

Crystal and Molecular Structure of Chondrine, $C_5H_9NO_3S$

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The crystal structure of chondrine has been determined and refined on the basis of data collected with an automatic diffractometer. The crystals are orthorhombic, space group $P2_12_12_1$, with cell dimensions $a=9.694$, $b=7.640$ and $c=9.249$ Å, with four molecules per unit cell. The structure was determined by interpretation of the Patterson function and was refined by the least-squares method to an R index of 0.034. The six-membered ring has the chair conformation with the S–O bond axial and the bond to the carboxyl group equatorial. The molecules are zwitterions in the crystal and are held together by a network of N–H \cdots O hydrogen bonds.

Introduction

The crystal and molecular structure of chondrine was undertaken as part of our continuing interest in the molecular conformation of cyclic sulfoxides. Chondrine was first isolated by Kuriyama, Takagi & Murata (1960) from the red alga *Chondria crassicaulis*. The compound was later found in a brown alga *Undaria pinnatifida* (Tominaga & Oka, 1963). The configuration of the carbon atom bearing the carboxyl group was known to be $L(R)$ (Carson, Boggs & Lundin, 1970) and n.m.r. data suggested a chair conformation with the carboxyl group equatorial. Chondrine is a lower homologue (one less methyl group) of cycloalliin, 5-(S)-methyl-1,4-thiazane-3(R)-carboxylic acid-1-(S)-oxide, a natural component of onions and important in its relationship to the flavor precursor of onions, trans (+)- S -(1-propenyl)-L-cysteine S -oxide. The crystal structure of cycloalliin as the hydrochloride hydrate has been determined (Palmer & Lee, 1966). In view of the interest in cyclic sulfoxides, particularly with reference to conformational problems, the structure of these unusual cyclic sulfoxide amino acids is important. In particular, knowledge of the configuration of the sulfoxide and the conformation of the ring are needed in order to validate empirical rules based on n.m.r. and infrared data which have been proposed for cyclic sulfoxides and applied to 1,4-thiazane S -oxides related to chondrine (Carson *et al.*, 1970).

Experimental

Crystals of chondrine suitable for X-ray analysis were grown from a water-ethanol mixture. They were almost isodimensional rectangular prisms. The crystal used for the determination of intensities had dimensions $0.18 \times 0.14 \times 0.16$ mm parallel to a , b and c respectively. Since the linear absorption coefficient for chondrine is 36.9 cm^{-1} (Cu $K\alpha$), the data were not corrected for absorption. The density, measured by flotation, was 1.58 g.cm^{-3} .

The unit cell dimensions were obtained by averaging the results obtained from θ - 2θ scans for $h00$, $0k0$ and $00l$ reflections, measured with a diffractometer. The crystal used for both the determination of cell dimensions and the collection of intensity data was mounted on the b axis. The crystallographic data are summarized below.

$C_5H_9NO_3S$	F.W. 163.20
Orthorhombic	Space group $P2_12_12_1$
$a=9.694$ (2) Å	$Z=4$
$b=7.640$ (2)	$F(000)=344$
$c=9.249$ (2)	$D_m=1.58 \text{ g.cm}^{-3}$
$\lambda(\text{Cu } K\alpha)=1.5418$ Å	$D_c=1.57 \text{ g.cm}^{-3}$
Number of independent reflections	658

Integrated intensities were obtained on an automatic diffractometer by using a θ - 2θ scan at 1° per min and subtracting a background calculated by averaging the two values obtained by counting for 20 sec at $\frac{1}{2}^\circ$ before the beginning of the scan and $\frac{1}{2}^\circ$ beyond the end of the scan. 1394 reflections were measured of which 658 were independent. Of these, four were measured as zero and the intensities of 15 others were less than $\sigma(I)$ where $\sigma(I)$ was calculated by the expression $\sigma(I)=[C+(T_c/2T_b)^2(B_1+B_2)+(0.05 I)^2]^{1/2}$. C is the total counts in scan time T_c , B_1 and B_2 are background counts taken for $T_b=20$ sec. The factor 0.05 was arbitrarily chosen to account for non-random errors.

Lorentz and polarization corrections were applied to the data, and a correction for secondary extinction was made in the final stages of refinement.

