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The Structures of DL-2,2′-Diamino-4,4′-dithiodibutyric Acid and DL-2-Amino-2′-ammonio-4,4′-dithiodibutyric Acid Monohydrogen Oxalate

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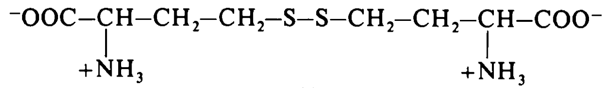
Abstract

The crystal structures of $C_8H_{16}N_2O_4S_2$ (HOMO) [$P2_1$, a = 12·858 (5), b = 7·951 (3), c = 5·944 (2) Å, β = 101·0 (1)°, Z = 2, U = 596·5 (4) Å^3; R = 0·050 for 1052 counter reflections] and of $C_8H_{17}N_2O_4S_2^+.C_2HO_4^-$ (HOMOX) [$P\bar{1}$, a = 12·110 (5), b = 11·686 (5), c = 5·557 (3) Å, α = 99·1 (1), β = 99·6 (1), γ = 98·9 (1)°, Z = 2, U = 752·3 (7) Å^3; R = 0·071 for 2291 counter reflections] have been determined from diffractometer data by Patterson and Fourier methods. The molecules of HOMO are in a nearly extended form and lie parallel to the x axis with a length approximately equal to the a parameter, being joined together by a three-dimensional system of hydrogen bonds roughly parallel to the three crystallographic axes. In addition, there are two C^α–H···O contacts along **b** in which the H···O distances (2·18, 2·33 Å) are significantly shorter than the sum of the van der Waals radii. In HOMOX the molecules run roughly in planes parallel to (1$\bar{1}$0) and packing is determined by a three-dimensional network of hydrogen bonds involving all the protonated amino and carboxyl groups, and by C^α–H···O contacts. The most remarkable conformational differences involve the torsion angles about C^α–C^β and C^β–C^γ. In the two halves of HOMO, C and N are antiperiplanar and +synclinal, and antiperiplanar and −synclinal with respect to C^γ, while in HOMOX they are +synclinal and −synclinal, and +synclinal and antiperiplanar. In both compounds the S atom is +synclinal in one half and antiperiplanar in the other with respect to C^α.

Introduction

The structure determinations of DL-homocystine (I) (DL-2,2′-diamino-4,4′-dithiodibutyric acid) (HOMO) whose proton ionization constants have been determined potentiometrically in aqueous solution (Braibanti, Leporati, Dallavalle & Mori, 1972) and of DL-homocystine monohydrogen oxalate (HOMOX) have been undertaken as part of a research programme on the structural properties of the S-containing amino acids. The aim of this work is to provide information about the conformation of the molecular backbone and hydrogen bonding in such systems.



$$^-OOC-\underset{\underset{+NH_3}{|}}{CH}-CH_2-CH_2-S-S-CH_2-CH_2-\underset{\underset{+NH_3}{|}}{CH}-COO^-$$

(I)

Experimental

Commercial DL-homocystine (Fluka AG Chemische Fabrik) was crystallized by very slow evaporation at 283 K from a saturated aqueous solution. The large, colourless, hexagonal plate-like crystals of HOMO were cut with a razor blade for the diffraction experiments. Needle-like crystals of HOMOX were grown by evaporation of an aqueous solution of DL-homocystine acidified with oxalic acid. The most significant crystal data are given in Table 1 and the *Abstract.*

The unit-cell parameters were determined from rotation and Weissenberg photographs and refined by least squares from diffractometer measurements.

Table 1. *Additional crystallographic data*

	(I) HOMO	(II) HOMOX
M_r	268·345	358·381
Stoichiometry	$C_8H_{16}N_2O_4S_2$	$C_8H_{17}N_2O_4S_2^+.C_2HO_4^-$
Space group*	$P2_1$	$P\bar{1}$
D_m (Mg m^{-3})	1·50	1·57
D_c (Mg m^{-3})	1·49	1·58
F(000)	284	376
μ (mm^{-1})	4·0375	3·5583
Radiation (λ = 1·54178 Å)	Cu $K\alpha$	Cu $K\alpha$
θ range (°)	0–70	0–70
Independent reflections	1090	2849
Observed reflections [$I \geq 2\sigma(I)$]	1052	2291

* From systematic absences and the structural analysis.

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The intensities were measured with an 'on-line' Siemens AED single-crystal diffractometer by using the ω–2θ scan technique with Ni-filtered Cu $K\alpha$ radiation, and corrected for Lorentz and polarization factors, but not for absorption or extinction effects.

Structure determination

Both structures were solved by the heavy-atom method, starting from the S atoms located from sharpened Patterson calculations. The refinements were carried out by block-diagonal least squares, first with isotropic, then with anisotropic thermal parameters. The difference Fourier syntheses at this first stage of refinement revealed all the H atoms, whose positional and isotropic thermal parameters were refined in the last cycles. For both compounds the weighting scheme was determined by plotting ΔF against $|\bar{F}_o|$; in the case of HOMO it was found that the best results were obtained using unit weights giving a final conventional $R(F) = 0{\cdot}050$ (observed reflections only), while for HOMOX the best scheme was $1/w = (A + BF_o)^2$ with $A = 0{\cdot}780$ and $B = 0{\cdot}0412$, giving a final conventional $R(F) = 0{\cdot}071$ (observed reflections only). The atomic scattering factors of Cromer & Mann (1968) were used for non-hydrogen atoms and those of Stewart, Davidson & Simpson (1965) for the H atoms. All the calculations were carried out on the CDC 6600 computer of the Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna), with the pro-

Table 2. *Final atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$) *with e.s.d.'s in parentheses, and equivalent isotropic thermal parameters* (*Hamilton*, 1959)

