with δ-lactones, and δ-lactones with δ-lactones. Both 2-bromo-α-santonin (Asher & Sim, 1965) and 2-bromo-β-santonin (Coggon & Sim, 1969) stack somewhat similarly in their crystals, but with α,β-unsaturated ketone units rather than lactones apparently interacting along the shortest axes in their unit cells.

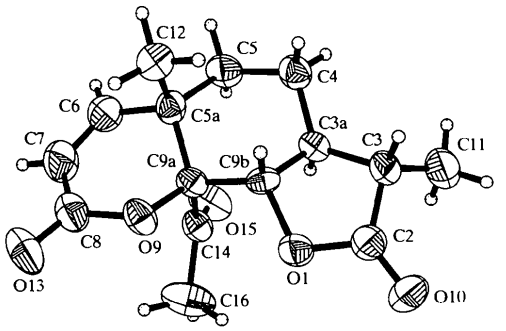

Fig. 1. The structure and atom-numbering scheme of molecule 1 of (I), drawn with 50% probability displacement ellipsoids.

Experimental

Compound (I) was prepared by $KMnO_4$ oxidation of α-santonin as described by Paknikar *et al.* (1994). Crystals were obtained by recrystallization from an ether–benzene (1:1) solution.

Crystal data

$C_{15}H_{18}O_5$
M_r = 278.29
Orthorhombic
$P2_12_12_1$
a = 6.4840 (11) Å
b = 15.2080 (11) Å
c = 28.047 (3) Å
V = 2765.7 (6) Å^3
Z = 8
D_x = 1.337 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 20–26°
μ = 0.100 mm^{-1}
T = 293 (2) K
Rod
0.25 × 0.13 × 0.10 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
5606 measured reflections
4856 independent reflections
2727 reflections with $I > 2\sigma(I)$

R_{int} = 0.028
θ_{max} = 25°
$h = -7 \rightarrow 7$
$k = -18 \rightarrow 18$
$l = -33 \rightarrow 33$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.118
S = 1.004
4856 reflections
362 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0479P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Extinction correction: none

H-atom parameters constrained

Scattering factors from *International Tables for Crystallography* (Vol. C)

Two Friedel-related octants of reflection data were collected to θ = 25°, resulting in 2500 Friedel pairs with $I > 3\sigma(I)$. Refinement of the Flack parameter (Flack, 1983) was unsuccessful; the absolute configuration was then based on that known for α-santonin (Cocker & McMurry, 1960).

Data collection: *CAD-4 Manual* (Enraf–Nonius, 1988). Cell refinement: *CAD-4 Manual*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992–1997). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*b*). Molecular graphics: *XP* in *SHELXTL* (Bruker, 1998). Software used to prepare material for publication: *SHELXL97*.

The title structure was determined by KJM as part of a course in Structural Chemistry taught in the Molecular Structure Laboratory, Department of Chemistry, University of Arizona, Tucson, AZ 85721, USA.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1090). Services for accessing these data are described at the back of the journal.

References

Asher, J. D. M. & Sim, G. A. (1965). *J. Chem. Soc.* pp. 6041–6055.
Bruker (1998). *SHELXTL*. Version 5.0. Bruker AXS Inc., Madison, Wisconsin, USA.
Cocker, W. & McMurry, T. B. H. (1960). *Tetrahedron*, **8**, 181–204.
Coggon, P. & Sim, G. A. (1969). *J. Chem. Soc. B*, pp. 237–242.
Enraf–Nonius (1988). *CAD-4 Manual*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Molecular Structure Corporation (1992–1997). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.8. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Paknikar, S. K., Malik, B. L., Bates, R. B., Caldera, S. & Wijayaratne, T. V. (1994). *Tetrahedron Lett.* **35**, 8117–8118.
Sheldrick, G. M. (1997*a*). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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DL-Cysteine at 298 K

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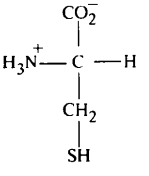
Abstract

In the room-temperature structure of DL-cysteine, $C_3H_7NO_2S$, the L-enantiomer has the *−gauche* confor-

mation [χ^1 = −62.3 (2)°], and this is the third conformation to be found in the cysteine molecule. In addition to three N—H···O hydrogen bonds, an intermolecular S—H···S contact exists with S···S = 3.854 (2) Å. Two hydrogen-bond cycles were identified, each consisting of two DL-pairs.

