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Structures of Three Stereoisomers of (4*S*)-3-(2-Chloro-3-hydroxy-4-methylpentanoyl)-4-(1-methylethyl)oxazolidine

BY DRAKE S. EGGLESTON,* AHMED ABDEL-MAGID, LENDON N. PRIDGEN AND IVAN LANTOS

Research and Development Division, Smith Kline & French Laboratories, 1500 Spring Garden Street, Philadelphia, Pennsylvania 19101, USA

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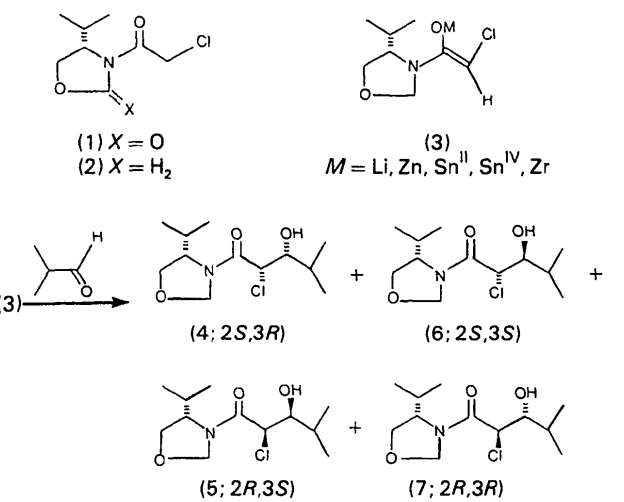
Abstract. $C_{12}H_{22}ClNO_3$, $M_r = 263{\cdot}77$: (4*S*)-3-[(2*S*,3*S*)-2-chloro-3-hydroxy-4-methylpentanoyl]-4-(1-methylethyl)oxazolidine, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}815$ (4), $b = 21{\cdot}414$ (4), $c = 6{\cdot}831$ (3) Å, $V = 1435{\cdot}6$ Å^3, $Z = 4$, $D_x = 1{\cdot}220$, $D_m = 1{\cdot}22$ g cm^{-3} (flotation in aqueous $ZnCl_2$), λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 2{\cdot}61$ cm^{-1}, $F(000) = 568$, $T = 273$ K, final $R = 0{\cdot}044$ for 1586 observed reflections; (4*S*)-3-[(2*R*,3*S*)-2-chloro-3-hydroxy-4-methylpentanoyl]-4-(1-methylethyl)oxazolidine, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}933$ (2), $b = 22{\cdot}574$ (5), $c = 6{\cdot}184$ (1) Å, $V = 1386{\cdot}6$ Å^3, $Z = 4$, $D_x = 1{\cdot}264$, $D_m = 1{\cdot}25$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 2{\cdot}70$ cm^{-1}, $F(000) = 568$, $T = 273$ K, final $R = 0{\cdot}041$ for 1301 observed reflections; (4*S*)-3-[(2*S*,3*R*)-2-chloro-3-hydroxy-4-methylpentanoyl]-4-(1-methylethyl)oxazolidine, triclinic, $P\bar{1}$, $a = 5{\cdot}790$ (4), $b = 5{\cdot}945$ (2), $c = 11{\cdot}884$ (3) Å, $\alpha = 95{\cdot}75$ (2), $\beta = 95{\cdot}45$ (4), $\gamma = 117{\cdot}80$ (4)°, $V = 355{\cdot}3$ Å^3, $Z = 1$, $D_x = 1{\cdot}233$, $D_m = 1{\cdot}23$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 2{\cdot}64$ cm^{-1}, $F(000) = 142$, $T = 273$ K, final $R = 0{\cdot}0387$ for 1876 observed reflections. The title isomers are synthetically prepared substituted oxazolidines containing an amide functionality. Molecular dimensions for the amide group indicate an appreciable contribution to the electronic structure from an ionic resonance form. A significant inductive effect on the oxazolidine C—O bond proximal to the amide group may also be posited. As a result of the peptide-like linkage, two distinct orientations of the carbonyl group relative to the oxazolidine ring are observed, both in solution and in the solid state. The oxazolidine ring conformations also differ between stereoisomers and may be described as a half-chair for the (*S*,*R*) diastereomer, and an envelope for both the (*R*,*S*) and (*S*,*S*) isomers.