	IUPAC designation	(I) HOMO				(II) HOMOX			
		x	y	z	B_{eq} (Å^2)	x	y	z	B_{eq} (Å^2)
S(1)	S^{δ}_{l}	4407 (1)	5000 (0)	1415 (4)	3·6	1674 (1)	607 (1)	−2282 (2)	4·1
S(2)	S^{δ}_{k}	5243 (1)	4538 (3)	4626 (3)	3·5	2141 (1)	746 (1)	1446 (2)	3·9
O(1)	O'_{l}	766 (3)	2313 (6)	4149 (7)	2·0	2931 (2)	−3373 (3)	−1908 (5)	3·8
O(2)	O''_{l}	1840 (4)	4274 (7)	6072 (7)	3·2	2269 (3)	−2530 (3)	1322 (5)	3·5
O(3)	O'_{k}	9259 (3)	4921 (6)	873 (7)	1·9	5780 (2)	3992 (3)	6439 (5)	3·1
O(4)	O''_{k}	8263 (4)	2906 (7)	−1066 (7)	3·4	5824 (3)	2074 (3)	5783 (5)	3·6
O(5)						3265 (2)	3764 (3)	7096 (4)	3·1
O(6)						1597 (2)	4037 (3)	5061 (4)	2·6
O(7)						827 (3)	4214 (4)	9315 (5)	5·0
O(8)						2438 (2)	3828 (3)	11222 (4)	2·9
N(1)	N_{l}	1152 (4)	3420 (7)	79 (8)	1·6	1025 (3)	−3641 (3)	−5187 (5)	2·8
N(2)	N_{k}	8887 (4)	3796 (7)	4907 (8)	1·8	4843 (3)	3785 (3)	1542 (5)	2·4
C(1)	C_{l}	1464 (4)	3436 (8)	4310 (9)	1·6	2190 (3)	−2983 (3)	−965 (6)	2·4
C(2)	C^{α}_{l}	1968 (4)	3790 (8)	2191 (9)	1·5	1029 (3)	−3024 (3)	−2595 (6)	2·4
C(3)	C^{β}_{l}	2929 (4)	2639 (9)	2303 (11)	2·2	740 (3)	−1793 (4)	−2564 (7)	3·1
C(4)	C^{γ}_{l}	3672 (5)	3087 (11)	654 (11)	3·0	1610 (4)	−966 (4)	−3465 (8)	3·8
C(5)	C_{k}	8606 (5)	3762 (8)	689 (9)	1·8	5473 (3)	3011 (3)	5228 (6)	2·4
C(6)	C^{α}_{k}	8122 (4)	3304 (9)	2805 (9)	1·6	4562 (3)	2784 (3)	2828 (6)	2·5
C(7)	C^{β}_{k}	7054 (4)	4190 (10)	2676 (11)	2·3	4411 (4)	1609 (4)	1107 (8)	3·4
C(8)	C^{γ}_{k}	6376 (5)	3301 (12)	4210 (11)	3·1	3653 (4)	638 (4)	1890 (9)	4·1
C(9)						2289 (3)	3924 (3)	6973 (6)	2·2
C(10)						1761 (3)	3997 (3)	9324 (6)	2·2
H(1)	H^{α}_{l}	206 (4)	512 (8)	219 (9)		37 (3)	−354 (4)	−212 (8)	
H(2)	$H^{\beta 1}_{l}$	339 (5)	265 (9)	382 (11)		−1 (4)	−184 (4)	−344 (9)	
H(3)	$H^{\beta 2}_{l}$	262 (5)	126 (10)	200 (11)		72 (4)	−154 (4)	−74 (8)	
H(4)	$H^{\gamma 1}_{l}$	435 (6)	221 (12)	68 (14)		249 (4)	−112 (4)	−310 (10)	
H(5)	$H^{\gamma 2}_{l}$	326 (5)	350 (9)	−89 (10)		150 (4)	−103 (4)	−511 (10)	
H(6)	H^{α}_{k}	807 (4)	189 (8)	281 (10)		375 (3)	278 (4)	333 (8)	
H(7)	$H^{\beta 1}_{k}$	719 (5)	542 (10)	307 (11)		403 (4)	171 (4)	−75 (8)	
H(8)	$H^{\beta 2}_{k}$	665 (5)	406 (10)	112 (11)		520 (4)	135 (4)	94 (9)	
H(9)	$H^{\gamma 1}_{k}$	591 (5)	219 (9)	356 (10)		369 (4)	−30 (5)	89 (10)	
H(10)	$H^{\gamma 2}_{k}$	672 (6)	293 (11)	588 (13)		376 (4)	61 (4)	367 (10)	
H(11)	H^{1}_{l}	46 (5)	409 (10)	6 (11)		128 (4)	−437 (4)	−516 (8)	
H(12)	H^{2}_{l}	131 (6)	377 (10)	−129 (12)		20 (4)	−389 (5)	−597 (10)	
H(13)	H^{3}_{l}	101 (4)	225 (8)	10 (10)		163 (4)	−324 (4)	−581 (9)	
H(14)	H^{1}_{k}	948 (5)	335 (11)	496 (13)		489 (4)	452 (4)	245 (8)	
H(15)	H^{2}_{k}	896 (4)	515 (8)	490 (9)		557 (3)	381 (3)	116 (7)	
H(16)	H^{3}_{k}	875 (6)	364 (11)	608 (12)		430 (4)	373 (4)	41 (8)	
H(17)	H''_{k}					660 (5)	226 (5)	677 (11)	
H(18)						206 (4)	387 (4)	1237 (9)	

grams written by Immirzi (1967). Final atomic coordinates are given in Table 2.*

Discussion

While each half of the molecule in the HOMO compound is related by a pseudo twofold symmetry axis for the central $C_i^\gamma-S_i^\delta-S_k^\delta-C_k^\gamma$ fragment and by a pseudo centre of symmetry for the remaining atoms, in the HOMOX compound there is only a pseudo twofold symmetry axis for the $C_i^\gamma-S_i^\delta-S_k^\delta-C_k^\gamma$ fragment as shown in Fig. 1. The distances and angles involving the amino acid residue of the two compounds are listed in Tables 3 and 4, and for the monohydrogen oxalate group in Table 5.

