

The Crystal and Molecular Structure of *meso*-3,3'-Dithiobisvaline Dihydrate

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(Received 19 October 1973; accepted 18 December 1973)

The crystal and molecular structure of *meso*-3,3'-dithiobisvaline dihydrate (alternatively named *meso*-3,3,3',3'-tetramethylcystine dihydrate or *meso*-penicillamine disulfide dihydrate) has been determined by X-ray diffraction methods using the 1161 unique and significant reflections for which $2\theta < 45^\circ$, and refined to an *R* index of 0.062. Counter methods with monochromatized Mo $K\alpha$ radiation were employed. Crystals form in the monoclinic space group $P2_1/c$ with cell dimensions $a = 12.586$ (6), $b = 9.949$ (10), $c = 12.432$ (7) Å, and $\beta = 92.29$ (5)°. All hydrogen atoms were found in a difference Fourier function, and their positional parameters were refined. Estimated standard deviations in non-hydrogen bond lengths range from 0.003 to 0.014 Å and, in angles, from 0.3 to 1.0°. The molecule is found to exist as a di-zwitterion, which is twisted such that the carboxylate groups approach each other. The backbone conformation differs from the helical sense found in other cystine compounds. The sulfur-sulfur bond length is 2.032 (3) Å, and the CSSC torsion angle is 119.4 (4)°. The packing is dominated by hydrogen bonds, in which both nitrogen atoms and all six oxygen atoms participate.

Introduction

Oxidative coupling of DL-3-mercaptovaline (Crooks, 1949) produces two diastereomers, *meso*- and *rac*-3,3'-dithiobisvaline, alternatively named penicillamine disulfide. This tetramethyl derivative of cystine, like cystine, forms complexes with transition metal ions (Warner & Seff, 1973; Suguiwa & Tanaka, 1970; Hawkins & Perrin, 1962). Structural information concerning these and other organic disulfides, and their transition metal complexes, is of possible biological interest because of the 'non-innocent' behavior which might be expected of organic disulfide ligands in the functioning of metalloenzymes (Hemmerich & Spence, 1966; Hemmerich, 1966). Comparisons of X-ray crystallographic data for organic disulfides and their corresponding transition metal complexes have led to some interesting correlations involving the stability of the complexes, the stereochemical features of the disulfide moiety, the nature of additional coordinating groups, and the size and stereochemical features of the accompanying chelate rings (Riley & Seff, 1972; Ottersen, Warner & Seff, 1973*a,b*, 1974*a*; Warner, Ottersen & Seff, 1974).

The structures of cystine and several of its derivatives have been determined crystallographically (Yakel & Hughes, 1954; Oughton & Harrison, 1959; Peterson, Steinrauf & Jensen, 1960; Steinrauf, Peterson & Jensen, 1958; Chaney & Steinrauf, 1968). Except for a brief report concerning D-penicillamine disulfide dihydrochloride (Rosenfield & Parthasarathy, 1971), nothing has been published concerning the crystal structures of cystines or any other disulfides with tertiary substitution at the carbons adjacent to the sulfur atoms. Such tertiary

substitution may have some interesting and important influences on the stereochemical features of the disulfide and its corresponding complexes, particularly with respect to the S-S bond and the CSSC torsion angle. Alkyl substitution at the carbon adjacent to the disulfide moiety is known to cause a significant hypochromic shift of the ultraviolet spectrum of this chromophore (Rosenthal & Oster, 1961), but it is not clear whether these shifts arise from steric repulsions of substituents leading to distortion of the S-S bond orbitals (Boyd, 1972).

The present work was carried out to evaluate the stereochemical features associated with tertiary substitution at the carbon adjacent to the disulfide moiety in organic disulfides. Additionally, this work will allow the identification of the diastereomers of non-optically active penicillamine disulfide, and may prove useful in the study of transition metal complexes of this ligand.

