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Structure of *N*-Acetyl-L-cysteine: X-ray ($T = 295$ K)* and Neutron ($T = 16$ K)† Diffraction Studies

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Abstract

N-Acetyl-L-cysteine, $C_5H_9NO_3S$, $M_r = 163 \cdot 20$, crystallizes in the space group $P1$, with $a = 5 \cdot 766$ (1), $b = 6 \cdot 433$ (1), $c = 5 \cdot 014$ (1) Å, $\alpha = 102 \cdot 80$ (2), $\beta = 102 \cdot 77$ (1), $\gamma = 95 \cdot 81$ (1)°, $Z = 1$ and final $R(F^2) = 0 \cdot 024$ for a total of 1232 independent reflections, at $T = 16$ K. The structure was first deduced from X-ray data obtained at 295 K. A subsequent neutron diffraction study carried out at 16 K has provided a more precise description of the hydrogen bonds than was possible from the X-ray experiment. The thiol group acts as both donor and acceptor, being involved in S–H⋯O and N–H⋯S interactions.

Introduction

The thiol or sulfhydryl group in cysteine residues has attracted a great deal of attention because of its ability to take part in a variety of biochemical reactions (Friedman, 1973; Jocelyn, 1972). The role of the thiol group as a possible hydrogen-bond donor and acceptor has been explored in a number of studies (Gordy &

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Stanford, 1940; Luck, 1965). Adman, Watenpaugh & Jensen (1975) have described a number of N—H···S type hydrogen bonds in proteins containing Fe—S clusters, but find no specific evidence for such interactions in cysteines involved in disulfide bridges or in single cysteines, based on a survey of some ten protein crystal structures. Early X-ray studies of monoclinic cysteine (Harding & Long, 1968) and glutathione (Wright, 1958) did not indicate any hydrogen bonding involving an SH group, but it must be borne in mind that the thiol protons were not located in this work. Evidence for the ability of the thiol group to take part in hydrogen bonding in solution has not been clear-cut (Edsall, 1965). More recently, in an IR spectroscopic investigation of self-association of thioloacetic and thiolobenzoic acids, de Alencastro & Sandorfy (1973) have shown that hydrogen bonds of the type S—H···O are formed in a 1:1 mixture of CCl_3F and $C_2F_4Br_2$ solvents. A neutron diffraction study of the orthorhombic modification of L-cysteine (Kerr, Ashmore & Koetzle, 1975) has indicated possible weak hydrogen bonding involving the disordered thiol group (S—H···O and S—H···S). In N-acetyl-L-cysteine, the thiol group is involved in short contacts with the carbonyl O of the carboxyl group and with the N atom, although the N···S and H···S distances determined in the room temperature X-ray diffraction study* appeared to be a bit longer than the values given by Donohue (1969) for N—H···S hydrogen bonds. We have undertaken a neutron diffraction study at $T = 16$ K, in order to determine accurate H-atom positions and to delineate the hydrogen bonding around S more completely. The present paper reports detailed results of both the neutron and X-ray investigations.

Experimental

Crystals of N-acetyl-L-cysteine were obtained by slow cooling of saturated aqueous solutions. Crystal data are summarized in Table 1. X-ray data were collected at a temperature of 295 ± 3 K on a General Electric XRD-5 manual diffractometer, using Cu $K\alpha$ radiation [$(\sin \theta/\lambda)_{max} = 0.639$ Å^{-1}]. Raw intensity data were corrected for Lorentz, polarization, and absorption (Coppens, 1970) effects, to yield values of F_o^2 for 819 independent reflections, of which 13 had intensities less than twice the background level and were excluded from the subsequent refinements.

A large crystal suitable for neutron diffraction measurements was mounted on an aluminum pin oriented approximately along the [3$\bar{1}$2] direction. The sample was placed in a closed-cycle He refrigerator†

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* A preliminary report of the X-ray work is presented by Kou & Parthasarathy (1976).

† Air Products and Chemicals, Inc. DISPLEX® Model CS-202.