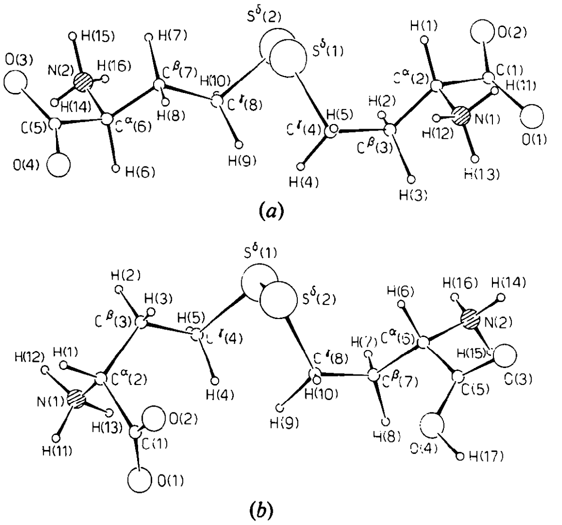

Fig. 1. Projections of molecules of (*a*) HOMO and (*b*) HOMOX.

There is good agreement between the corresponding bond lengths in the two halves of the molecules, the differences not being significant. In contrast, significant differences are observed for some angles, *i.e.* the starred values of Δ/σ in Table 3. In the same table are shown the weighted means calculated for the corresponding four-value sets.

A large spread in the values of $C-C^\alpha-C^\beta$ has also been observed in other amino acid residues (see Table 6). The bond angles at S observed in several S—S amino acids fall in the range 99·5–105·7°, so the value found in HOMO (105·3°) is near the upper limit. The S—S and S—C bond lengths are in the class of disulphide compounds with a C—S—S—C torsion angle near 90°. These distances seem to be roughly linearly correlated, the S—S bond length increasing with the decrease of S—C.

The molecular conformations about the C—C bonds are shown in Fig. 2.

In Table 6 the torsion angles are compared, together with other relevant parameters, with those of other structurally known cystine derivatives, following the nomenclature of the IUPAC–IUB Commission on Biochemical Nomenclature (1970). In HOMOX both $C^\alpha CO'O''$ groups are planar, the maximum deviation being 0·002 Å for C(1) and 0·009 Å for C(5); in

Table 3. *Bond distances* (Å) *and angles* (°) *in the amino acid molecules* (*e.s.d.'s in parentheses*)

	(I) HOMO			(II) HOMOX			
	C(1)C(2) ···S(1)	C(5)C(6) ···S(2)	Δ/σ	C(1)C(2) ···S(1)	C(5)C(6) ···S(2)	Δ/σ	Weighted means
C—O′	1·257 (7)	1·237 (8)	1·9	1·223 (5)	1·203 (5)	2·8	†
C—O″	1·258 (7)	1·253 (7)	0·5	1·279 (4)	1·297 (5)	2·8	†
$C-C^\alpha$	1·548 (8)	1·549 (9)	0·1	1·530 (5)	1·540 (5)	1·4	1·538 (5)
$C^\alpha-N$	1·504 (7)	1·488 (7)	1·6	1·504 (5)	1·489 (5)	2·1	1·496 (5)
$C^\alpha-C^\beta$	1·529 (8)	1·532 (8)	0·3	1·530 (6)	1·511 (6)	2·2	1·524 (6)
$C^\beta-C^\gamma$	1·536 (10)	1·547 (10)	0·8	1·519 (7)	1·512 (7)	0·7	1·524 (8)
$C^\gamma-S$	1·802 (8)	1·813 (8)	1·0	1·837 (5)	1·833 (5)	0·6	1·827 (8)
S—S	2·037 (3)			2·028 (2)			2·031 (4)
O′—C—O″	126·5 (6)	127·1 (6)	0·7	126·7 (7)	125·6 (4)	1·4	126·2 (4)
$O'-C-C^\alpha$	118·1 (5)	118·3 (5)	0·3	119·3 (4)	119·9 (5)	0·9	118·9 (5)
$O''-C-C^\alpha$	115·3 (5)	114·6 (6)	0·9	114·1 (5)	114·4 (5)	0·4	114·6 (4)
$C-C^\alpha-C^\beta$	108·4 (5)	110·3 (5)	2·7	112·0 (4)	116·9 (5)	7·7*	111·9 (1·7)
$C-C^\alpha-N$	108·1 (5)	108·4 (5)	0·4	108·7 (4)	106·3 (4)	4·2*	107·8 (6)
$N-C^\alpha-C^\beta$	110·4 (5)	111·3 (5)	1·3	111·7 (4)	111·5 (4)	0·4	111·3 (3)
$C^\alpha-C^\beta-C^\gamma$	115·4 (6)	111·2 (6)	4·9*	113·0 (6)	112·5 (4)	0·7	112·9 (8)
$C^\beta-C^\gamma-S$	113·3 (5)	113·0 (6)	0·4	114·4 (4)	114·9 (5)	0·8	114·0 (5)
$C^\gamma-S-S$	103·9 (3)	105·3 (2)	3·9*	102·9 (2)	103·5 (3)	1·7	104·0 (6)

* Significant differences (see text).

† The averaged value is not considered as the carboxyl groups are not in the same chemical situation.

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* Lists of structure factors and thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35854 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

HOMO only the C(6)C(5)O(3)O(4) group is planar, the maximum deviation being 0·007 Å for C(5), while the other group, C(2)C(1)O(1)O(2), deviates significantly from planarity and here again the C(carboxyl) atom has the greatest deviation (0·17 Å). While in HOMO the carboxyl groups are nearly perpendicular to the C,C^α,C^β planes in order to have minimum hindrance, in HOMOX one carboxyl group is nearly eclipsed with respect to N and the other shows a tendency to be eclipsed with respect to C^β {τ[O(4)—C(5)—C(6)—C(7)] = −15·2°} (Fig. 2*a*,*a*′,*f*,*f*′). This last conformation was not found in any other known cystine derivative.