Experimental

The starting material, DL-penicillamine, alternatively named DL-mercaptovaline or 3,3-dimethylcysteine, was obtained from Sigma Chemical Company. Penicillamine disulfide dihydrate (3,3'-dithiobisvaline dihydrate; 3,3,3',3'-tetramethylcystine dihydrate) was prepared by aeration of a basic aqueous solution of DL-penicillamine in the presence of ferric chloride (Crooks, 1949). The first crude fraction was recrystallized by dissolving in a minimum amount of 1*N* lithium hydroxide and neutralizing with 1*N* hydrochloric acid. The resulting solution was kept at 8°C for 5 days. The clusters of colorless, plate-like crystals were isolated, washed with acetone and dried under vacuum at room temperature for 8 h; m.p. 206–207°C. Due to twinning, some difficulty was encountered in finding a crystal suitable for crystallographic analysis.

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Standard deviations were assigned to individual reflections according to the formula,

$$\sigma(I) = [\omega^2(CT + B_1 + B_2) + (pI)^2]^{1/2}$$

where ω is the scan rate, CT is the total integrated count, B_1 and B_2 are the background counts, and the intensity is $I = \omega(CT - B_1 - B_2)$. A value of 0.02 was assigned to the empirical parameter p to account for instrument instability. The weights, w , used in the least-squares calculations were the reciprocal squares of $\sigma(F_o)$. Of the 2051 symmetry independent reflections measured, those for which $2\theta < 45^\circ$, 1161 had intensities greater than three times their standard deviations, $\sigma(I_o)$. All remaining reflections were excluded from further calculations. The intensities were corrected for Lorentz and polarization effects (Ottersen, 1973); the contribution of the monochromator crystal was calculated assuming it was half perfect and half mosaic in character. An absorption correction was not made ($\mu = 3.45 \text{ cm}^{-1}$); the transmission coefficients are estimated to show a total range of less than 0.04.

The atomic scattering factors of Doyle & Turner (1968) were used for C^o , N^o , O^o , and S^o . The latter was modified to account for the real part of the anomalous dispersion correction (*International Tables for X-ray Crystallography*, 1968). The atomic scattering factor used for hydrogen was that of Stewart, Davidson & Simpson (1965).

Crystal data

meso-3,3'-Dithiobisvaline dihydrate or *meso*-3,3,3',3'-tetramethylcystine dihydrate, $C_{10}H_{24}N_2O_6S_2$, monoclinic, $P2_1/c$, $a = 12.586$ (6), $b = 9.949$ (10), $c = 12.432$ (7) Å, and $\beta = 92.29$ (5)°. Figures in parentheses are estimated standard deviations in the units of

the least significant digit given for the corresponding parameter. $V = 1556 \text{ Å}^3$; $M = 332.4$; D_{obs} (floatation) = 1.41 g cm^{-3} ; $D_{\text{calc}} = 1.419 \text{ g cm}^{-3}$; $Z = 4$; $F(000) = 712$.

Structure determination

The positions of the two sulfur atoms were indicated on a three-dimensional Patterson function. Positions for all other non-hydrogen atoms were found by successive Fourier refinements, using the fast-Fourier program *ALFF* (Hubbard, Quicksall & Jacobson, 1971).

The structure model was refined to $R_1 = 0.12$ ($R_1 = (\sum |F_o - |F_c||) / \sum F_o$, $R_2 = [\sum w(F_o - |F_c|)^2 / \sum wF_o^2]^{1/2}$). The introduction of anisotropic thermal parameters for all non-hydrogen atoms followed by least-squares refinement reduced R_1 to 0.084. The program used (*UCLALS4*) was that of Gantzel, Sparks & Trueblood (1960) which minimizes $\sum w(\Delta F)^2$.

Positions for all hydrogen atoms were found on a difference Fourier synthesis. All 24 hydrogen atoms were included in the least-squares refinement with an estimated isotropic temperature factor of 5.0 Å^2 .

Full-matrix least-squares refinement of all positional parameters and anisotropic thermal parameters of all non-hydrogen atoms converged to give the final error indices $R_1 = 0.062$ and $R_2 = 0.066$. The 'goodness-of-fit', $\{[\sum w(F_o - |F_c|)^2] / (m - s)\}^{1/2}$, is 1.12. The number of observations, m , is 1161; the number of parameters, s , is 253. In the final cycles of least-squares, all shifts in parameters for non-hydrogen atoms were less than 3% of their standard deviations. Shifts in parameters for the hydrogen atoms were less than 10% of their e.s.d.'s. The two largest peaks on the final difference Fourier function had densities of approximately 0.7 e Å^{-3} and 0.5 e Å^{-3} , and are found at positions (at which hydrogen atoms cannot be, on the basis of

Table 2. Fractional atomic coordinates and thermal parameters with estimated standard deviations (all $\times 10^4$)

See Fig. 1 for the identities of the atoms. The e.s.d. is in units of the least significant digit given for the corresponding parameter.