Table 1. Crystal data

D_n ($T = 16$ K)	1.552 Mg m^{-3}		
D_x (room temperature)	1.482 Mg m^{-3}		
D_m (flotation bromoform/benzene)	1.48 Mg m^{-3}		
μ (X-ray)*	3.442 mm^{-1}		
μ (neutron)†	0.2318 mm^{-1}		

Cell constants	16 K‡	295 K§	Δ
a	5.766 (1) Å	5.885 (1) Å	−0.119 Å
b	6.433 (1)	6.523 (1)	−0.090
c	5.014 (1)	5.092 (1)	−0.078
α	102.80 (2)°	103.87 (3)°	−1.07°
β	102.77 (1)	102.02 (2)	+0.75
γ	95.81 (1)	96.47 (2)	−0.66
V	174.65 (6) Å^3	182.87 (7) Å^3	−8.22 Å^3

* Sample crystal volume 0.018 mm^3.
† Calculated with mass absorption coefficients for C, N, O and S atoms taken from International Tables for X-ray Crystallography (1968). For H atoms, 2.39 m^2 kg^{-1} was used for the effective mass absorption coefficient due to incoherent scattering, corresponding to an incoherent cross-section of 40 barn.
‡ Neutrons, $\lambda = 1.0450$ (2) Å.
§ Cu $K\alpha$, X-rays, $\lambda = 1.54051$ Å.

and mounted on an automated four-circle diffractometer (Dimmler, Greenlaw, Kelley, Potter, Rankowitz & Stubblefield, 1976; McMullan, Andrews, Koetzle, Reidinger, Thomas & Williams, 1976) at the Brookhaven High Flux Beam Reactor. Experimental details of the neutron study together with parameters describing the subsequent refinements are given in Table 2. A Be (002) monochromator was used to select a neutron beam of wavelength 1.0450 (2) Å (based on KBr, $a_0 = 6.6000$ Å at $T = 298$ K). The temperature recorded during data collection was 16 ± 0.5 K. Cell dimensions were refined by a least-squares procedure based on the setting angles of 29 high-angle ($2\theta > 95°$) reflections. Intensities were measured for all reciprocal space with $2\theta \leq 110°$, except for limited regions of χ at high 2θ comprising about 200 independent reflections, which were inaccessible due to constraints of the refrigerator assembly. Background scattering from the aluminum pin and refrigerator was inconsequential. A $\theta/2\theta$ step-scan technique was employed, and the scan range varied according to $\Delta 2\theta = (2.23 + 1.59 \tan \theta)°$ for the

Table 2. Neutron experimental and refinement parameters

Crystal weight	17.34 mg
Crystal volume at room temperature	11.64 mm^3
Number of neutron reflections measured	2543
Agreement factor on averaging	0.012
$R_c = \sum \langle \Delta F_o^2 \rangle / \sum \langle F_o^2 \rangle$	
Number of independent reflections (m)	1232
Number of variable parameters (n)	172
Range of $\sin \theta/\lambda$	0.0–0.784 Å^{-1}
$R(F^2) = \sum w|F_o^2 - k^2|F_c|^2| / \sum F_o^2$	0.024*
$wR(F^2) = [\sum w(F_o^2 - k^2|F_c|^2)^2 / \sum wF_o^4]^{1/2}$	0.027*
$S(F^2) = [\sum w(F_o^2 - k^2|F_c|^2)^2 / k^4 (m - n)]^{1/2}$	1.308

* $R(F) = wR(F) = 0.013$.

high-angle data ($2\theta \geq 60°$) and fixed at $\Delta 2\theta = 3\cdot 0°$ for the low-angle data. The step size was adjusted to give approximately 75 steps in each scan. As a general check on experimental stability, the intensities of two reflections were monitored every 100 measurements. These did not vary to any significant degree during the entire period of data collection.

