The environment of the carbon atoms (below 4 Å) has been closely examined for possible hydrogen bonding. The hydrogen atoms could not be localized. The intramolecular contacts C···O (2·63 Å) and C···Cl(1) (3·40 Å) are short but the angles are unfavourable [S–C···O = 32·4° and S–C···Cl(1) = 67·4°]. The shortest C···O intermolecular contacts are 3·48 Å with an angle S–C···O of 118·7°. The long intermolecular C···Cl(1) [3·58 Å, angle S–C···Cl(1) = 177·3°] and C···Cl(2) [3·51 Å, angle S–C···Cl(2) = 101·2°] contacts do not suggest that hydrogen bonding would be very important in this crystal.

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A Refinement of the Crystal Structure of *N,N'*-Diglycyl-L-cystine Dihydrate

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Abstract. The structure of the title compound has been re-refined by full-matrix least squares, including anisotropic thermal parameters for the heavy atoms. Bond distances and angles are near to the previously published values, except for the angle C–C–S which is now no longer anomalously small. A revised scheme for the hydrogen bonding at the water molecule is suggested.

Introduction. During a survey of the geometries of the disulfide linkages in cystines, various derivatives of it, and related compounds (Donohue, 1976), it was noted that while there was generally good agreement among the values of various molecular features in these compounds, the value of 105·0 (2·1)° reported for the C–C–S bond angle in the diglycylcystine molecule (Yakel & Hughes, 1954, hereinafter YH) differed markedly from the average of 114·6 (1·9)° for fifteen other observed values of this feature. In their full-matrix least-squares refinement YH used one fixed isotropic temperature factor of 3·5 Å^2 which had been determined by the Wilson method. We decided that further refinement of this structure was necessary in order to learn whether the C–C–S bond angle was really abnormally small in this peptide.

YH reported that the crystals are monoclinic, space group $A2$, with two molecules in a unit cell having $a = 12·26$ (1), $b = 4·84$ (1), $c = 17·17$ (1) Å, and $\beta = 124·4$ (3)°. The molecules lie across crystallographic twofold axes.

The list of observed structure factors was obtained from the Library of Congress. It was found to contain 657 observed F_{hkl} instead of 630 as stated by YH. The ratio of number of observations to number of variables in least-squares refinements of the heavy atoms with anisotropic thermal motion is thus 6·1. Our full-matrix least squares began with three cycles with individual isotropic temperature factors, on the 12 heavy atoms. The weighting scheme used was that of Hughes (1941), with $4F_{\min}$ equal to 6·8. YH did not state which weighting scheme they used, presumably it was the same one. The structure factors were those in *International Tables for X-ray Crystallography* (1974). The initial three cycles reduced R to 15·6%. Three cycles with anisotropic temperature parameters were then calculated, reducing R to 11·3%. The 11 H atoms were then introduced at fixed assumed positions, with isotropic temperature factors of 5·0 Å^2, and an additional six cycles calculated. The parameter shifts in the last

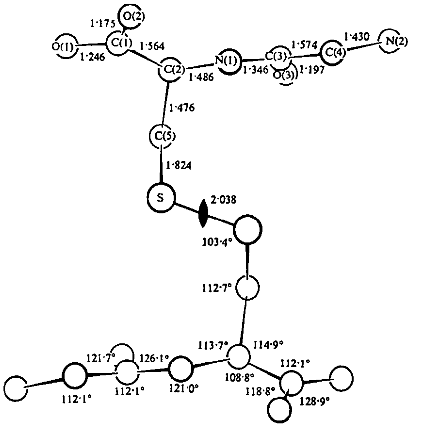

Fig. 1. Bond distances (Å) and angles (°). The view of the molecule is down its twofold axis. Standard errors on the bond distances are in the range 0·01 to 0·02 Å except for S–S, which is 0·003 Å, and on the bond angles 1·0 to 2·0° except for S–S–C, which is 0·4°.