Comment

For each of the 20 naturally occurring amino acids, an X-ray analysis is known. In most cases, X-ray investigations for the L-form, the racemic DL-form and some simple derivatives of a single amino acid have been carried out. For cysteine, two crystal structures of the L-form are known, namely, a monoclinic and an orthorhombic modification. For the monoclinic form, a room-temperature investigation based on film data (H atoms not determined; Harding & Long, 1968) and a 123 K study (Görbitz & Dalhus, 1996) are reported. For the orthorhombic form, room temperature X-ray (Kerr & Ashmore, 1973) and neutron data (Kerr *et al.*, 1975) have been published. Surprisingly, the structure of the DL-form has not previously been investigated. In our program of comparative charge-density studies of different amino acids, one of the two sulfur-containing amino acids was intended to be included and DL-cysteine, (I), was considered as a suitable representative.



(I)

Crystallization experiments (slow evaporation from an aqueous/ethanol solution) yielded well suited crystals of (I). However, upon cooling of the crystals for high resolution charge-density data collection, all crystals were mechanically destroyed at a temperature of about 217 K. Since this observation could be reproduced for several crystals, we suspect a phase transition to occur at this temperature, although this was not investigated further. Therefore, we were unable to collect a low-temperature data set, but we report here on the room-temperature structure of DL-cysteine.

An *ORTEP*II (Johnson, 1976) representation of the molecular structure with the atomic numbering scheme is shown in Fig. 1. The C—C and C—N bond lengths in (I) compare to within 3σ with the values for the previous cysteine structures. The C—S distance of 1.798 (2) Å is somewhat shorter than that found in the previous X-ray studies, but it is similar to the value for the C—S bond found using neutron techniques [1.796 (8) Å]. It has already been mentioned by Görbitz & Dalhus (1996) that the C—S bond might be affected by thermal motion (or disorder, as found in the neutron structure). If a rigid body motion correction is applied (Schomaker & Trueblood, 1968; Spek, 1990), the C—S distance is lengthened to 1.813 Å for DL-cysteine, while all other bonds become almost uniformly longer, by 0.01 Å.

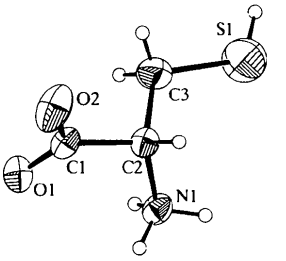


Fig. 1. The molecular structure (*ORTEP*II; Johnson, 1976) of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

With regard to the C—O bonds, it seems that they are influenced by the hydrogen-bonding environment. Atom O2, having the longer C—O length [1.251 (2) Å], is involved in two N—H···O hydrogen bonds, while C—O1 [1.240 (2) Å] is an acceptor of only one N—H···O hydrogen bond. The same situation is found in the orthorhombic L-cysteine structure.

The molecular conformation in (I) can be described by two torsion angles around C2—C3 (χ^1; N1—C2—C3—S1) and C1—C2 (ψ^1; O1—C1—C2—N1). In the L-enantiomer of DL-cysteine, the conformation around C2—C3 is *−gauche* [χ^1 = −62.3 (2)°], and this is the third conformation to be found in cysteine. In the previous cysteine structures, the *+gauche* conformation was found in the orthorhombic form of L-cysteine and in one of the two crystallographically independent molecules of the monoclinic form, while the second molecule was *trans*. The value for the torsion angle around

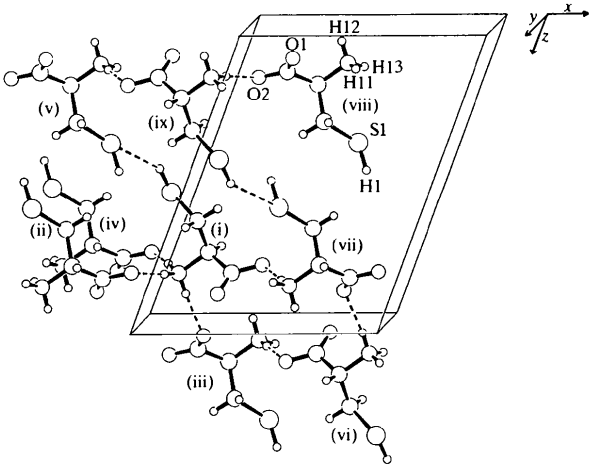


Fig. 2. Packing illustration (*SCHAKAL*88; Keller, 1988) for (I) in a projection of the lattice onto the *xz* plane [symmetry codes: (i) *x*, *y*, *z*; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, 2-z$; (iv) $x-\frac{1}{2}, -\frac{1}{2}-y, z$; (v) $-\frac{1}{2}-x, \frac{1}{2}+y, 1-z$; (vi) $1-x, 1-y, 1-z$; (vii) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (viii) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$; (ix) $-x, 1-y, 1-z$].