Integrated intensities of reflections were obtained from the scan profile data by a method described by Takusagawa & Koetzle (1978). The intensities were corrected for absorption by a modification of the analytical method of de Meulenaer & Tompa (1965) (Alcock, 1970; Templeton & Templeton, 1973). Squared structure factors were obtained as $F_o^2 = I \sin 2\theta$ and averaged for Friedel-related reflections. The variance of each reflection was estimated as follows: $\sigma^2(F_o^2) = \sigma_{count}^2 + AF_o^8 + BF_o^4 + C$. Constants A, B and C were determined by a least-squares procedure minimizing the quantity $\sum [\langle \Delta F_o^2 \rangle - \sigma(F_o^2)]^2$, where

$$\langle \Delta F_o^2 \rangle = \sum_{i=1}^{n'} |\langle F_o^2 \rangle - F_{oi}^2|/n'$$

and n' is the number of observations for a given reflection hkl and its Friedel equivalent. The resulting values on an absolute scale are $A = 3\cdot 21 \times 10^{-10}$, $B = 2\cdot 08 \times 10^{-4}$ and $C = 6\cdot 23 \times 10^{-3}$ (with F^2 expressed in barn: 1 barn $\equiv 10^{-28}$ m^2).

Refinement

The structure was first deduced from the X-ray data. Chemical and stereochemical criteria were used to select a plausible molecular model, starting from an F_o

synthesis with all positive coefficients (the S atom was positioned at the origin) and removing peaks caused by the false center of inversion. The structure was refined by block-diagonal least-squares techniques, with anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms, to yield an overall agreement factor $R = \sum |k|F_o| - |F_c||/ \sum k|F_o| = 0\cdot 057$ for 806 independent X-ray reflections. The function minimized was $\sum w[|F_o| - (1/k)|F_c|]^2$; the differential synthesis weighting of $w = 1/f_C$ was used, where f_C is the scattering factor of the C atoms.

X-ray coordinates of non-H atoms were used as initial values for the refinement based on the neutron data. After three cycles of full-matrix refinement of positional and thermal parameters, a ΔF synthesis showed all H-atom positions. Positional parameters for all atoms except S, which remained fixed at the origin, and anisotropic thermal parameters were varied together with the coherent neutron scattering lengths of S and N atoms and a type I isotropic extinction correction parameter (Becker & Coppens, 1975). The least-squares procedure minimized $\sum w(F_o^2 - k^2 F_c^2)^2$ and was carried out with a modified version of program *ORFLS* by Busing, Martin & Levy (1962). Weights were chosen as $w = 1/\sigma^2(F_o^2)$. The most significant extinction correction value (on F^2) is $0\cdot 35$ for the reflection $1\bar{1}1$. Final positional and equivalent isotropic thermal parameters for both the X-ray and neutron refinements are listed in Table 3.* Neutron

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* Lists of anisotropic thermal parameters and structure factors and a stereoscopic view of the molecule have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36053 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Fractional atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