Table 4. *Bond distances* (Å) *and angles* (°) *involving hydrogen atoms* (*e.s.d.'s in parentheses*)

	(I) HOMO		(II) HOMOX	
	C(1)C(2) ···S(1)	C(5)C(6) ···S(2)	C(1)C(2) ···S(1)	C(5)C(6) ···S(2)
C^α–H^α	1·06 (6)	1·13 (6)	1·02 (4)	1·07 (4)
C^β–$H^{\beta 1}$	0·98 (6)	1·01 (8)	0·95 (5)	1·09 (4)
C^β–$H^{\beta 2}$	1·17 (8)	0·98 (6)	1·02 (4)	1·06 (5)
C^γ–$H^{\gamma 1}$	1·11 (9)	1·10 (7)	1·10 (5)	1·16 (6)
C^γ–$H^{\gamma 2}$	1·02 (6)	1·05 (7)	0·89 (6)	0·98 (6)
N–H^1	1·04 (7)	0·84 (7)	0·95 (5)	0·91 (4)
N–H^2	0·92 (8)	1·08 (6)	1·00 (4)	0·94 (4)
N–H^3	0·95 (6)	0·76 (8)	0·95 (5)	0·82 (4)
O″–H″				0·98 (6)
C–C^α–H^α	104 (3)	106 (3)	114 (3)	108 (2)
N–C^α–H^α	105 (3)	107 (3)	102 (3)	110 (2)
C^β–C^α–H^α	120 (3)	114 (3)	108 (2)	104 (2)
C^α–C^β–$H^{\beta 1}$	112 (4)	109 (4)	111 (3)	108 (3)
C^α–C^β–$H^{\beta 2}$	108 (3)	108 (4)	101 (3)	112 (3)
C^γ–C^β–$H^{\beta 1}$	104 (4)	113 (4)	112 (3)	109 (3)
C^γ–C^β–$H^{\beta 2}$	111 (3)	105 (4)	113 (3)	109 (3)
$H^{\beta 1}$–C^β–$H^{\beta 2}$	106 (6)	111 (6)	106 (4)	106 (4)
C^β–C^γ–$H^{\gamma 1}$	115 (5)	119 (3)	116 (3)	114 (3)
C^β–C^γ–$H^{\gamma 2}$	112 (4)	120 (4)	115 (3)	118 (3)
S–C^γ–$H^{\gamma 1}$	99 (4)	95 (3)	107 (3)	106 (3)
S–C^γ–$H^{\gamma 2}$	96 (4)	103 (4)	105 (3)	97 (3)
$H^{\gamma 1}$–C^γ–$H^{\gamma 2}$	119 (5)	102 (6)	100 (4)	106 (4)
C^α–N–H^1	112 (4)	112 (5)	111 (3)	116 (3)
C^α–N–H^2	116 (5)	108 (3)	104 (3)	110 (2)
C^α–N–H^3	107 (4)	120 (6)	110 (3)	106 (3)
H^1–N–H^2	100 (6)	110 (6)	103 (4)	103 (4)
H^1–N–H^3	110 (5)	105 (8)	99 (4)	103 (5)
H^2–N–H^3	113 (6)	102 (7)	129 (4)	119 (4)
C–O″–H″				112 (4)

Table 5. *Bond distances* (Å) *and angles* (°) *in the monohydrogen oxalate group* (*e.s.d.'s in parentheses*)

C(9)–C(10)	1·544 (5)	C(10)–O(7)	1·196 (6)
C(9)–O(5)	1·217 (5)	C(10)–O(8)	1·285 (4)
C(9)–O(6)	1·277 (4)	O(8)–H(18)	0·84 (5)
O(5)–C(9)–O(6)	127·7 (5)	O(7)–C(10)–O(8)	125·5 (5)
O(5)–C(9)–C(10)	119·6 (4)	O(7)–C(10)–C(9)	121·8 (5)
O(6)–C(9)–C(10)	112·7 (5)	O(8)–C(10)–C(9)	112·7 (5)
		C(10)–O(8)–H(18)	105 (3)

The α-NH_3^+ groups are staggered with respect to the substituents at C^α, as shown in Fig. 2(*b*),(*b*′),(*g*),(*g*′). In HOMO the conformation about the C^α—C^β bonds shows that: (i) the C^γ atoms are antiperiplanar to the carboxyl C atoms taking the most favourable position (Fig. 2*c*,*c*′); (ii) the two conformations are twisted by 15 and 20° relative to the perfectly staggered one, so as to have minimum interaction with the N atoms.

Different conformations are found in HOMOX: the torsion about the C(2)—C(3) bond shows a +synclinal and −synclinal conformation which should be the most unlikely one, but it is common in several compounds with a S atom in the γ position (column χ_1, Table 6). A third type of conformation has been found in the other half of the HOMOX molecule with the C^γ atom [C(8)] antiperiplanar to the N atom. This conformation has not been found in the other compounds of Table 6 (Fig. 2*h*,*h*′).

Only two types of conformation around the C^β—C^γ bonds have been found in HOMO and HOMOX. The torsions about the C^β—C^γ bonds show two different situations for S in the two halves of each molecule. In one half the S atom is antiperiplanar to C^α so as to have a maximum S···C distance, and hence a minimum interaction, and in the other the S atom is +synclinal to C^α (Fig. 2*d*,*d*′,*i*,*i*′). In both halves of the two compounds a quite perfect staggered (+synclinal) conformation about C^γ—S^δ is observed (Fig. 2*e*,*e*′,*j*,*j*′). In the other compounds this conformation is significantly twisted, the torsion angle lying in the range 66·9–95·2°. HOMO and HOMOX have a right-handed disulphide chirality (Fig. 1).