Determination of the structure

A three-dimensional Patterson synthesis yielded the atomic coordinates of sulfur and two other atoms, which were subsequently identified as C(1) and C(3). Three cycles of full-matrix least-squares calculations resulted in an R index, defined as $\sum||F_o|-|F||/\sum|F_o|$, of

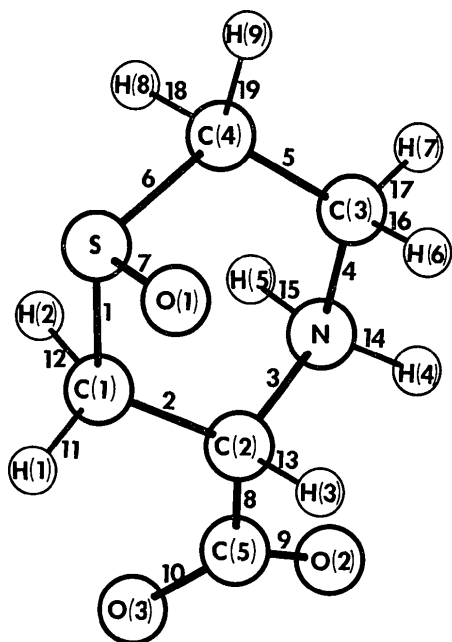


Fig. 1. The structure of chondrine with the atom and bond numbering system used in this investigation.

EF appears to be 4×10^{-7} . This correction gave a final R index of 0.034. The final values for the positional and thermal parameters and their standard deviations are listed in Table 1. The observed and calculated structure factors are given in Table 2.

The residual electron density distribution shows a number of small peaks, the largest of which is $0.20 \text{ e.}\text{\AA}^{-3}$.

Description of the structure

The molecular structure of chondrine and the atom numbering system used in this investigation are shown in Fig. 1. A stereoscopic drawing of the molecule, which illustrates its conformation, was made with the ORTEP program (Johnson, 1965) and is shown in Fig.

2. The absolute configuration about the C(2) carbon atom is known to be $L(R)$ (Carson *et al.*, 1970). From Fig. 2 it is evident that the six-membered ring has the chair conformation and the carboxyl group is oriented equatorially, in agreement with the conclusions based on an n.m.r. study of chondrine (Carson *et al.*, 1970). The sulfoxide bond is axially oriented, which agrees with the orientation found in cycloalliin (Palmer & Lee, 1966).^{*} The thermodynamic arguments which have been used to suggest that the axial orientation for the oxygen atom in thianes is preferred (Lambert & Keske, 1966; Lambert, Bailey & Mixan, 1972) is valid for the two known naturally occurring cyclic sulfoxides, chondrine and cycloalliin.

The Fourier difference synthesis, used to locate the hydrogen atoms, showed two significant electron peaks near the nitrogen atom and none near either carboxyl oxygen atom. Consequently, it is concluded that the chondrine molecule occurs as the zwitterion in the crystal.

The two hydrogen atoms bonded to nitrogen form hydrogen bonds, one to the sulfoxide oxygen atom, and the other to the carboxyl oxygen atom O(3). The carboxyl oxygen atom, O(2), does not participate in hydrogen bonding. The network of hydrogen bonds which help to hold the chondrine molecules together in the crystal is shown in Fig. 3, which is a projection of the structure onto the (101) plane. The hydrogen bond distances and angles listed in Table 3 indicate that the hydrogen bond formed by the carboxyl oxygen atom is somewhat stronger than that formed by the sulfoxide oxygen atom.

Table 3. *Hydrogen bond distances and angles in chondrine*

E.s.d.'s for the distance are 0.005 \AA and for the angles 3.0° .

	Distance	Angle
N-H(4)···O(1')	2.770 Å	149°
N-H(5)···O(3')	2.660	173

^{*} The y parameters given in Table 1 of their paper are incorrect: they should all have negative signs. The drawings in the paper, Figs. 1 and 2, do show the correct stereoisomer.

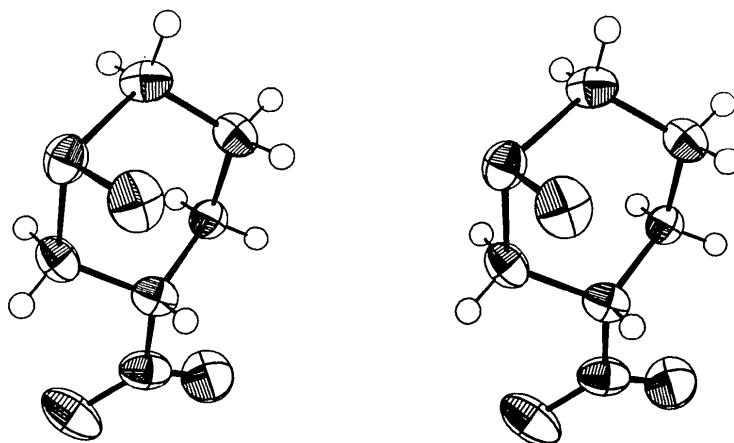


Fig. 2. A stereoscopic view of chondrine. The thermal ellipsoids are drawn at the 50% probability level.

