5 (1·0)
N(2)——Cα(2)—C′(2)	110·6 (0·5)	107·2 (1·0)
N(2)——Cα(2)—Cβ(2)	108·2 (0·5)	105·8 (1·0)
Cα(2)—C′(2) —O″(2)	113·0 (0·5)	109·5 (1·0)
Cα(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)
Cα(2)—Cβ(2)—Cγ(2)	113·4 (0·6)	112·4 (1·1)
Cβ(2)—Cγ(2)—Cδ2(2)	119·4 (0·7)	121·8 (1·9)
Cβ(2)—Cγ(2)—Cδ1(2)	119·3 (0·7)	118·4 (1·2)
Cγ(2)—Cδ2(2)–Cε2(2)	117·3 (1·0)	123·1 (2·1)
Cδ2(2)–Cε2(2) –Cγ(2)	120·8 (1·4)	116·5 (2·5)
Cε2(2) –Cζ(2)—Cε1(2)	119·8 (1·3)	120·9 (2·4)
Cζ(2)—Cε1(2) –Cδ1(2)	120·3 (1·2)	122·9 (2·0)
Cε1(2) –Cδ1(2)–Cγ(2)	120·5 (0·9)	116·9 (1·5)
Cδ1(2)–Cγ(2)—Cγ2(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 non-hydrogen 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 Cα(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*-toluenesulfonic 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 (±0·01 Å). It is noteworthy that the substituents, the methyl carbon atom C(7) and sulfur atom, lie +0·08 and +0·12 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 $ArSO_3^-$ group is found in an eclipsed conformation (Huber, 1969) while the $ArSO_3H$ group is found in a skew conformation (Dexter, 1972).

In the peptide molecule the six atoms of the phenyl ring and the Cβ(2) atom form a plane (±0·02 Å; χ^2 = 10·0).‡ For the five atoms [Cα(1), C′(1), O(1), N(2), and Cα(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 Cα(2) 0·037 Å above the mean plane. Both terminal N(1) and Cβ(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 Cα(2) atom form a plane (χ^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 ($\varphi = -57°$, $\psi = -47°$), while at the glycyl end it has an extended chain ($\varphi = 180$, $\psi = 180°$) conformation.

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

	Rotation bond	Gly-L-phe TsOH	Gly-L-phe-gly
ψ_1	Cα(1)–C′(1)	−179·0°	132·6°
ω_1	C′(1) –N(2)	−174·5	−175·4
φ_2	N(2)—Cα(2)	−60·8	−126·3
ψ_2 or ψ'_T	Cα(2)–C′(2)	−40·2	134·3
ω_2	C′(2) –N(3)	—	−179·7
φ_3	N(3)—Cα(3)	—	84·3
ψ'_T	Cα(3)–C′(3)	—	−0·7
χ_1	Cα(2)–Cβ(2)	35·9	5·3
χ_2	Cβ(2)–Cγ(2)	78·5	−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

* 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.

† 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.

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 × 10^3.

Peptide		Carboxyl group		Phe phenyl ring		Tosylate phenyl ring	
Atoms	Deviation	Atoms	Deviation	Atoms	Deviation	Atoms	Deviation
Cα(1)	0·027 (6)	O″(2)	0·002 (6)	Cγ(2)	0·000 (7)	C(1)	0·019 (8)
C′(1)	−0·005 (5)	O′(2)	0·003 (6)	Cδ(2)	−0·015 (12)	C(2)	−0·007 (8)
O(1)	−0·009 (4)	C′(2)	−0·007 (6)	Cε1(2)	−0·003 (17)	C(3)	−0·007 (8)
N(2)	−0·049 (5)	Cα(2)	0·002 (7)	Cζ(2)	0·021 (14)	C(4)	0·010 (6)
Cα(2)	0·037 (6)			Cε2(2)	−0·007 (11)	C(5)	0·002 (7)
						C(6)	−0·017 (8)
Cβ(2)*	−0·046 (7)			Cδ2(2)	−0·011 (9)	S*	0·126 (1)
N(1)*	−0·049 (5)			Cβ(2)	0·014 (7)	C(7)*	0·078 (13)
A	−0·4737		−0·5403		0·0750		0·0683
B	−0·5258		0·8408		0·3471		0·3468
C	−0·7069		−0·0341		−0·9348		−0·9354
D	−6·216		−1·2457		−0·1093		−0·1713
χ^2	168·		1·8		14·5		14·5

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

to the *a* axis. Each 'extended' peptide molecule, as seen in the *h*0*l* projection, has a nonpolar (benzene ring) and a polar end. Twofold axes in the peptide sheet lie between the polar ends of two hydrogen-bonded 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 the tosylate molecules. This arrangement establishes bimolecular layers of alternating pairs of peptide and tosylate molecules which lie parallel to **c** (Fig. 2).

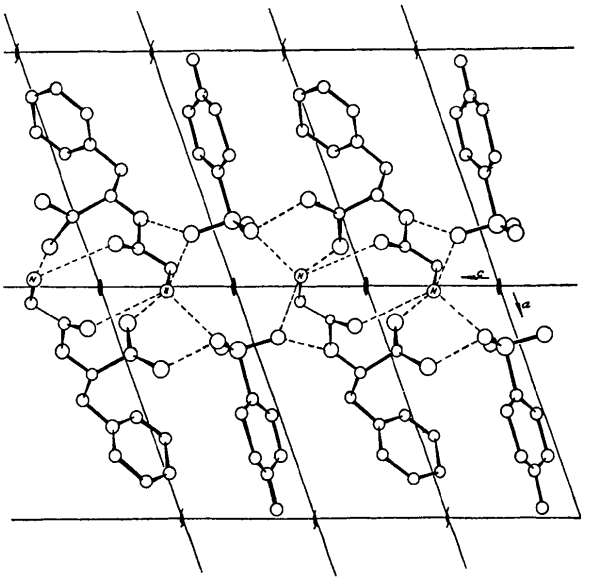


Fig. 3. Hydrogen-bonding network viewed along **b**.