The conformations of the ends of the two molecules are determined by the intermolecular interactions involving the carboxyl O atoms and the protonated amino groups (Table 7). The dihedral angle between the planes of the glycine-like groups of HOMO is 3·3 (3), and 57·9 (4)° for HOMOX.

In HOMO the molecules are in an extended form and lie parallel to the *x* axis with a length approximately equal to the *a* parameter, in order to have the polar groups facing (Fig. 3). Packing is determined by N—H···O hydrogen bonds roughly parallel to the three crystallographic axes and there are two C^α—H···O interactions, with H···O distances less than the sum of the van der Waals radii, providing additional links between the molecules (Table 7).

The conformation and the hydrogen-bonding arrangement of the COO^- and NH_3^+ groups in the two halves of the HOMO molecule are practically mirror related (Fig. 2*b*,*b*′).

The S atoms lie roughly in planes parallel to (100) with all distances greater than 4·0 Å while in HOMOX they lie roughly in planes parallel to (010) with the S···S contacts [3·647 (3) Å] very near to the sum of the van der Waals radii.

In HOMOX the amino acid molecules run roughly in

Table 6. *Comparison of relevant bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *in methionine and cystine derivatives*

	ψ_1 $\tau[\mathrm{N–C^{\alpha}–C–O'}]$	ψ_2 $\tau[\mathrm{N–C^{\alpha}–C–O''}]$	χ_1 $\tau[\mathrm{N–C^{\alpha}–C^{\beta}–C^{\gamma}}]$	χ_2 $\tau[\mathrm{C^{\alpha}–C^{\beta}–C^{\gamma}–S^{\delta}}]$	χ_{3-j}* $\tau[\mathrm{C^{\beta}–C^{\gamma}–S^{\delta}–S^{\delta}}]$	χ_{4-j}* $\tau[\mathrm{C^{\gamma}–S^{\delta}–S^{\delta}–C^{\gamma}}]$	S–S	S–C	S–S–C	*R* (%)	References
HOMO D moiety	30·5 (7)	−152·5 (5)	75·1 (7)	70·0 (7)	59·4 (5)	80·2 (4)	2·037 (3)	1·802 (8)	103·9 (3)	5·0	(*a*)
L moiety	−26·3 (8)	155·0 (5)	−80·1 (7)	167·2 (5)	57·2 (6)			1·813 (8)	105·3 (2)		
HOMOX D moiety	3·2 (8)	−176·5 (5)	−63·1 (7)	−155·3 (5)	61·6 (6)	73·9 (4)	2·028 (2)	1·837 (5)	102·9 (2)	7·1	(*a*)
L moiety	41·2 (8)	−140·4 (6)	−154·8 (5)	70·7 (7)	62·2 (6)			1·833 (5)	103·5 (3)		
					$\tau[\mathrm{C^{\beta}–C^{\gamma}–S^{\delta}–C^{\varepsilon}}]$						
α-DL-Methionine	−33·7	149·6	−60·1	177·0	80·5			1·79 1·77		21·0	(*b*)
β-DL-Methionine	−29·4	148·4	−61·0	−176·4	−169·6			1·80 1·78		23·0	(*b*)
L-Methionine	−17·4 (1·4) −34·3 (1·4)	163·7 (1·0) 150·8 (1·1)	−166·1 (1·0) −165·6 (1·5)	174·2 (9) 73·6 (2·0)	179·7 (1·2) 73·6 (2·0)			1·829 (16) 1·803 (27) 1·789 (26) 1·715 (31)		8·9	(*c*)
			$\tau[\mathrm{N–C^{\alpha}–C^{\beta}–S^{\gamma}}]$		$\tau[\mathrm{C^{\alpha}–C^{\beta}–S^{\gamma}–S^{\gamma}}]$	$\tau[\mathrm{C^{\beta}–S^{\gamma}–S^{\gamma}–C^{\beta}}]$					
Tetragonal L-cystine	−7·5 (1·5) 8·0 (1·6)	174·6 (1·1) −175·7 (1·1)	64·3 (1·2) 51·2 (1·3)		75·1 (9) 66·9 (1·0)	69·3 (6)	2·042 (7)	1·830 (13) 1·800 (13)	105·7 (4) 104·2 (5)	9·7	(*d*)
Hexagonal L-cystine†	−16·2 (2·1)	166·8 (1·5)	57·3 (1·8)		80·6 (1·4)	75·7 (9)	2·040 (9)	1·786 (17)	104·2 (7)	11·7	(*e*)
N,N′-Diglycyl-L-cystine dihydrate	2·8 (2·2)	178·4 (1·4)	60·1 (1·7)		−95·2 (1·2)	−84·4 (9)	2·037 (7)	1·824 (18)	103·4 (5)	10·7	(*f*)
L-Cystine dihydrochloride	9·5 (2)	−171·2 (1)	69·2 (2)		−88·8 (2)	−81·7 (2)	2·038 (4)	1·816 (3)	103·7 (2)	3·4	(*g*)
L-Cystine dihydrochloride	9·4 (4)	−171·4 (3)	69·4 (3)		−89·2 (4)	−81·7 (4)	2·040 (9)	1·810 (7)	104·0 (4)	5·5	(*h*)
							2·038 (4)‡	1·815 (4)‡	103·8 (2)‡		
Cu$^{\mathrm{II}}$ doped L-cystine dihydrochloride dihydrate	144·9 (4) −4·6 (6)	−38·6 (5) 173·2 (3)	−55·8 (4) −85·1 (4)		−80·6 (3) −70·8 (3)	−79·9 (2)	2·040 (2)	1·832 (5) 1·818 (4)	103·3 (1) 99·5 (2)	5·1	(*i*)
L-Cystine dihydrobromide dihydrate	144·4 (1·1) −0·3 (1·5)	−41·0 (1·3) 173·3 (9)	−54·9 (1·1) −85·3 (1·0)		−82·4 (9) −70·0 (8)	−79·8 (6)	2·044 (5)	1·804 (13) 1·820 (11)	102·3 (4) 100·1 (4)	5·0	(*j*)
3,3,3′,3′-Tetramethyl-D-cystine dihydrochloride	25·2 (8) −2·9 (8)	−153·7 (6) 178·6 (5)	55·8 (5) 42·0 (6)		69·6 (4) 67·1 (4)	114·7 (3)	2·049 (3)	1·866 (7) 1·865 (6)	105·4 (2) 105·4 (2)	4·3	(*k*)
L-Cystine dimethyl ester dihydrochloride monohydrate	−3·4 (2·0) −39·3 (1·9)	178·6 (1·1) 144·2 (1·3)	−75·9 (1·4) −51·7 (1·4)		−79·2 (1·1) −77·4 (1·0)	−84·4 (7)	2·045 (4)	1·805 (15) 1·808 (12)	100·0 (5) 103·1 (5)	10·3	(*l*)
L-Cystinediamide dihydrochloride	−8·2 (2·5)	165·9 (1·6)	65·0 (2·0)		−94·6 (1·6)	−81·4 (1·0)	2·051 (9)	1·757 (23)	102·9 (7)	12·4	(*m*)
Average							2·038 (2)	1·826 (5)	103·5 (4)		