The temperature factor is $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	1112 (2)	804 (2)	4079 (2)	55 (2)	77 (2)	87 (2)	-9 (3)	65 (3)	-9 (4)
S(2)	1320 (2)	2156 (2)	2880 (2)	56 (2)	87 (3)	63 (2)	-12 (4)	-14 (3)	-24 (4)
O(3)	3999 (7)	-410 (6)	5826 (6)	164 (8)	85 (8)	72 (6)	54 (14)	-116 (11)	12 (12)
O(4)	3216 (12)	1428 (9)	5539 (7)	365 (19)	115 (11)	76 (7)	24 (23)	-161 (18)	-19 (15)
O(5)	3639 (4)	6030 (6)	3712 (5)	60 (4)	78 (7)	68 (4)	-17 (9)	28 (7)	10 (10)
O(6)	3206 (5)	5247 (6)	5304 (5)	75 (4)	87 (7)	48 (5)	-10 (9)	10 (7)	-7 (9)
O(7)	5685 (5)	3004 (6)	3462 (5)	72 (4)	75 (6)	51 (4)	4 (9)	-21 (7)	18 (9)
O(8)	4222 (4)	1115 (6)	1977 (4)	71 (5)	106 (8)	46 (4)	13 (10)	20 (7)	-32 (9)
N(9)	3976 (5)	-1108 (7)	3728 (6)	41 (4)	93 (9)	52 (5)	-6 (10)	3 (7)	-32 (11)
N(10)	3575 (5)	3603 (7)	2834 (5)	46 (5)	102 (9)	43 (5)	15 (11)	13 (8)	1 (11)
C(11)	2048 (6)	-604 (8)	3891 (7)	30 (5)	71 (9)	62 (7)	-15 (11)	10 (9)	-13 (13)
C(12)	1900 (6)	-1150 (9)	2758 (7)	39 (5)	90 (10)	61 (6)	-24 (12)	-10 (9)	-43 (14)
C(13)	1694 (7)	-1602 (9)	4705 (8)	58 (6)	83 (10)	79 (8)	-3 (13)	17 (11)	37 (15)
C(14)	3204 (6)	-67 (9)	4093 (6)	45 (6)	104 (10)	45 (6)	3 (13)	9 (9)	-39 (13)
C(15)	3520 (8)	309 (9)	5241 (7)	90 (7)	54 (10)	33 (6)	-12 (14)	0 (11)	-7 (13)
C(16)	1737 (6)	3777 (7)	3507 (7)	42 (5)	51 (9)	64 (7)	3 (11)	0 (9)	-19 (12)
C(17)	1112 (7)	3996 (10)	4533 (8)	48 (6)	124 (12)	102 (9)	1 (14)	56 (11)	-85 (18)
C(18)	1423 (7)	4783 (10)	2621 (10)	57 (7)	91 (12)	153 (13)	24 (15)	-63 (15)	46 (20)
C(19)	2941 (5)	3803 (7)	3804 (6)	33 (5)	68 (9)	38 (5)	7 (11)	12 (8)	-11 (11)
C(20)	3304 (6)	5146 (8)	4319 (7)	43 (5)	76 (10)	36 (6)	8 (12)	13 (9)	-9 (13)

nearest neighbor approaches) in the vicinity of the carboxylate groups. They may be associated with the delocalized electron density of these groups, or may be due to the inadequacy of the anisotropic model to properly represent the electron density of the oxygen atoms, which have large thermal motion. The largest remaining peaks on the difference Fourier function had a density of less than $0.3 \text{ e } \text{Å}^{-3}$; the standard deviation of the electron density is calculated to be $0.1 \text{ e } \text{Å}^{-3}$.

The overdetermination ratio, m/s , excluding the unrefined thermal parameters of hydrogen atoms, is 4.5. Table 1 is a tabulation of the observed and calculated structure factors ($\times 10$), and the final parameters of the non-hydrogen atoms are listed in Table 2. Positional parameters for the hydrogen atoms are given in Table 3. Standard deviations were calculated from the correlation matrix ignoring standard deviations in cell parameters.