C1—C2 [ψ^1 = −29.2 (2)°] is in the range of values found in the previously reported cysteine structures (−4.5 to −35.3°).

A summary of intermolecular contacts indicating hydrogen bonds is given in Table 2 and the hydrogen-bond network is illustrated in Fig. 2. The three H atoms of the charged amino group form distinct N—H···O hydrogen bonds to three neighbouring molecules. Of special interest is the neighbourhood of the thiol group, since in the monoclinic and orthorhombic L-cysteine structures S—H···O and S—H···S contacts were reported. In DL-cysteine we find an S—H···S contact with an S···S distance of 3.854 (2) Å and this is comparable to the S···S distance [3.79 (2) Å] of the disordered sulfur in the neutron structure of the orthorhombic L-cysteine, but is significantly shorter than the value of 4.080 (1) Å reported by Görbitz & Dalhus (1996) in the monoclinic L-cysteine form. A short S—H···O contact does not exist in DL-cysteine, the shortest intermolecular S···O distance being 3.673 (3) Å.

In contrast to the previously investigated pure enantiomeric cysteines, hydrogen bonds constitute connections between D and L pairs of cysteine in the present structure. If both the N—H···O and S—H···S linkages are considered, two hydrogen bond cycles are established, each containing four molecules. The sequences for cycles 1 and 2 are displayed in Fig. 3, showing also that each cycle contains two DL-pairs. Repeated cycles of type 1 form a head-to-head double sheet structure of only N—H···O linkages extending in the x direction and situated around z = 0, 1... The connection between the z = 0 and z = 1 sheets is *via* the cycle 2 sequence containing both N—H···O and S—H···S interactions. Neighbouring sheets in the y direction are linked *via* the third N—H···O hydrogen bond, N1—H13···O2. Through this pattern, N—H···O-rich regions are seen around z = 0, 1... separated by tail-to-tail related S—H···S-rich regions around $z = \frac{1}{2}$.

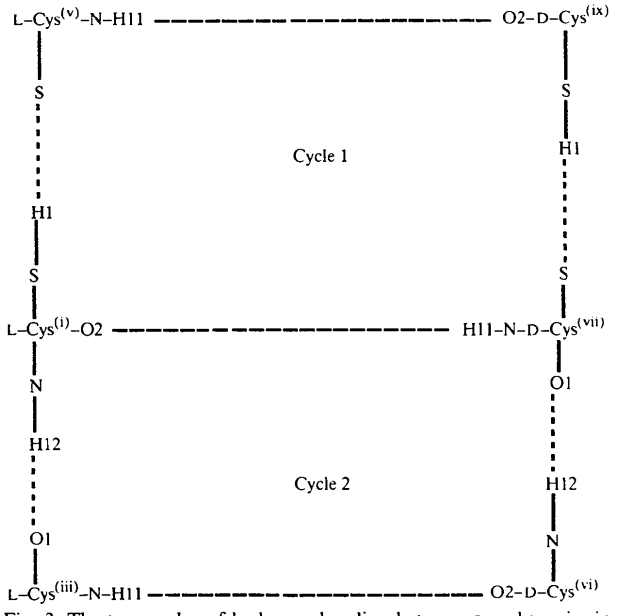


Fig. 3. The two cycles of hydrogen bonding between D and L pairs in (I). Symmetry codes are as in Fig. 2.

Experimental

Crystals of (I) suitable for X-ray analysis were prepared by slow evaporation from a water–ethanol solution.

Crystal data

$C_3H_7NO_2S$
M_r = 121.16
Monoclinic
$P2_1/a$
a = 9.877 (1) Å
b = 4.737 (1) Å
c = 12.877 (1) Å
β = 112.044 (2)°
V = 558.44 (14) Å^3
Z = 4
D_x = 1.441 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 6183 reflections
θ = 1.71–31.32°
μ = 0.470 mm^{-1}
T = 298 (2) K
Plate
0.46 × 0.34 × 0.08 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
6183 measured reflections
1699 independent reflections
1294 reflections with $F > 4\sigma(F_o)$
R_{int} = 0.020
θ_{max} = 31.32°
h = −13 → 14
k = −6 → 6
l = −18 → 18
Intensity decay: 2.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.202
S = 1.060
1699 reflections
65 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.1228P)^2 + 0.1858P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.97 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C1—O1	1.240 (2)	C2—N1	1.485 (2)
C1—O2	1.251 (2)	C2—C3	1.523 (3)
C1—C2	1.539 (2)	C3—S1	1.798 (2)
O1—C1—O2	126.28 (18)	N1—C2—C1	109.19 (14)
O1—C1—C2	117.53 (15)	C3—C2—C1	107.33 (15)
O2—C1—C2	116.07 (17)	C2—C3—S1	115.80 (15)
N1—C2—C3	110.79 (15)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—H11···O2^{ii}	0.89	1.92	2.809 (2)	175
N1—H12···O1^{iii}	0.89	1.89	2.781 (2)	174
N1—H13···O2^{iv}	0.89	1.96	2.829 (2)	165
S1—H1···S1^{v}	1.16	2.83	3.854 (2)	146