Introduction. During our study on the effect of metal chelation on the stereoselectivity of aldol condensations of the metal enolates of (+)-(4*S*)-3-chloroacetyl-4-(1-methylethyl)-2-oxazolidinone (1) with aldehydes, we found the need to carry out the reaction with (2) in which the ring carbonyl is absent. The condensation of Li, Zn, Sn^{II}, Sn^{IV} and Zr enolates (3) with isobutyraldehyde gave the four diastereomeric products (4), (5), (6) and (7) in different ratios with (4) being the major component in all cases (Abdel-Magid, Pridgen, Eggleston & Lantos, 1986).



The determination of both the relative and absolute stereochemistry of the newly formed centers in the four products could not be achieved by spectroscopic methods. Rotational isomerization about the amide function complicated the ^{1}H and ^{13}C NMR spectra so that each compound appeared as a mixture of two isomers at ambient temperature. Single-crystal X-ray diffraction studies established both the absolute stereochemistry of each molecule and its conformation in the solid state. The crystal structures also revealed specifics of the molecular bonding, most notably the 'peptide-like' nature of the amide bond and the metrical adjustments which accompany adoption of either a *cisoid* or *transoid* orientation of the amide carbonyl relative to the oxazolidine ring. Structure determinations of the three chlorohydrins (4), (5) and (6) are dicussed here.

Experimental. Crystals of all three molecules grown by slow evaporation from ether/hexane solutions and

* Author to whom correspondence should be addressed.

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mounted in quartz capillaries for data collection. Intensity data measured on an Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo radiation, ω–2θ scan mode used for each crystal as indicated by peak shape analysis. Cell constants measured from angular settings of 25 reflections with $30 \le 2\theta(\text{Mo}) \le 35°$. Data corrected for Lorentz–polarization effects. Empirical absorption correction based on ψ scans of reflections with $80 \le \chi \le 90°$ applied. All three structures solved with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All refinements by full-matrix least squares (on F) with anisotropic thermal parameters for non-H atoms. H atoms treated as indicated below. The function minimized was $\sum w(|F_o|-|F_c|)^2$, where $w = 4F_o^2/\sigma^2(I)$ with $\sigma^2(I) = \sigma^2(I)_c + p(I)_c^2$ (Corfield, Doedens & Ibers 1967), $\sigma^2(I)_c$ is the variance determined by counting statistics, and p (indicated below for each structure) is a small percentage value which dampens the weights of large intensities to prevent them from biasing the least-squares refinement. For non-H atoms, values of the neutral-atom scattering factors and of f' and f'' were taken from *International Tables for X-ray Crystallography* (1974); H-atom scattering factors from Stewart, Davidson & Simpson (1965). All programs from the Enraf–Nonius (1979) *SDP* with local modifications.