Table 3. Fractional atomic coordinates ($\times 10^3$) for hydrogen atoms

See Fig. 1 for the identities of atoms. The e.s.d. is in units of the least significant digit given for the corresponding parameter.

	<i>x</i>	<i>y</i>	<i>z</i>
H(21)	606 (7)	368 (10)	379 (7)
H(22)	579 (7)	221 (10)	375 (8)
H(23)	388 (8)	97 (10)	132 (7)
H(24)	481 (7)	86 (10)	192 (8)
H(25)	384 (7)	-183 (10)	419 (8)
H(26)	396 (7)	-132 (10)	308 (8)
H(27)	465 (7)	-66 (10)	408 (8)
H(28)	424 (8)	344 (10)	307 (8)
H(29)	348 (7)	412 (11)	236 (8)
H(30)	337 (7)	288 (11)	247 (8)
H(31)	126 (7)	-138 (10)	263 (8)
H(32)	203 (7)	-31 (10)	217 (8)
H(33)	245 (7)	-194 (10)	271 (8)
H(34)	179 (7)	-133 (10)	544 (8)
H(35)	207 (7)	-241 (10)	482 (8)
H(36)	97 (7)	-193 (10)	465 (8)
H(37)	327 (7)	90 (10)	340 (8)
H(38)	125 (7)	489 (10)	480 (8)
H(39)	136 (7)	351 (10)	517 (8)
H(40)	44 (7)	396 (10)	427 (8)
H(41)	166 (7)	562 (10)	301 (8)
H(42)	70 (7)	490 (10)	260 (8)
H(43)	179 (7)	435 (10)	195 (7)
H(44)	320 (7)	303 (10)	441 (8)

Discussion

Bond lengths and angles involving only non-hydrogen atoms are given in Fig. 1, where the numbering of the atoms is indicated. Average bond lengths and angles involving hydrogen atoms are given in Table 4.

The substituted cystine molecule is found to be the *meso*-compound (see Fig. 1), which exists as a di-zwitterion; three hydrogen atoms were located around each nitrogen atom. All bond lengths and angles, except the O(3)-C(15) bond length, are in good agreement with those reported for other cystine compounds

Table 4. Average bond distances (Å) and bond angles ($^\circ$) involving hydrogen

The e.s.d., in parentheses, is in units of the least significant digit given for the corresponding parameter.

	Average value	Number averaged	Range
O-H	0.87 Å	4	0.79 (9)–0.92 (9) Å
N-H	0.90	6	0.79 (10)–1.04 (9)
C-H	1.01	14	0.85 (9)–1.28 (9)
N-C-H	106 $^\circ$	2	104 (4)–108 (5) $^\circ$
C-N-H	108	6	96 (5)–118 (6)
C-C-H	109	16	98 (6)–120 (6)
H-O-H	111	2	109 (9)–115 (8)
H-N-H	110	6	97 (10)–120 (8)
H-C-H	109	12	93 (8)–126 (7)