| | Neutron values (16 K) | | | | X-ray values (room temperature) | | | |
	x	y	z	B (Å^2)	x	y	z	B (Å^2)
S	0·0000	0·0000	0·0000	0·57 (2)	0·000000	0·000000	0·000000	2·74 (9)
O(1)	0·5255 (2)	−0·3050 (2)	0·0809 (2)	0·64 (1)	0·5127 (8)	−0·3032 (6)	0·079 (1)	3·02 (11)
O(2)	0·2321 (2)	−0·4600 (2)	0·2343 (2)	0·76 (1)	0·224 (1)	−0·4546 (8)	0·225 (2)	4·32 (15)
O(3)	0·5082 (2)	0·3107 (2)	0·7944 (2)	0·63 (1)	0·5034 (9)	0·3122 (7)	0·788 (1)	3·09 (11)
N	0·5400 (2)	0·0844 (2)	0·3979 (2)	0·50 (1)	0·5285 (8)	0·0850 (7)	0·3935 (9)	2·06 (11)
C(1)	0·3669 (2)	−0·3027 (2)	0·2334 (2)	0·47 (1)	0·3575 (9)	−0·2996 (8)	0·226 (1)	2·13 (11)
C(2)	0·3617 (2)	−0·0827 (2)	0·4208 (2)	0·44 (1)	0·3514 (9)	−0·0802 (8)	0·412 (1)	1·99 (11)
C(3)	0·1060 (2)	−0·0283 (2)	0·3556 (2)	0·52 (1)	0·103 (1)	−0·0271 (9)	0·348 (1)	2·34 (12)
C(4)	0·6030 (2)	0·2736 (2)	0·5915 (2)	0·45 (1)	0·594 (1)	0·2747 (8)	0·586 (1)	2·22 (11)
C(5)	0·7962 (2)	0·4335 (2)	0·5597 (2)	0·67 (1)	0·783 (1)	0·430 (1)	0·555 (2)	3·00 (15)
H(1)	0·5216 (3)	−0·4609 (2)	−0·0344 (3)	1·48 (2)	0·43 (2)	−0·41 (2)	−0·08 (3)	6·00 (100)
H(2)	0·4039 (3)	−0·0983 (2)	0·6397 (3)	1·37 (2)	0·39 (2)	−0·09 (2)	0·63 (3)	6·00 (100)
H(3A)	0·0993 (3)	0·1203 (2)	0·5059 (3)	1·67 (2)	0·10 (1)	0·11 (2)	0·50 (2)	3·00 (100)
H(3B)	−0·0184 (3)	−0·1597 (2)	0·3772 (3)	1·68 (2)	−0·03 (1)	−0·12 (1)	0·38 (1)	1·00 (100)
H(S)	0·1386 (4)	0·1888 (3)	0·0352 (4)	2·46 (3)	0·15 (3)	0·14 (3)	0·00 (3)	1·00 (100)
H(N)	0·6143 (3)	0·0584 (2)	0·2311 (3)	1·82 (2)	0·60 (1)	0·06 (1)	0·26 (2)	2·00 (100)
H(5A)	0·7460 (3)	0·5938 (2)	0·6026 (4)	2·27 (3)	0·77 (3)	0·60 (3)	0·66 (3)	7·00 (100)
H(5B)	0·8330 (3)	0·3944 (3)	0·3528 (3)	2·27 (3)	0·78 (3)	0·40 (3)	0·35 (3)	7·00 (100)
H(5C)	0·9606 (3)	0·4395 (3)	0·7200 (4)	2·41 (3)	0·94 (2)	0·40 (2)	0·65 (2)	3·00 (100)

scattering lengths used for C, H and O atoms are $b_C = 6\cdot648$, $b_H = -3\cdot740$ and $b_O = 5\cdot803$ fm (Shull, 1972). The refined scattering lengths for S and N were found to be $2\cdot90$ (3) and $9\cdot29$ (3) fm respectively, which are in good agreement with values of $b_S = 2\cdot847$ (1) and $b_N = 9\cdot36$ (2) fm presented by Koester (1977).

Discussion

The molecular structure of *N*-acetyl-L-cysteine in the crystalline state and the atomic nomenclature used in this paper are illustrated in Fig. 1 (Johnson, 1976). Bond distances and angles from the neutron diffraction study shown in Fig. 2 are consistent with corresponding dimensions determined by neutron diffraction in amino acids (Koetzle & Lehmann, 1976) and peptides (Freeman, Paul & Sabine, 1970; Griffin & Coppens, 1975; Koetzle, Hamilton & Parthasarathy, 1972; Kvick, Al-Karaghouli & Koetzle, 1977). For *N*-acetyl-L-cysteine, the differences in bond distances and angles between the neutron and X-ray studies are given in Fig. 3. The neutron bonding parameters agree quite well with those determined in the X-ray study, except for the C(1)–O(1), C(1)–O(2) and C(4)–C(5) distances and the expected discrepancies in parameters involving H atoms. In the following discussion, reference is made mainly to the more precise neutron parameters. The reported bond distances are not corrected for thermal motion, and the apparent foreshortening of the C(1)–O(1), C(1)–O(2) and C(4)–C(5) bonds in the X-ray study is an effect of the large rigid-body librations of the carboxyl and methyl groups at room temperature.