All the data referred to the structures obtained from the literature have been recalculated from the atomic coordinates and standard deviations quoted in the papers.

References: (*a*) present work, (*b*) Mathieson (1952), (*c*) Torii & Iitaka (1973), (*d*) Chaney & Steinrauf (1974), (*e*) Oughton & Harrison (1959), (*f*) Stallings & Donohue (1976), (*g*) Jones, Bernal, Frey & Koetzle (1974), (*h*) Gupta, Sequeira & Chidambaram (1974), (*i*) Kominami, Riesz, Akiyama & Silverton (1976), (*j*) Rosenfield & Parthasarathy (1975*b*), (*k*) Rosenfield & Parthasarathy (1975*a*), (*l*) Vijayalakshmi & Srinivasan (1975), (*m*) Chaney & Steinrauf (1968).

* $j = 0$ for the first five compounds; $j = 1$ for the others.

† This structure has been completely refined by least squares using the F_o's published in the paper. In the original paper the authors did not choose the conventional origin.

‡ Weighted mean between the values of the two independent structures of L-cystine dihydrochloride.

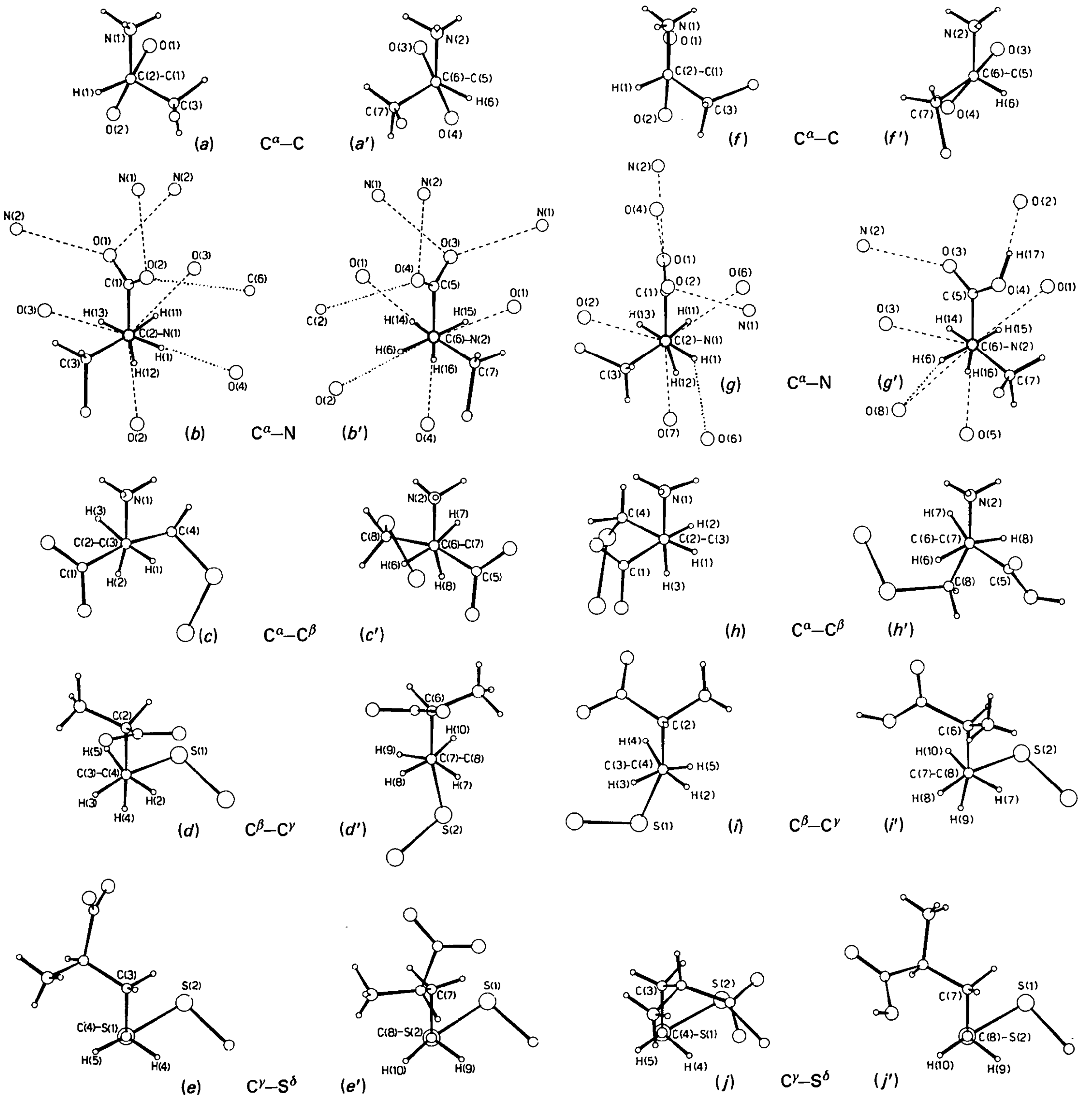

Fig. 2. Conformations about the most significant bonds in HOMO and HOMOX. Dotted lines refer to C$^{\alpha}$–H···O contacts while broken lines refer to the N–H···O and O–H···O hydrogen bonds.