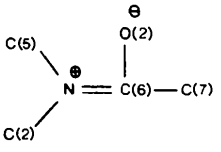
For the (2*S*,3*S*) diastereomer: 2955 intensity data $2\theta(\text{Mo}) \le 60°$, $0 \le h \le 13$, $0 \le k \le 30$, $0 \le l \le 9$, no systematic fluctuations in three intensity standards measured every 3 h of exposure time (17 times; 025, $3\bar{7}4$, 2,10,$\bar{4}$; average $F = 137{\cdot}87$, 95·43, 117·09; max. deviation = 2·1, 2·9, 2·4%), 1586 observed reflections with $I \ge 3\sigma(I)$. The approximate crystal dimensions were $0{\cdot}30 \times 0{\cdot}20 \times 0{\cdot}50$ mm; min. and max. transmission coefficients were 0·967 and 0·998, respectively. Non-H atoms located from an E map and subsequent difference Fourier synthesis. Twofold disorder for one of the methyl C atoms refined with occupancies of 67% and 33% for atoms C(14) and C(14′), respectively, based on relative heights in a difference Fourier map and near equivalency of isotropic thermal parameters. All H atoms, except those attached to disordered C, located from difference Fourier maps and all except those attached to C(13) allowed to refine in final stages of least squares. An extinction coefficient, of the type described by Zacharisen (1963), included in the later stages refined to $9{\cdot}07\,(4) \times 10^{-7}$. For the weighting scheme $p = 0{\cdot}05$. Final $R = 0{\cdot}0443$, $wR = 0{\cdot}0562$, $S = 1{\cdot}39$. Coordinates were inverted and refinement gave $R = 0{\cdot}0455$ and $wR = 0{\cdot}0577$ thus, for a refinement with 1586 observations and 228 variables, the enantiomorphic structure may be rejected at greater than the $1/2\sigma$ level based on Hamilton's R-factor-ratio test (Hamilton, 1965). [The configuration at atom C(4) also is consistent with the known configuration of the starting material L-valinol.] In the final least-squares cycle $(\Delta/\sigma)_{\max} = 0{\cdot}06$; max. and min. heights in a final difference Fourier map 0·287 and $-0{\cdot}278$ e Å^{-3}. A refinement using 2106 observations with $I \ge 0{\cdot}01\sigma(I)$ gave $R = 0{\cdot}0624$, $wR = 0{\cdot}0613$.

For the (2*R*,3*S*) diastereomer: 2330 intensity data $2\theta(\text{Mo}) \le 60°$, $0 \le h \le 14$, $0 \le k \le 31$, $0 \le l \le 8$, three intensity standards measured every 3 h of exposure time (15 times; 672, $6\bar{4}3$, 3,14,3; average $F = 92{\cdot}43$, 97·02, 100·74; max. deviation = 2·6, 2·5, 2·6%) showed no systematic fluctuations, 1301 observed reflections with $I \ge 3\sigma(I)$. Approximate crystal dimensions $0{\cdot}50 \times 0{\cdot}30 \times 0{\cdot}20$ mm; min. and max. transmission coefficients were 0·961 and 0·997, respectively. An E map gave starting positions for 6 of the 17 non-H atoms. Subsequent least-squares refinement and difference Fourier map revealed the remaining atoms. All H atoms were located from difference Fourier maps and all were allowed to refine with isotropic thermal parameters. An extinction coefficient, of the type described by Zacharisen (1963), included in the later stages refined to $1{\cdot}13\,(1) \times 10^{-6}$. For the weighting scheme, $p = 0{\cdot}05$. Final $R = 0{\cdot}0413$, $wR = 0{\cdot}0484$, $S = 1{\cdot}12$. Coordinates were inverted and refinement gave $R = 0{\cdot}0420$, $wR = 0{\cdot}0491$ for a refinement with 1301 observations and 243 variables. In the final least-squares cycle $(\Delta/\sigma)_{\max} = 0{\cdot}13$; max. and min. heights in a final difference Fourier map 0·212 and $-0{\cdot}230$ e Å^{-3}. A refinement using 1927 observations with $I \ge 0{\cdot}01\sigma(I)$ gave $R = 0{\cdot}0751$, $wR = 0{\cdot}0623$.