Torsion angles and the molecular conformation are shown in Fig. 4. The amide group shows small deviations from planarity: displacements of individual atoms from the least-squares plane are listed in Table 4. C(2) is essentially coplanar with the carboxyl group C(1), O(1) and O(2); the bond angles around C(1) accordingly sum to $360\cdot0°$.
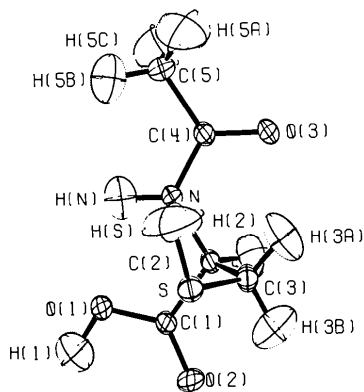

Fig. 1. Molecular view of *N*-acetyl-L-cysteine at 16 K. Thermal ellipsoids are drawn at the 97% probability level. A full stereoscopic drawing has been deposited.
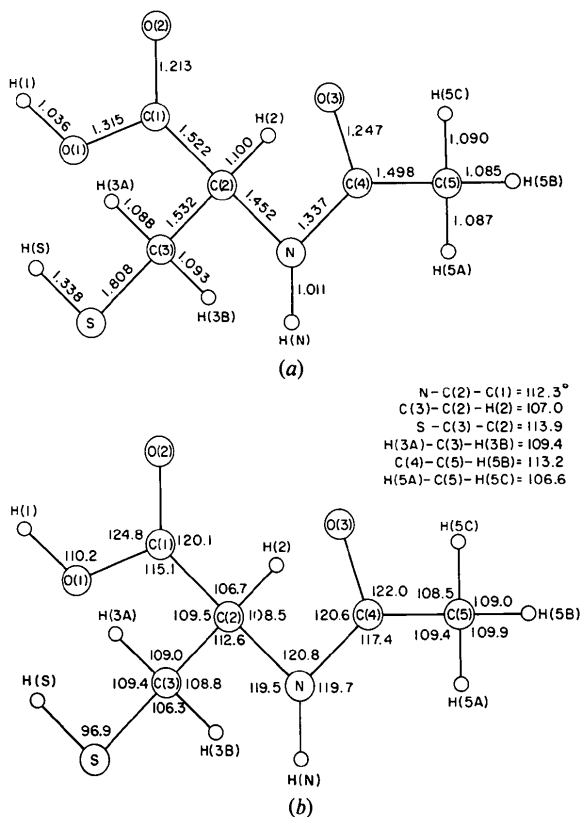

(a)

N–C(2)–C(1) = 112.3°
C(3)–C(2)–H(2) = 107.0
S–C(3)–C(2) = 113.9
H(3A)–C(3)–H(3B) = 109.4
C(4)–C(5)–H(5B)= 113.2
H(5A)–C(5)–H(5C)= 106.6

(b)

Fig. 2. (a) Bond distances (Å) at 16 K (neutron values). E.s.d.'s are $0\cdot002$ Å or less. (b) Bond angles (°) at 16 K (neutron). E.s.d.'s are $0\cdot2°$ or less.
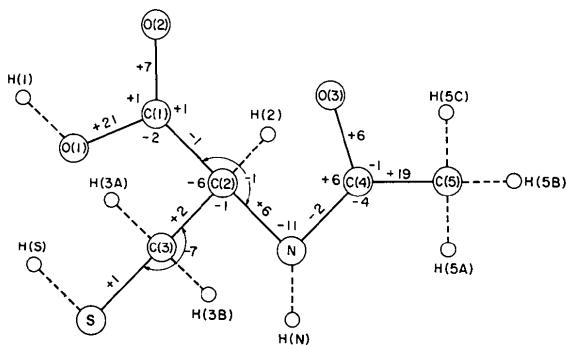

Fig. 3. Differences between the neutron and X-ray results for bond distances $[D = D(N) - D(X)]$ and angles $[A = A(N) - A(X)]$. Units for distances and angles are $0\cdot001$ Å and $0\cdot1°$ respectively. Estimated pooled standard deviations are $0\cdot006$–$0\cdot008$ Å and $0\cdot4$–$0\cdot6°$.