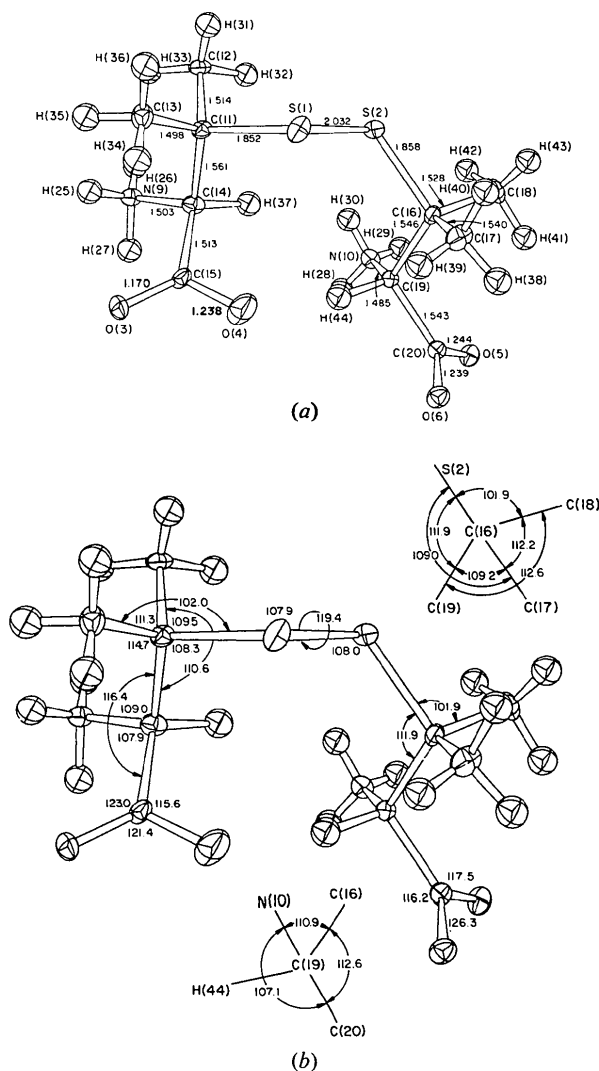


Fig. 1. The 3,3'-dithiovaline molecule. Ellipsoids of 15% probability are used (Johnson, 1965). Bond lengths are given in (a) and bond angles in (b). The standard deviations in the bond lengths and angles which do not involve hydrogen atoms are, in $\text{Å} \times 10^3$ and $^\circ$: S-S, 3; S-C, 8; N-C, 9 to 11; other bonds, 9 to 14; S-S-C, 0.3; S-C-C, 0.5 or 0.6; N-C-C, 0.5 to 0.7; other angles, 0.6 to 1.0.

and also with those reported for valines (Torii & Iitaka, 1970). The O(3)–C(15) bond length of 1.170 (12) Å is significantly shorter than the value of 1.25 Å usually found for C–O bonds in carboxylate groups (Mostad, Ottersen & Rømming, 1971), and appears foreshortened due to the large thermal motion of the O(3)–C(15)–O(4) group. The C–H bonds C(14)–H(37) and C(19)–H(44) are noticeably long, averaging 1.2 (1) Å.

The sulfur–carbon bond lengths (average 1.855 Å) are significantly longer than those commonly found (Cox & Jeffrey, 1951; Ottersen, Warner & Seff, 1973*b*, 1974*b*). [The sum of the covalent radii is 1.81 Å; Pauling (1960)]. Long sulfur–carbon bonds have also been reported for other cystine compounds; L-cystine dihydrobromide: 1.862 (30) Å (Peterson, Steinrauf & Jensen, 1960), L-cystine dihydrochloride: 1.865 Å (Steinrauf, Peterson & Jensen, 1958), *N,N'*-diglycyl-L-cystine: 1.87 (2) (Yakel & Hughes, 1954).

The conformation of the molecule differs from the helical one found in other cystine compounds; it is twisted so that the two carboxylate groups approach each other [O(4)···O(6): 3.81 Å] as is shown in Fig. 1. Chaney & Steinrauf (1968) suggest that the molecular packing of cystines is largely controlled by their backbone conformation and to smaller extent by their hydrogen bonding interactions. The conformational difference between the present compound and other cystines may reflect the difference between the *meso*-cystine and the L-cystine conformation. Steric interactions between the groups on C(11) and C(16), the tertiary carbons adjacent to the sulfurs might also influence the backbone conformation.

The torsion angle around the sulfur–sulfur bond is 119.4 (4)° (selected torsion angles are given in Table 5) which is significantly larger than the value of 112.8° reported for D-penicillamine disulfide dihydrochloride (Rosenfield & Parthasarathy, 1971) or the values reported for other cystines and for other disulfides (Hordvik, 1966; Lee, 1972). Although CSSC torsion angles of 105 to 110° have been reported (Foss, Johnsen & Tvedten, 1958; Foss & Johnsen, 1965), values between 80 and 100° are usually observed. Repulsion between the lone-pair electrons is expected to be at a

minimum when the torsion angle is 90° (Bergson, 1957). The exceptionally large torsion angle found here is probably caused by steric repulsion between groups on the two tertiary carbons, and may account for the hypochromic shift of the ultraviolet spectrum (Boyd, 1972) of this and other tertiary substituted disulfides.

Table 5. Selected torsion angles (°)

E.s.d.'s are in the units of the least significant digit given for the corresponding parameter.