For the (2*S*,3*R*) diastereomer: 2166 intensity data, $2\theta(\text{Mo}) \le 60°$, $-8 \le h \le 8$, $-8 \le k \le 8$, $0 \le l \le 16$. Data were corrected for decay using the program *CHORT*, min. and max. correction factors were 1·000 and 1·318, respectively. The approximate crystal dimensions were $0{\cdot}40 \times 0{\cdot}40 \times 0{\cdot}20$ mm; min. and max. transmission coefficients were 0·880 and 0·998, respectively. An E map gave starting positions for 12 of the 17 non-H atoms; the remaining atoms were located from a difference Fourier map. All H atoms were located from difference Fourier maps and were refined with isotropic thermal parameters. An extinction coefficient, of the type described by Zacharisen (1963), included in the later stages refined to $1{\cdot}1\,(3) \times 10^{-6}$. For the weighting scheme, $p = 0{\cdot}06$. Assignment of the enantiomorph was made relative to the other structures. The data were averaged to remove symmetry-equivalent reflections, the agreement factors were 1·4% on I and 1·4% on F_o. The refinement converged to $R = 0{\cdot}0387$, $wR = 0{\cdot}051$, for 1876 intensities with $I \ge 3\sigma(I)$. In the final cycle $(\Delta/\sigma)_{\max} = 0{\cdot}04$; max. and min. heights in a final difference Fourier map 0·280 and $-0{\cdot}232$ e Å^{-3}. A refinement using 2019 observations with $I \ge 0{\cdot}01\sigma(I)$ gave $R = 0{\cdot}0419$, $wR = 0{\cdot}0525$.

Discussion. The molecular structure of each molecule is displayed in a separate *ORTEP* (Johnson, 1965) diagram, Figs. 1–3. Final positional parameters are

listed in Tables 1–3.* Selected bond distances and angles are presented in Table 4. Overall, analogous bond distances and angles between structures are equivalent within the error of the experiments. There is a notable asymmetry in the two chemically distinct bond distances involving atom O(3) in all structures. Thus, the C(2)–O(3) bonds are distinctly shorter than their C(4)–O(3) counterparts. Shortening of the C(2)–O(3) bond(s) may arise from an inductive effect caused by the amide group. The N–C(6) bond lengths of 1·333 (3), 1·327 (5) and 1·343 (4) Å for the (*S,R*), (*R,S*) and (*S,S*) molecules, respectively, combined with the relatively long amide-carbonyl bond lengths [C(6)–O(2)] of 1·235 (3), 1·226 (5) and 1·230 (4) Å, respectively, suggest an appreciable contribution to the structures of the ionic resonance form:



These values are similar to average dimensions cited for peptide linkages (Benedetti, 1977), to which ionic resonance forms are known contributors, and are consistent with restricted rotational freedom about the N–C(6) bond which has been observed in extensive NMR experiments on these oxazolidines (Abdel-Magid, Pridgen, Eggleston & Lantos, 1986). The result of this peptide-like linkage is the possible observation of '*cis*' and '*trans*' isomers about the N–C(6) bond. As may be seen from the figures, in the three molecules discussed here both '*cis*' and '*trans*' conformations are represented with O(2) *trans* to C(2) in the (*S,R*) and (*S,S*) diastereomers and *cis* to C(2) in the (*R,S*) structure. In the (*R,S*) structure, presumably as a result of the adoption of this *cisoid* conformation, there has been a considerable adjustment in the exocyclic angles involving the N atom. Thus, for the two '*trans*' molecules, the C(2)–N–C(6) and C(5)–N–C(6) angles are equivalent whereas for the '*cis*' molecule the C(2)–N–C(6) angle has narrowed considerably from an average of 126·5 (2) to 118·6 (3)°, and the C(5)–N–C(6) angle of 131·2 (3)° is considerably wider than the 120·9 (3) and 122·5 (2)° angles observed for the '*trans*' structures. Adoption of the *cisoid* conformation in the (*R,S*) structure also leads to widening of the N–C(6)–C(7) angle to 118·7 (4)° as compared to an average of 116·7 (3)° for the two *transoid* structures.