planes parallel to (1$\bar{1}$0) in such a way that the polar residues and the oxalic groups face parallel to the (010) plane, so determining a layer of N–H···O and O–H···O hydrogen bonds (Fig. 4). In addition, the $C_2HO_4^-$ anions, in which bond lengths and angles are normal (Table 5), are hydrogen bonded together in chains running parallel to the *z* axis with O(8)···O(6) = 2·507 (4) Å hydrogen bonds *trans* to each other. These chains are interlinked by N–H···O hydrogen bonds as shown in Fig. 5.

In HOMOX one of the protons, H(16), of N(2) appears to be shared by two acceptor atoms, O(5$^{\rm i}$) and O(8$^{\rm i}$), but the angular values are in favour of hydrogen bonding with O(5$^{\rm i}$). Generally, the H–*D*···*A* angles are greater in HOMOX and the same can be said for the *D*···*A* distances (Table 7). Additional linkage is provided by C$^{\alpha}$–H···O contacts, in which the C$^{\alpha}$···O distances are shorter and the H–C$^{\alpha}$···O angles and the H···O distances are greater in HOMOX (Table 7).

Extensive use of the Cambridge Crystallographic Data Files has been made.

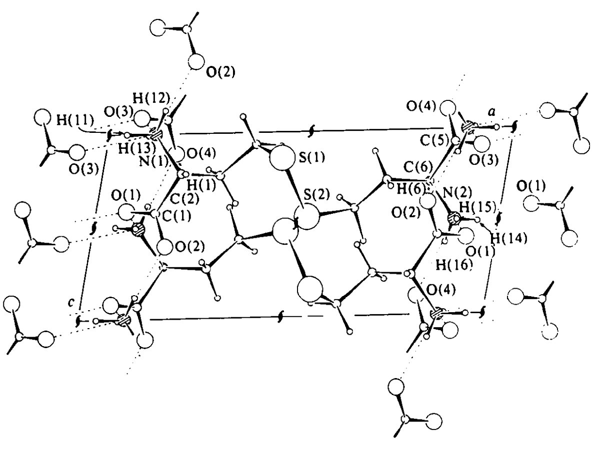

Fig. 3. Projection of the HOMO structure along [010].

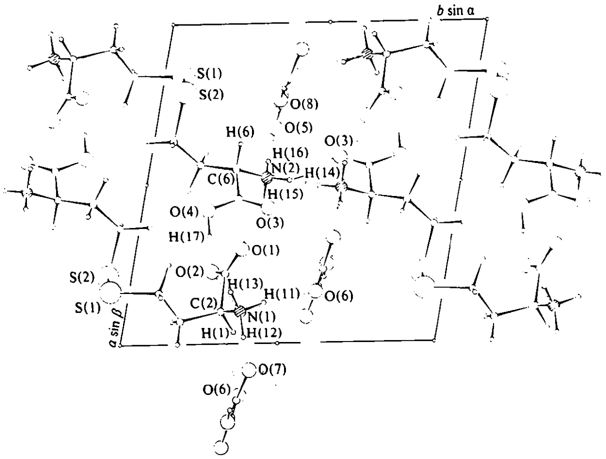

Fig. 4. Projection of the HOMOX structure along [001].

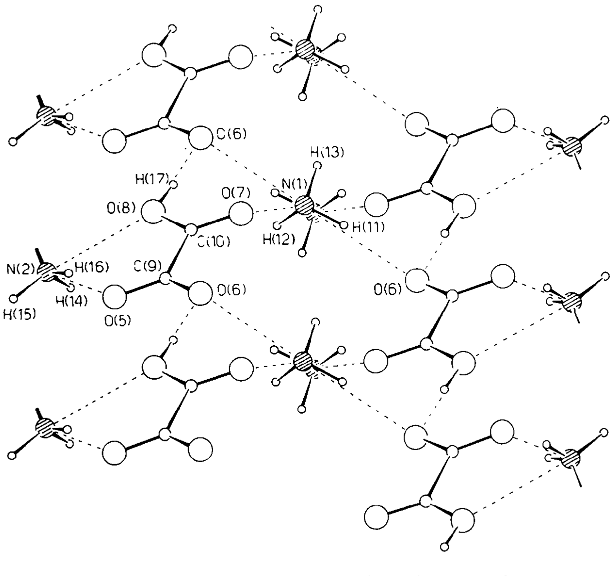

Fig. 5. N–H···O interactions involving ribbons of hydrogen-bonded monohydrogen oxalate anions.

Table 7. *Possible hydrogen-bond distances* (Å) *and angles* (°) *and* C^α–H···O *contacts*

D–H···*A*	*D*···*A*	H···*A*	∠H–*D*···*A*	∠*D*–H···*A*
(1) HOMO				
Hydrogen bonds				
N(1)–H(11)···O(3^{iii})	2·830 (7)	1·83 (7)	12 (4)	162 (6)
N(1)–H(12)···O(2^{i})	2·779 (7)	1·87 (8)	6 (5)	170 (7)
N(1)–H(13)···O(3^{v})	2·868 (7)	1·95 (6)	12 (4)	162 (5)
N(2)–H(14)···O(1^{iv})	2·801 (7)	1·99 (7)	11 (5)	164 (7)
N(2)–H(15)···O(1^{vi})	2·870 (7)	1·82 (6)	11 (3)	162 (4)
N(2)–H(16)···O(4^{ii})	2·758 (7)	2·00 (8)	7 (6)	171 (9)
C^α–H···O contacts				
C(2)–H(1)···O(4^{vii})	3·342 (9)	2·33 (6)	15 (3)	159 (4)
C(6)–H(6)···O(2^{viii})	3·272 (9)	2·18 (6)	12 (3)	162 (4)