The neutron thermal parameters have been fit to general rigid-body motions described by **T**, **L**, and **S** tensors (Schomaker & Trueblood, 1968). When the H atoms are excluded from the rigid body, the r.m.s. error of fit, $\langle \Delta U_{ij}^2 \rangle^{1/2}$, is $0\cdot0005$ Å^2. On the other hand, when the H atoms are included in the calculation, $\langle \Delta U_{ij}^2 \rangle^{1/2}$ is increased to $0\cdot0061$ Å^2. This fact suggests that the backbone of the molecule can be considered to behave
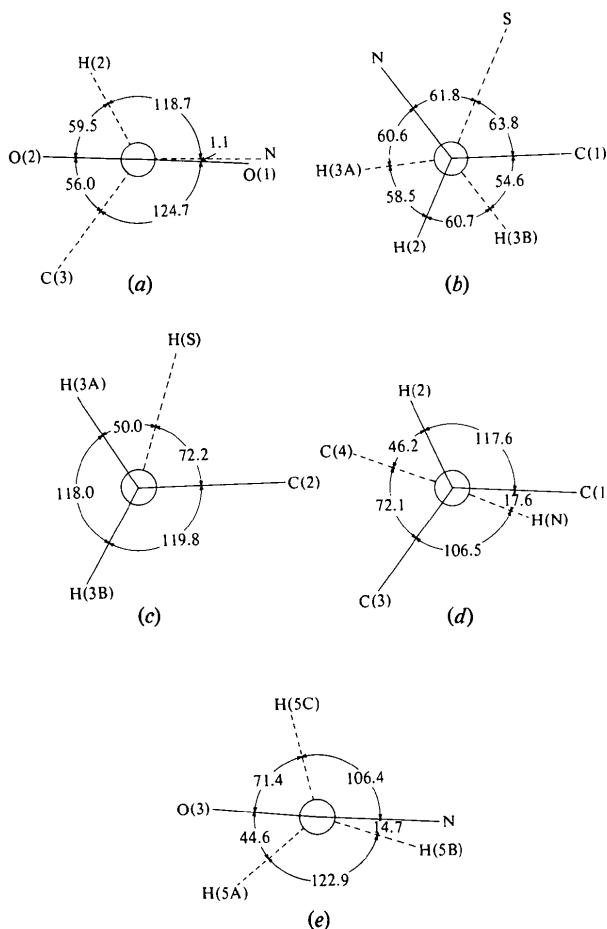
Fig. 4. Torsion angles (°) around bonds: (a) C(1)–C(2), (b) C(2)–C(3), (c) C(3)–S, (d) C(2)–N, (e) C(4)–C(5) (neutron values). E.s.d.'s are 0·2° or less.

Table 4. *Deviations* (Å) *from the least-squares plane through the amide group* [N, H(N), C(4), O(3)] *and* C(2), C(5) (*neutron results*)

The equation of the plane is $3·7865x - 3·8429y + 2·4503z - 2·6934 = 0$.

O(3)	−0·017 (2)	O(1)	0·667 (3)
N	0·002 (1)	O(2)	0·527 (4)
C(2)	0·025 (2)	C(1)	0·431 (3)
C(4)	−0·012 (2)	H(1)	0·969 (4)
C(5)	0·027 (2)	H(2)	0·781 (3)
H(N)	−0·026 (3)	H(5A)	−0·673 (3)
S	−2·693 (3)	H(5B)	−0·190 (3)

as a rigid body, but as might be expected the H atoms are moving somewhat independently from the backbone. When the methyl group C(4)–C(5)–H(5A,5B,5C) is taken as a rigid body, the largest principal axis of **L** corresponds to a r.m.s. libration of $L_1 = 6·8°$ about the C–C bond, and $\langle \Delta U_{ij}^2 \rangle^{1/2}$ is 0·0020 Å². This calculation indicates that the

C(5)–H(5A,5B,5C) distances should be increased by 0·017 Å to allow for effects of thermal motion, while the corresponding corrections calculated for bond distances in the non-H backbone are less than 0·002 Å.