The interatomic bond distances and angles are given in Tables 4 and 5 respectively. All the bond distances are very similar to those reported for cycloalliin, except for the C–O bonds of the carboxyl group. In cycloalliin, these two bonds are 1.311 and 1.195 Å, whereas in chondrine they are 1.260 and 1.224 Å. This difference is presumably due to the fact that in cycloalliin the carboxyl group is not ionized, and therefore there is less resonance between the C–O bonds than there is in the ionized carboxyl group of chondrine. The S–O distance of 1.495 Å in chondrine is in good agreement with the value of 1.492 Å reported for cycloalliin (Palmer & Lee, 1966), 1.493 Å reported for (+)-methyl-*p*-tolyl sulfoxide (De la Camp & Hope, 1970), and 1.488 Å reported for (+)-*S*-methyl-L-cysteine sulfoxide (Hine, 1962).

Table 4. *Interatomic distances in chondrine*

E.s.d.'s are 0.005 Å for the heavy atoms and 0.1 Å for hydrogen atoms. The bond numbers refer to Fig. 1.

Bond no.	Bond distance (Å)	Bond no.	Bond distance (Å)
1	1.806	11	0.85
6	1.795	12	1.09
2	1.505	13	0.80
5	1.490	14	0.86
3	1.483	15	0.94
4	1.483	16	0.88
8	1.543	17	0.81
7	1.495	18	0.99
9	1.224	19	0.97
10	1.260		

The bond angles in chondrine and cycloalliin agree fairly well. The C(1)–S–C(4) angle of 95.9° is consistent with the observations reported for other sulfoxides of 96.9, 96.7 and 97.6°. The only large discrepancy between chondrine and cycloalliin is the angle C(1)–C(2)–C(5) which has the value 114.0° in chondrine and 109.8° in cycloalliin. No obvious explanation for this difference is apparent. In chondrine the C–S–O angles are both slightly less than tetrahedral, the two S–C–C angles slightly greater, and the C–N–C angle considerably greater than the tetrahedral value. A very similar distortion of the ring angles was observed in cycloalliin (Palmer & Lee, 1966). The bond distances and bond

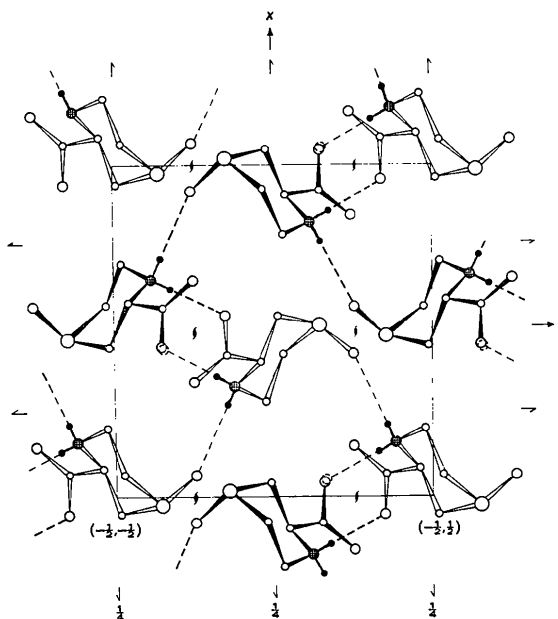


Fig. 3. Projection of structure onto the (101) plane. The four N–H...O hydrogen bonds formed by each molecule are illustrated. The nitrogen atoms are shown as hatched circles; the sulfur, oxygen and carbon atoms as open circles of decreasing size; and the hydrogen atoms involved in hydrogen bonds as solid circles.

Table 5. *Interatomic bond angles for chondrine*

E.s.d.'s are 0.10° for angles involving heavy atoms and 3.0° for angles involving hydrogen atoms. The bond numbers refer to Fig. 1.