* Lists of structure factor amplitudes, anisotropic thermal parameters, H-atom coordinates, and complete bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43048 (66 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

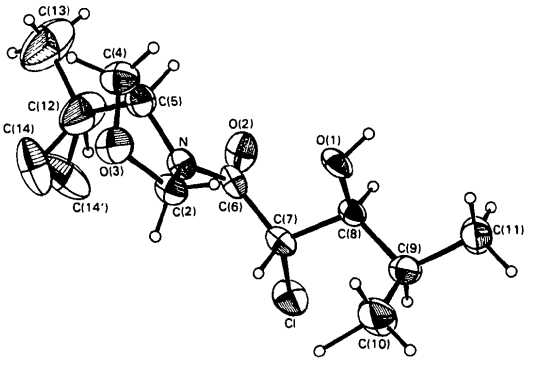


Fig. 1. Molecular conformation and numbering scheme for (4*S*)-3-[(2*S*,3*S*)-2-chloro-3-hydroxy-4-methylpentanoyl]-4-(1-methylethyl)oxazolidine. Probability ellipses are drawn at the 50% level, H atoms as spheres of arbitrary size. Atoms C(14) and C(14′) indicate the twofold disorder for this methyl C atom.

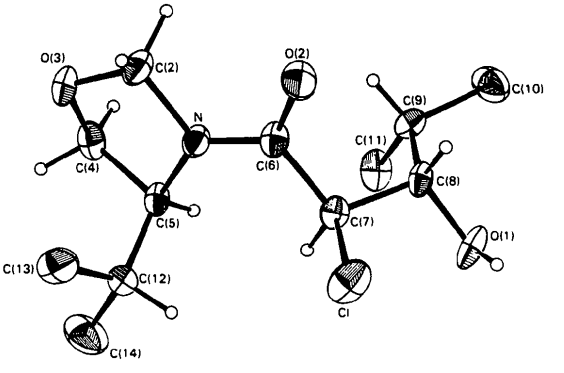


Fig. 2. Molecular conformation and numbering scheme for (4*S*)-3-[(2*R*,3*S*)-2-chloro-3-hydroxy-4-methylpentanoyl]-4-(1-methylethyl)oxazolidine. Probability ellipses are drawn at the 50% level, H atoms are spheres of arbitrary size. H atoms attached to methyl C atoms are omitted for clarity.

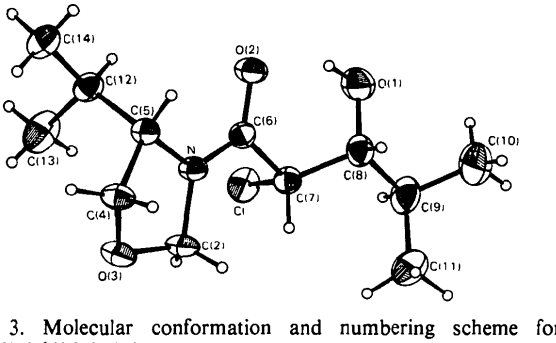


Fig. 3. Molecular conformation and numbering scheme for (4*S*)-3-[(2*S*,3*R*)-2-chloro-3-hydroxy-4-methylpentanoyl]-4-(1-methylethyl)oxazolidine. Probability ellipses are drawn at the 50% level, H atoms as spheres of arbitrary size.

Bond angles internal to the oxazolidine ring are notably asymmetric with the angle at C(5) in all cases severely compressed from normal tetrahedral values [average = 99·8 (4)°]. This internal angular compression is apparent in a number of other structurally characterized oxazolidines (Turley, 1972; Neelkantan & Molin-Case, 1971; Bellan, Rossi, Chezeau, Roques, Cormain & Declercq, 1978) regardless of the ring conformation adopted. Coincident with this internal angular compression is a marked widening of the C(4)–C(5)–C(12) angle over normal tetrahedral values with an average in these structures of 115·9 (4)°.