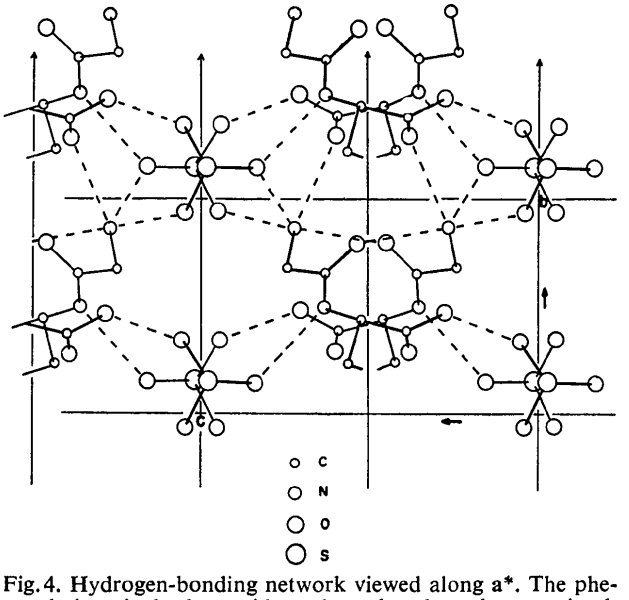


Fig. 4. Hydrogen-bonding network viewed along **a***. The phenyl rings in both peptide and tosylate have been omitted.

Table 10. *Hydrogen bonds*

Donor	Acceptor	Symmetry operation on acceptor			Length Å
N(1)	O(1)S	x	$1+y$	$1+z$	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 NH_3^+ 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 Hδ1(2) and H′ε2(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 Hζ(2) and Hε2(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_3^+ 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 z coordinates 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.

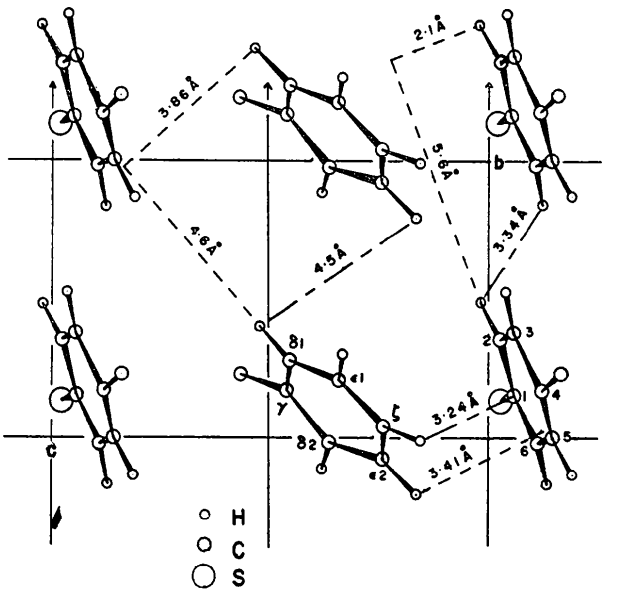


Fig. 5. Packing of phenyl rings as viewed along a^* axis. The hydrogen positions are shown for purposes of packing. They were not established experimentally.

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
Cα(1)	0·769	0·755	0·748
C′(1)	0·687	0·645	0·638
O(1)	0·595	0·551	0·546
N(2)	0·724	0·658	0·653
Cα(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
Cβ(2)	0·711	0·596	0·595
Cγ(2)	0·638	0·495	0·500
Cδ1(2)	0·671	0·494	0·514
Cε1(2)	0·595	0·391	0·430
Cζ(2)	0·498	0·303	0·333
Cε2(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	0·058	−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, $z'=z-\dfrac{\chi_{tos}(35{\cdot}99)(\sin 19{\cdot}12-\sin 3{\cdot}8)}{9{\cdot}679}$.

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The Crystal Structure of Sborgite, $NaB_5O_6(OH)_4.3H_2O$

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The crystal structure of sborgite (space group $C2/c$, cell parameters $a=11{\cdot}119$, $b=16{\cdot}474$, $c=13{\cdot}576$ Å, $\beta=112°50'$) 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 $[B_5O_6(OH)_4]^-$ characterized by the double ring built up from one BO_4 tetrahedron and three BO_3 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 $NaB_5O_8.5H_2O$, synthesized and studied by Sborgi in his researches on the ternary system Na_2O–B_2O_3–H_2O. 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 single-crystal investigations, were obtained following the suggestions of Cipriani (1957). Unit-cell constants were determined from the least-squares refinement of powder data.

Sborgite, $NaB_5O_8.5H_2O$ M.W. 295·17

Monoclinic, space group $C2/c$ or Cc ($C2/c$ established by intensity statistics)

$a=11{\cdot}119$ (8) Å
$b=16{\cdot}474$ (14)
$c=13{\cdot}576$ (9)
$\beta=112°50$ (2)'

Unit-cell volume, $V=2291{\cdot}9$ Å^3 $Z=8$

$D_m=1{\cdot}713$ g.cm^{-3}, as determined by Sabelli, $D_c=1{\cdot}711$ g.cm^{-3}, $F(000)=1200$, $\mu=17{\cdot}0$ cm^{-1} (Cu $K\alpha$).

The intensity data were recorded with nickel-filtered Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ 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 ($\mu R=0{\cdot}382$ for Cu $K\alpha$ radiation). Eleven layers with a as rotation axis ($h=0$ through 10) were recorded