The crystal structure is illustrated in Fig. 5, and Fig. 6 outlines the hydrogen-bonding scheme. The hydrogen atom H(1) of the carboxyl group forms a hydrogen bond to the acetyl oxygen O(3) of a neighboring molecule [H(1)···O(3) 1·513 (2) Å]; this hydrogen bonding is a common specific feature for *N*-acyl amino acids (Chen & Parthasarathy, 1978). These moderately strong hydrogen bonds link molecules head-to-tail to form infinite chains along the [011] direction. These chains are joined by weak S–H(S)···O(2) [2·216 (2) Å] and N–H(N)···S [2·747 (2) Å] hydrogen bonds to form a three-dimensional network. The H(S)···O distance of 2·216 (2) Å observed here is considerably shorter than the analogous contact of 2·40 (2) Å found in orthorhombic L-cysteine (Kerr *et al.*, 1975). In addition to the interaction with S, the amide hydrogen H(N) possesses a shorter intra-
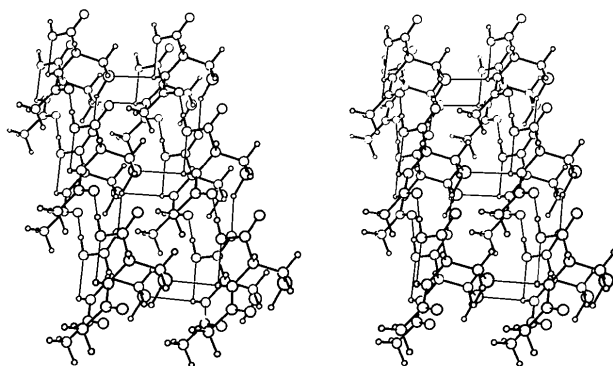

Fig. 5. Stereoscopic illustration of the molecular packing, viewed approximately along [001]. Thin lines denote hydrogen bonds.
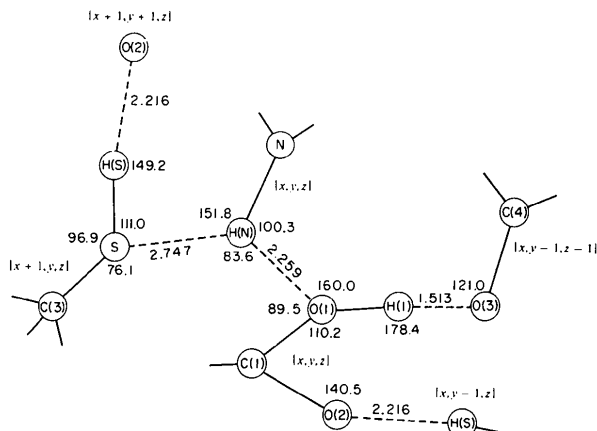

Fig. 6. Outline of the hydrogen-bonding scheme. E.s.d.'s for distances and angles are 0·002 Å and 0·2° respectively (neutron values).

molecular contact with O(1); this may be regarded as a bifurcated interaction (Koetzle *et al.*, 1972). Intramolecular N—H···O contacts similar to that found here are observed in many amino acids, *e.g.* α-glycine (Jönsson & Kvick, 1972).

The H(N)···S distance of 2·747 (2) Å is substantially shorter than 3·0 Å, the sum of normal van der Waals radii (Bondi, 1964),* and is similar to the H···S distances for a bifurcated $O-D\overset{\cdot\cdot}{\underset{\cdot}{\cdot}}\overset{S}{\underset{S}{}}$ interaction in Schlippe's salt where Raman spectroscopic data indicate that all D and H atoms are involved in hydrogen bonding (Mereiter, Preisinger & Guth, 1979). Thus, this contact may be considered to be a weak hydrogen bond. The orientation of the S···H(N) vector with respect to the thiol group ($\theta = 24\cdot2°$, $\varphi = 154\cdot7°$) falls in the normal range for electrophilic contacts, as described by Rosenfield, Parthasarathy & Dunitz (1977).

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* The X-ray value of the H···S distance is 2·92 (8) Å.

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