Table 1. *Positional parameters and equivalent isotropic temperature factors with e.s.d.'s in parentheses for* (4*S*)-3-[(2*S*,3*S*)-2-*chloro*-3-*hydroxy*-4-*methylpentanoyl*]-4-(1-*methylethyl*)*oxazolidine*

$B_{eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	B_{eq}(Å²)
Cl	0·4560 (1)	0·04182 (5)	0·0716 (1)	3·56 (1)
O(1)	0·3760 (2)	0·0586 (1)	0·6344 (3)	2·78 (4)
O(2)	0·3677 (3)	−0·0677 (1)	0·3194 (4)	3·41 (5)
O(3)	0·7034 (3)	−0·0638 (1)	0·7601 (4)	3·48 (5)
N	0·5493 (3)	−0·0564 (1)	0·5150 (4)	2·34 (4)
C(2)	0·6486 (3)	−0·0197 (1)	0·6289 (4)	2·54 (5)
C(4)	0·6002 (4)	−0·1089 (2)	0·7960 (6)	3·47 (7)
C(5)	0·5336 (4)	−0·1187 (2)	0·5997 (4)	2·79 (6)
C(6)	0·4576 (3)	−0·0340 (2)	0·3870 (4)	2·41 (5)
C(7)	0·4703 (3)	0·0347 (1)	0·3320 (4)	2·19 (6)
C(8)	0·3579 (3)	0·0721 (2)	0·4326 (5)	2·07 (5)
C(9)	0·3651 (4)	0·1428 (2)	0·3930 (6)	2·86 (6)
C(10)	0·5024 (4)	0·1703 (2)	0·4459 (9)	4·69 (9)
C(11)	0·2491 (4)	0·1758 (2)	0·5005 (6)	3·66 (8)
C(12)	0·5885 (6)	−0·1696 (2)	0·4699 (8)	6·3 (1)
C(13)	0·5582 (7)	−0·2330 (2)	0·5587 (8)	8·4 (2)
C(14)	0·7312 (8)	−0·1619 (4)	0·407 (1)	6·6 (2)
C(14′)	0·640 (1)	−0·1638 (7)	0·282 (2)	5·9 (4)

Table 2. *Positional parameters and equivalent isotropic temperature factors with e.s.d.'s in parentheses for* (4*S*)-3-[(2*R*,3*S*)-2-*chloro*-3-*hydroxy*-4-*methylpentanoyl*]-4-(1-*methylethyl*)*oxazolidine*

$B_{eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	B_{eq}(Å²)
Cl	0·8217 (1)	0·16708 (5)	0·0532 (2)	3·18 (2)
O(1)	0·8219 (3)	0·2860 (1)	0·2888 (4)	2·51 (5)
O(2)	1·1382 (3)	0·1788 (1)	0·0421 (5)	2·75 (6)
O(3)	1·2696 (3)	0·0522 (1)	0·4514 (5)	2·31 (5)
N	1·1170 (3)	0·1201 (1)	0·3298 (5)	1·81 (6)
C(2)	1·2491 (4)	0·0937 (2)	0·2867 (7)	2·28 (8)
C(4)	1·1904 (4)	0·0711 (2)	0·6313 (7)	2·29 (7)
C(5)	1·0605 (4)	0·0954 (2)	0·5299 (6)	1·70 (6)
C(6)	1·0737 (4)	0·1632 (2)	0·2014 (6)	1·86 (6)
C(7)	0·9395 (4)	0·1926 (2)	0·2521 (7)	1·79 (6)
C(8)	0·9491 (4)	0·2605 (2)	0·2412 (6)	1·75 (7)
C(9)	1·0500 (4)	0·2845 (2)	0·4052 (7)	1·94 (7)
C(10)	1·0081 (5)	0·2719 (2)	0·6376 (7)	2·67 (8)
C(11)	1·0707 (5)	0·3508 (2)	0·3730 (8)	3·18 (9)
C(12)	0·9495 (4)	0·0495 (2)	0·4892 (7)	2·22 (8)
C(13)	0·9934 (4)	−0·0012 (2)	0·3443 (8)	2·92 (9)
C(14)	0·8937 (5)	0·0261 (2)	0·7032 (9)	4·0 (1)

The conformation of the oxazolidine ring is best described as a half-chair in the (2*S*,3*R*) structure, with atoms N, C(2) and C(5) coplanar; atom O(3) lies 0·290 (3) Å to one side of the plane and atom C(4) lies 0·303 (2) Å to the other side of the plane. The oxazolidine ring adopts an envelope conformation with atoms N, C(2), C(4) and C(5) nearly coplanar and atom O(3) 0·485 (3) and 0·453 (2) Å out of the plane for the (2*S*,3*S*) and (2*R*,3*S*) structures, respectively.