Bond angle	Bond angle	Bond angle	Bond angle	Bond angle	
1,6	95.9°	1,12	108°	4,16	105°
1,7	106.4	1,11	105	4,17	112
6,7	106.6	2,11	111	5,16	118
1,2	113.2	2,12	107	5,17	112
2,3	110.4	11,12	112	16,17	97
2,8	114.0	2,13	108	5,18	109
3,8	107.0	3,13	110	5,19	109
3,4	114.8	8,13	107	6,18	111
4,5	112.2	3,14	114	6,19	101
5,6	112.4	3,15	110	18,19	115
8,9	117.0	4,14	109		
8,10	115.3	4,15	109		
9,10	127.7	14,15	99		

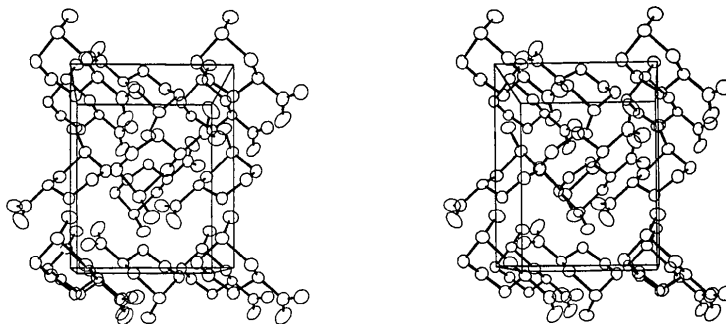


Fig. 4. A stereoscopic drawing of the unit cell of chondrine. The structure is viewed parallel to the *a* axis. The thermal ellipsoids are scaled to include 50% probability.

angles involving the hydrogen atoms are known with only approximate accuracy. The values reported are typical of those obtained by X-ray diffraction for other organic molecules.

The packing of the molecules is illustrated by the stereoscopic view of the unit cell shown in Fig. 4. This view shows clearly how one carboxyl oxygen and the sulfoxide oxygen atom point toward the NH₂ group, while the second carboxyl oxygen atom occupies an open part of the structure. The chondrine molecules pack together to form a compact structure which enables the maximum number of intermolecular hydrogen bonds to be formed between the oxygen atoms and the NH₂ group.

The thermal parameters for the heavy atoms are sufficiently small to suggest that the chondrine molecules are rather firmly held in the crystal by the N-H...O hydrogen bonds, the electrostatic attraction of the zwitterions, and van der Waals forces. There is no appreciable oscillation about the C(2)-C(5) bond, as verified by the small size of the 50% probability ellipsoids for O(2) and O(3) shown in Fig. 4.

The closest intermolecular approaches between heavy atoms, which are not hydrogen bonded, are 3.117 Å for O(1)...C(3'), and 3.306 Å for O(1)...C(4'); these distances are normal. Several additional intermolecular distances occur between 3.38 and 3.50 Å.

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The Crystal Structures of Two Solvates of 5,5',6,6'-Tetrachloro-1,1',3,3'-Tetraethylbenzimidazolocarboyanine Iodide

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The title compound, C₂₅H₂₇N₄Cl₄I, DYE, is an efficient spectral sensitizer of silver halide photographic systems and is known to form *J*-aggregates with ease. We have determined the crystal structures of the 2:1 methanol:DYE solvate (DYEM) and the 1:1 acetonitrile:DYE solvate (DYEA) from single-crystal X-ray intensity data collected with an automated diffractometer. DYEM is monoclinic, *P*2₁/*a*, with *a* = 22.547 (9), *b* = 11.036 (5), *c* = 13.375 (5) Å, β = 107.48 (1)° and *Z* = 4; DYEA is triclinic, *P*1, with *a* = 10.392 (3), *b* = 8.242 (2), *c* = 9.284 (2) Å, α = 93.92 (2), β = 107.81 (1), γ = 77.71 (2)° and *Z* = 1. The structures were solved by the heavy-atom technique and refined by block-diagonal least-squares methods. The final *R* values are 0.033 for DYEM and 0.040 for DYEA. The distances and angles for the cations in the two structures agree very well with each other and with the usual accepted values. In spite of the extensive conjugation the cations are only approximately planar. In both structures, the cations pack plane to plane, and end to end on edge in sheets parallel to (100) separated by sheets containing the anions and solute molecules. There is a remarkable similarity of the (100) projections of the cation sheets in the two structures to each other and to the arrangement of ions in (111) faces of AgBr.

Introduction

Spectral sensitization, the process by which the photographic or photoconductive sensitivity of a material is

extended into spectral regions outside its intrinsic absorption region, was discovered a century ago by Vogel (1873). Since then, the effect, which is indispensable to photographic technology, has been studied intensively