Symmetry codes: (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, 2 - z$; (iv) $x - \frac{1}{2}, -\frac{1}{2} - y, z$; (v) $-\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1996). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *SCHAKAL*88 (Keller, 1988) and *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1312). Services for accessing these data are described at the back of the journal.

References

Görbitz, C. H. & Dalhus, B. (1996). *Acta Cryst.* C**52**, 1756–1759.
Harding, M. M. & Long, H. A. (1968). *Acta Cryst.* B**24**, 1096–1102.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA.
Keller, E. (1988). *SCHAKAL*88. *Fortran Program for the Graphic Representation of Molecular and Crystallographic Models*. University of Freiburg, Germany.
Kerr, K. A. & Ashmore, J. P. (1973). *Acta Cryst.* B**29**, 2124–2127.
Kerr, K. A., Ashmore, J. P. & Koetzle, T. (1975). *Acta Cryst.* B**31**, 2022–2026.
Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–77.
Sheldrick, G. M. (1997*a*). *SHELXS*97. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1996). *SMART* and *SAINT*. *Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

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1:1 Adducts of 4-picoline with methylcatecholborane and phenylcatecholborane

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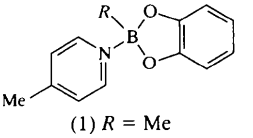
Abstract

In the title compounds, 2-methyl-2-(4-methylpyridine)-1,3,2-benzodioxaborole, $C_{13}H_{14}BNO_2$, and 2-(4-methylpyridine)-2-phenyl-1,3,2-benzodioxaborole, $C_{18}H_{16}BNO_2$, boron has a distorted tetrahedral coordination geometry, the two O—B—C angles being greater and all other angles at boron smaller than the ideal tetrahedral value. Both structures contain two crystallographically independent molecules, and all corresponding geometrical parameters in them are essentially the same, except for minor torsional variations. Bond lengths involving boron are similar to those of related adducts of phenylcatecholborane, and longer than those in the parent compound itself and related compounds with trigonal planar boron.

Comment

In conjunction with our recent work on coordination of phosphines and amines to diborane(4) compounds (Nguyen *et al.*, 1995; Clegg *et al.*, 1997), we have also investigated the formation of adducts between Lewis bases and organoboranes containing the catecholboryl unit bound to alkyl and aryl groups. Because of their facile preparation (Wieber & Künzel, 1974), methyl- and phenylcatecholboranes were chosen as model substrates. NMR studies of these three-coordinate boron compounds have been reported by Goetz *et al.* (1981). Our findings show a similar Lewis acidity to that observed for the diborane(4) compound $B_2(cat)_2$ (cat = 1,2-$O_2C_6H_4$). Thus, no evidence for adduct formation was observed in reactions between the catecholboryl derivatives and phosphines, even with the highly basic PMe_3, and only amines were capable of coordinating to the B atom. We report here the structures of the adducts 2-methyl-2-(4′-methylpyridine)-1,3,2-benzodioxaborole, (1), and 2-phenyl-2-(4′-methylpyridine)-1,3,2-benzodioxaborole, (2), formed between these organoboranes and 4-picoline. These adducts have been discussed previously (Wieber & Künzel, 1974), but only very limited data were reported for them.



(1) *R* = Me
(2) *R* = Ph

Both crystal structures contain two independent molecules in the asymmetric unit (Figs. 1 and 2). In each case there are no significant differences between the two molecules other than unimportant variations in the orientations of substituents attached to boron as measured by torsion angles around B—C and B—N bonds. Corresponding molecular-geometry parameters for the two compounds are also essentially the same (Tables 1 and 2). There are no particularly short intermolecular contacts. The B atom in each case has distorted tetrahedral coordination; the catecholate chelating group gives an O—B—O angle which is smaller than the ideal tetrahedral angle, and the two