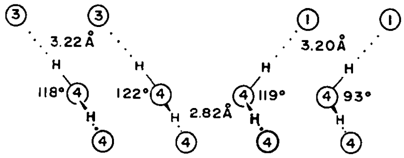

Fig. 2. Four possible orientations of the water molecule.

cycle were all insignificant, and the final R was 10·7%, or about four percentage points smaller than the values reported by YH.

The final positional parameters for the heavy atoms are presented in Table 1. The average differences between these values and those of YH are 0·037, 0·042, and 0·019 Å, for x, y, and z, respectively, with maximum deviations of 0·098, 0·089, and 0·055 Å.*

Discussion. The new molecular dimensions are shown in Fig. 1, which is a view of one molecule down c. Excluding S–S, the average change in a bond length from the YH values is 0·019, maximum, 0·05 Å; the average change in a bond angle is 2·0, maximum, 7·6°, which occurs in the case of C(2)–C(5)–S. The increase in the value of the y coordinate of C(5) from 0·7101 to 0·7285 is almost entirely responsible for this angle, now 112·7°, being close to the value observed in the other disulfides. Inasmuch as YH were the very first to determine the structure of a cystine derivative it is scarcely surprising that they were unable to recognize that the value which they obtained for this bond angle was anomalously small.

Table 1. *Positional parameters and their standard errors*

All values have been multiplied by 10^4.

	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$
S	307 (3)	10000 (–)	−441 (2)
C(1)	3416 (11)	10237 (49)	211 (7)
C(2)	2911 (12)	8361 (41)	687 (8)
C(3)	3076 (11)	8472 (56)	2187 (7)
C(4)	3194 (12)	10484 (44)	2951 (8)
C(5)	1557 (13)	7285 (41)	40 (8)
N(1)	3120 (10)	9833 (39)	1521 (5)
N(2)	3563 (13)	9061 (39)	3797 (7)
O(1)	3299 (11)	9095 (33)	−483 (7)
O(2)	3909 (9)	12368 (31)	562 (6)
O(3)	2970 (15)	6026 (35)	2226 (9)
O(4)	633 (12)	5753 (41)	2553 (9)

Not shown in Fig. 1 is the C–S–S–C torsion angle of 84·4°, close to the average of 82·4 (5·7)° in the other disulfides. It might appear that this new value is greatly different from the value of 101° given by YH, but they actually gave the *dihedral* angle, which is the supplement of the more commonly cited torsion angle. Nevertheless, the value 101° has not infrequently been termed the torsion angle in this molecule by subsequent authors.

The hydrogen bonding by the peptide is essentially the same as described by YH, with the $-NH_3^+$ group entering into three hydrogen bonds in neighboring molecules, the NH···O distances being 2·762, 2·805, and 2·833 Å. A fourth O atom, O(2) of molecule *A* (the designation of YH), is 2·931 Å from N(2), but lies close to an extension of the C(4)–N(2) bond, and thus is not favorably located for participation in a hydrogen bond. The H atom of the amide N atom, N(1), forms, at best, a very weak hydrogen bond, to O(3) in the molecule directly above, with NH···O 3·277 Å. Van der Waals contacts of the methylene H atoms of C(5) with the S atoms of adjacent molecules prevent a closer approach, as pointed out by YH.

The hydrogen bonding by the water molecule, O(4), is somewhat less simple than described by YH, as there are four close O atom candidates, O(3) of molecule *M* at 3·22 Å, O(1) of molecule *A* at 3·20 Å, and two other water molecules related to the reference molecule by the screw axis, and thus $b/2$ above and below it. There are thus four possibilities for the orientation of the H_2O molecule, as shown in Fig. 2, all of which involve one long OH···O bond and one normal OH···O bond. [Of the remaining two possibilities, in O(4)···O(4)···O(4) it is impossible to position two H atoms per water molecule, and O(3)···O(4)···O(1) not only involves two long hydrogen bonds but also has an unfavorably small bond angle of 73°.]

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* The list of temperature factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31682 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.