Key to symmetry operations

(i)	$x, y, -1+z$	(v)	$1-x, -\frac{1}{2}+y, \bar{z}$
(ii)	$x, y, 1+z$	(vi)	$1-x, \frac{1}{2}+y, 1-z$
(iii)	$-1+x, y, z$	(vii)	$1-x, \frac{1}{2}+y, \bar{z}$
(iv)	$1+x, y, z$	(viii)	$1-x, -\frac{1}{2}+y, 1-z$

D–H···*A*	*D*···*A*	H···*A*	∠H–*D*···*A*	∠*D*–H···*A*
(2) HOMOX				
Hydrogen bonds				
N(1)–H(11)···O(6^{iii})	2·921 (5)	1·98 (5)	6 (3)	171 (4)
N(1)–H(12)···O(7^{iv})	2·842 (5)	2·00 (5)	27 (3)	140 (4)
N(1)–H(13)···O(2^{i})	2·981 (6)	2·11 (5)	20 (3)	151 (4)
N(2)–H(14)···O(3^{vii})	2·923 (5)	2·08 (5)	19 (3)	153 (4)
N(2)–H(15)···O(1^{v})	2·791 (5)	1·96 (4)	22 (2)	147 (3)
N(2)–H(16)···O(5^{i})	2·855 (5)	2·06 (4)	11 (3)	165 (5)
N(2)–H(16)···O(8^{i})	2·897 (5)	2·39 (5)	45 (3)	121 (4)
O(4)–H(17)···O(2^{vi})	2·513 (5)	1·54 (5)	6 (3)	171 (6)
O(8)–H(18)···O(6^{ii})	2·507 (4)	1·68 (5)	8 (3)	167 (5)
C^α–H···O contacts				
C(2)–H(1)···O(6^{iv})	3·203 (5)	2·58 (3)	45 (2)	119 (3)
C(6)–H(6)···O(8^{i})	3·074 (5)	2·41 (4)	43 (2)	119 (3)

Key to symmetry operations

(i)	$x, y, -1+z$	(v)	$1-x, \bar{y}, \bar{z}$
(ii)	$x, y, 1+z$	(vi)	$1-x, \bar{y}, 1-z$
(iii)	$x, -1+y, -1+z$	(vii)	$1-x, 1-y, 1-z$
(iv)	$\bar{x},\bar{y},\bar{z}$		

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The Structure of 1,6-Anhydro-β-D-allopyranose: Allosan

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Abstract

The crystal structure of allosan, 1,6-anhydro-β-D-allopyranose, $C_6H_{10}O_5$, is monoclinic, space group $P2_1$ with $a = 10 \cdot 974$ (2), $b = 6 \cdot 850$ (2), $c = 14 \cdot 213$ (2) Å and $\beta = 109 \cdot 30$ (2)° ($Z = 6$, $V = 1008 \cdot 4$ Å^3 and $D_{\rm calc} = 1 \cdot 60$ Mg m^{-3}). The structural parameters, describing the three crystallographically independent allosan molecules, were refined with the 1744 most significant reflections, $d \geq 0 \cdot 71$ Å, to a conventional linear R value of 0·029. The three molecules have different types of intra- and intermolecular hydrogen-bonding schemes, which are obviously of relevance for the deviations observed between the three molecular conformations. Assuming a similar coexistence of different conformers also in solution offers a plausible structural explanation for the anomalous NMR T_1 values observed for allosan. The conformations of the pyranose and anhydro rings of all three allosan molecules are partially flattened $^3C_0$ chair and E_0 envelope, respectively. Two of the hydroxyl groups are axial relative to the pyranose ring at C(2) and C(4), and the third is equatorial at C(3).

Introduction

Allosan, 1,6-anhydro-β-D-allopyranose, shows NMR parameters which differ significantly from those observed for other 1,6-anhydro sugars (Bock, Hall & Pedersen, 1981) assuming a rigid chair conformation. In the 1,6-anhydro sugars whose structures have been determined so far (for references see *e.g.* Noordik & Jeffrey, 1977), the conformations of the pyranose rings have always been flattened chairs ($^3C_0$). In view of the pattern of the three hydroxyl substituents in allosan, such a conformation would yield several short intramolecular contacts between the hydroxyl groups, indicating different possibilities for intramolecular hydrogen bonds. The present investigation was undertaken in order to elucidate whether the anomalous NMR relaxation data of allosan can be ascribed to structural effects.

Experimental

A single crystal of dimensions 0·08 × 0·12 × 0·50 mm was selected from a crystalline specimen obtained by slow evaporation of an aqueous solution. Investigations of the single crystal by X-ray photographic and diffractometer techniques suggested $P2_1$ as the most probable noncentrosymmetric space group. Preliminary unit-cell parameters, $a = 10 \cdot 974$ (2), $b = 6 \cdot 850$ (2), $c = 14 \cdot 213$ (2) Å and $\beta = 109 \cdot 30$ (2)°, were determined from observed θ values of 17 high-order reflections. The preliminary unit-cell volume of 1008·4 Å^3 indicates that the number (Z) of allosan molecules per unit cell is six, since a volume of 167·3 Å^3 per molecule was observed in the structure of the closely related substance levoglucosan (Park, Kim & Jeffrey, 1971).

The intensities of all the 3158 unique reflections with $\theta \leq 30°$ were collected on a computer-controlled diffractometer (CAD-4), using graphite-monochromatized Mo $K\alpha$ radiation and a scintillation detector with a pulse-height discriminator set to accept 95% of the incident radiation. The intensities, collected with the ω–2θ scan techniques, using a scan interval of 0·7° +

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