Relative to their respective oxazolidine rings, the isopropyl groups have remarkably similar orientations in each structure. One of the methyl groups adopts a *transoid* orientation relative to the N atom [average torsion angle −175·7 (8)°] whereas the other methyl C atom adopts the positive *gauche* conformation relative to N [average torsion angle 57·2 (8)°]. While the g^+ position is sterically least favorable for valine residues in peptides and proteins (Benedetti, Morrelli, Nemethy & Scheraga, 1983), the absence of the peptide carbonyl group in a cyclized oxazolidine would appear to relax the steric demand on the β-branched isopropyl side chain.

Table 3. *Positional parameters and equivalent isotropic temperature factors with e.s.d.'s in parentheses for* (4*S*)-3-[(2*S*,3*R*)-2-*chloro*-3-*hydroxy*-4-*methylpentanoyl*]-4-(1-*methylethyl*)*oxazolidine*

$B_{eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	B_{eq}(Å²)
Cl	0·722	0·056	0·056	3·254 (9)
O(1)	0·6862 (4)	0·5165 (4)	0·1849 (2)	3·72 (5)
O(2)	0·3777 (3)	0·3553 (3)	−0·0227 (2)	2·66 (3)
O(3)	−0·1185 (3)	−0·4745 (3)	−0·1905 (2)	2·84 (3)
N	0·1397 (3)	−0·0707 (3)	−0·0912 (2)	2·02 (3)
C(2)	0·0367 (4)	−0·3462 (4)	−0·0824 (2)	2·54 (4)
C(4)	−0·2284 (4)	−0·3168 (4)	−0·2266 (2)	2·45 (4)
C(5)	−0·0018 (4)	−0·0412 (4)	−0·1931 (2)	1·95 (3)
C(6)	0·3139 (4)	0·1297 (3)	−0·0131 (2)	1·95 (3)
C(7)	0·4342 (4)	0·0671 (4)	0·0916 (2)	2·16 (4)
C(8)	0·5000 (4)	0·2648 (4)	0·1990 (2)	2·73 (4)
C(9)	0·6021 (6)	0·1988 (6)	0·3068 (2)	3·85 (6)
C(10)	0·6467 (9)	0·3986 (8)	0·4085 (3)	5·4 (1)
C(11)	0·4203 (9)	−0·0705 (6)	0·3279 (3)	5·22 (9)
C(12)	0·1747 (4)	0·0636 (4)	−0·2841 (2)	2·39 (4)
C(13)	0·2852 (5)	−0·1089 (6)	−0·3284 (3)	3·92 (6)
C(14)	0·0260 (5)	0·1167 (5)	−0·3812 (2)	3·30 (5)

Table 4. *Selected bond lengths* (Å) *and angles* (°)

	(2*S*,3*S*)	(2*R*,3*S*)	(2*S*,3*R*)
O(2)–C(6)	1·230 (4)	1·226 (5)	1·235 (3)
O(3)–C(2)	1·410 (4)	1·399 (5)	1·408 (3)
O(3)–C(4)	1·421 (4)	1·428 (5)	1·433 (3)
N–C(2)	1·475 (4)	1·465 (5)	1·477 (3)
N–C(5)	1·461 (4)	1·468 (5)	1·469 (3)
N–C(6)	1·343 (4)	1·327 (5)	1·333 (3)
C(2)–N–C(6)	126·5 (3)	118·6 (3)	126·5 (2)
C(5)–N–C(6)	120·9 (3)	131·2 (3)	122·5 (2)
C(2)–N–C(5)	110·4 (3)	109·9 (3)	110·5 (2)
N–C(5)–C(4)	100·4 (3)	99·2 (3)	99·7 (2)
N–C(5)–C(12)	112·9 (3)	113·1 (3)	112·6 (2)
C(4)–C(5)–C(12)	118·0 (4)	115·4 (3)	115·8 (2)
N–C(6)–C(7)	116·9 (3)	118·7 (4)	116·4 (2)