Dihedral angles	
C(11)–S(1)–S(2)–C(16)	119.4 (4)°
S(1)–S(2)–C(16)–C(17)	39.0 (4)
S(1)–S(2)–C(16)–C(19)	81.8 (4)
S(2)–S(1)–C(11)–C(12)	53.6 (4)
S(2)–S(1)–C(11)–C(14)	67.1 (4)
S(1)–C(11)–C(14)–C(15)	69.2 (6)
S(1)–C(11)–C(14)–N(9)	168.6 (6)
S(2)–C(16)–C(19)–C(20)	179.6 (6)
S(2)–C(16)–C(19)–N(10)	59.6 (6)
O(3)–C(15)–C(14)–N(9)	24.9 (9)
O(4)–C(15)–C(14)–N(9)	156.7 (10)
O(5)–C(20)–C(19)–N(10)	29.2 (8)
O(6)–C(20)–C(19)–N(10)	152.5 (8)

According to Hordvik (1966), a relationship exists between the sulfur–sulfur bond length and torsion angle in disulfides. When this angle is 90°, favorable π overlap is at a maximum. The current result [2.032 (3) Å] is shorter than the value (2.06 Å) to be expected for this torsion angle (Hordvik, 1966). Apparently short sulfur–sulfur bond lengths have also been reported for other disulfides (Lee, 1972).

A view of the packing in the crystal is given in Fig. 2. Hydrogen bonds (see Table 6), which involve both nitrogens, all four carboxylate oxygens, and the two water molecules, form a three-dimensional network of interactions between the molecules. All possible donors have been utilized, as is usual for α -amino acids. A close (3.24 Å) linear C(19)–H(44)–O(4) contact is noted.

This work was supported by the National Institutes of Health (grant no. GM-18813-02). We are also indebted to the University of Hawaii Computing Center for their assistance.

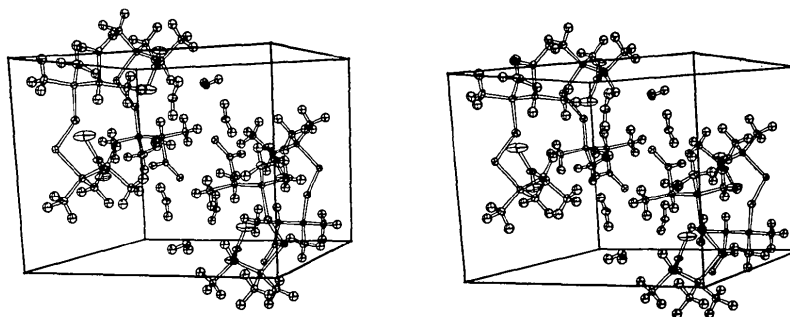


Fig. 2. A stereoview (Johnson, 1965) illustrating the packing of the molecules in the crystal. The *a* axis is horizontal and the *c* axis is vertical in the plane of the paper. Ellipsoids of 15% probability are used.

Table 6. Hydrogen bonds

The coordinates of the acceptor atoms are related to those given in Table 1 by the symmetry operation given. The standard deviations are about 0.012 Å in O···O, 0.010 Å in N···O, 0.10 Å in H···O distances, and about 6° in the angles.

Donor (D)	Acceptor (A)	Symmetry operation	D···A (Å)	H···A (Å)	D-H···A (°)
O(7)—H(21)	O(6)	1-x, 1-y, 1-z	2.675	1.78	167
O(7)—H(22)	O(3)	1-x, -y, 1-z	2.753	1.89	171
O(8)—H(23)	O(6)	x, 0.5-y, -0.5+z	2.754	1.92	150
O(8)—H(24)	O(5)	1-x, -0.5+y, 0.5-z	2.859	2.14	149
N(9)—H(25)	O(5)	x, -1+y, z	2.878	2.22	131
N(9)—H(26)	O(7)	1-x, -0.5+y, 0.5-z	2.910	2.09	152
N(9)—H(27)	O(3)	1-x, -y, 1-z	2.996	2.01	157
N(10)—H(28)	O(7)	x, y, z	2.802	1.92	171
N(10)—H(29)	O(4)	x, 0.5-y, -0.5+z	2.871	2.35	124
N(10)—H(30)	O(8)	x, y, z	2.827	2.16	132

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