The conformation at the C(7)–C(8) bond is markedly different for the (2*R*,3*S*) isomer compared to the other two analogs. The C(6)–C(7)–C(8)–C(9) torsion angle of −61·0 (5)° contrasts with the transplanar arrangement observed in the (2*S*,3*S*) and (2*S*,3*R*) structures for which the torsion angles are 177·6 (5) and 175·9 (4)°, respectively. The observed conformations presumably reflect the most favorable arrangements dictated by formation of H-bonding interactions of the hydroxyl group at C(8).

The crystal structures are stabilized by H-bonding interactions which differ between structures. In the (2*S*,3*R*) structure an intramolecular H bond exists between the carbonyl O(2) atom and the hydroxyl group at C(8). The associated metrical parameters are O(1)···O(2) = 2·700 (3), HO(1)···O(2) = 1·95 (5) Å with an angle at H of 151 (4)°. In the (2*R*,3*S*) structure there is an intermolecular H bond between the donor atom O(1) and the acceptor carbonyl O. The associated metrical parameters are O(1)···O(2) = 2·855 (4) Å, HO(1)···O(2) = 2·14 (5) Å with an angle at H of 159 (5)°. One intermolecular H bond also exists in the (2*S*,3*S*) structure with associated metrical parameters of O(1)···O(2) = 2·711 (3) Å, HO(1)···O(2) = 1·90 (4) Å and an angle at H of 176 (3)°.

The disorder model for the isopropyl methyl group C(14) in the (2*S*,3*S*) structure, while successfully modeling the electron density of the data set, is less than satisfying structurally. In particular, atom C(14) is not in a tetrahedral relationship relative to C(13). Large extensions of the thermal ellipsoids for C(13) and C(12) suggest a disorder in the atomic position for these atoms as well, although no separate occupancy sites could be resolved. Since there are no particularly close intermolecular contacts to explain the observed disorder [shortest intermolecular contacts are 3·54 (2) and 3·93 (1) Å for atoms C(14′) and C(14), respectively], a possible explanation for the current observations is that restrictions on the vibrational and librational motion of this isopropyl group are minimal in an open space within the solid-state structure.

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Structure of Tetramethylthiuram Disulfide (1) and Refinement of Tetraethylthiuram Disulfide (2)

BY YU WANG,* JU-HSIOU LIAO AND CHUEN-HER UENG

Department of Chemistry, National Taiwan University, Taipei, Taiwan

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Abstract. (1), $C_6H_{12}N_2S_4$, $M_r = 240$, monoclinic, $C2/c$, $a = 9·653$ (1), $b = 9·923$ (1), $c = 11·804$ (2) Å, $\beta = 99·38$ (1)°, $V = 1115·5$ (4) Å^3, $Z = 4$, $D_m = 1·45$ (3), $D_x = 1·43$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·774$ mm^{-1}, $F(000) = 504$, $T = 300$ K, final $R = 0·038$ for 1034 observed reflections. (2), $C_{10}H_{20}N_2S_4$, $M_r = 296$, monoclinic, $P2_1/c$, $a = 11·108$ (2), $b = 15·873$ (2), $c = 8·637$ (3) Å, $\beta = 92·55$ (2)°, $V = 1521·3$ (5) Å^3, $Z = 4$, $D_m = 1·29$ (3), $D_x = 1·30$ Mg m^{-3}. λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·580$ mm^{-1}, $F(000) = 632$, $T = 300$ K, final $R = 0·036$ for 2850 observed reflections. The corresponding

* To whom all correspondence should be addressed.

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