

## Références

- AUBRY, A., MARRAUD, M., PROTAS, J. & NÉEL, J. (1971). *C.R. Acad. Sci. Paris, Sér. C*, **273**, 959–961.
- AUBRY, A., MARRAUD, M., PROTAS, J. & NÉEL, J. (1972). *C.R. Acad. Sci. Paris, Sér. C*, **274**, 1378–1381.
- AUBRY, A., MARRAUD, M., PROTAS, J. & NÉEL, J. (1973a). *C.R. Acad. Sci. Paris, Sér. C*, **276**, 579–582.
- AUBRY, A., MARRAUD, M., PROTAS, J. & NÉEL, J. (1973b). *C.R. Acad. Sci. Paris, Sér. C*, **276**, 1089–1092.
- BYSTROV, V. F., PORTNOVA, S. L., TSETLIN, V. T., IVANOV, V. T. & DVCHINNIKOV, YU. A. (1969). *Tetrahedron*, **25**, 493–515.
- CHEN, C. Y. S. & SWENSON, C. A. (1969). *J. Phys. Chem.* **73**, 1363–1366, 2999–3008.
- FERBER, E. & BRÜCKNER, H. (1943). *Chem. Ber.* **70**, 1019–1027.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- ICHIKAWA, T. & IITAKA, Y. (1969). *Acta Cryst.* **B25**, 1824–1833.
- IUPAC-IUB COMMISSION ON BIOLOGICAL NOMENCLATURE (1970). *Biochem. Wash.* **9**, 3471–3479.
- RAMACHANDRAN, G. N., CHANDRASEKHARAN, R. & KOPPLE, K. D. (1971). *Biopolymers*, **10**, 2113–2131.
- RAMACHANDRAN, G. N. & SASISEKHARAN, V. (1968). *Advanc. Protein Chem.* **23**, 283–437.
- THONG, C. M., CANET, D., GRANGER, P., MARRAUD, M. & NÉEL, J. (1969). *C.R. Acad. Sci. Paris, Sér. C*, **269**, 580–583.

*Acta Cryst.* (1973). **B29**, 2580

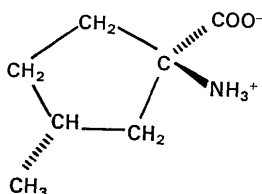
## The Crystal Structure of an Isomer of 1-Amino-3-methylcyclopentanecarboxylic Acid

BY H. L. CARRELL, BARBARA GALLEN AND JENNY PICKWORTH GLUSKER

*The Institute for Cancer Research, Fox Chase Center for Cancer and Medical Sciences, Philadelphia, Pa., U.S.A.*

(Received 23 April 1973; accepted 11 June 1973)

The crystal structure of the isomer of 1-amino-3-methylcyclopentanecarboxylic acid that inhibits the methionine adenosyltransferase reaction was studied by X-ray diffraction, using three-dimensional data. The crystals are monoclinic, space group *A2*. There are four molecules of the amino acid,  $C_7H_{13}O_2N$ , and two water molecules per unit cell. The unit-cell dimensions are  $a = 13.618$  (3),  $b = 6.093$  (1),  $c = 10.217$  (2) Å,  $\beta = 95.93$  (2)°,  $V = 843.2$  Å<sup>3</sup>. The calculated and measured densities are 1.20 and 1.21 g cm<sup>-3</sup> respectively. 872 three-dimensional diffractometer data were collected with Cu  $K\alpha$  radiation. The structure was solved by direct methods and refined by a full-matrix least-squares procedure to the final residual  $R = 0.064$  for the 589 data with non-zero weights. All hydrogen atoms were located and were refined isotropically. The structure determination showed that the carboxyl group and methyl group lie on the same side of the ring system, *i.e.* that the 1*R*:3*R* or 1*S*:3*S* isomer is the active inhibitor. However, since the compound was prepared from a 3*R* ketone it is assumed that the inhibitor is the 1*R*:3*R* isomer.



### Experimental

The synthesis of 1-amino-3-methylcyclopentanecarboxylic acid from 3*R*-cyclopentanone was carried out by Dr H. Doshan, Department of Pharmacology and Experimental Therapeutics, The Johns Hopkins University, according to the procedure of Zelinsky & Stodnikoff (1906). Details will be published by A. W. Coulter, J. B. Lombardini & Paul Talalay. Crystals were grown from aqueous solution as fragile flat laminated plates. The crystal data are summarized in Table 1. A crystal, 0.2 × 0.2 × 0.03 mm, was used to collect three-dimensional data on a Syntex automated

diffractometer with monochromatic Cu  $K\alpha$  radiation. The variable  $\theta$ - $2\theta$  scan technique was used. Intensities were measured for 872 unique reflections. Measurements on three standard reflections during the data collection indicated no intensity fall-off during exposure to X-rays. Values for  $\sigma(I)$  were derived from counting statistics and measured instrumental uncertainties. There were 283 reflections for which the measured intensity,  $I_{\text{obs}}$ , was less than  $2\sigma(I_{\text{obs}})$ . When  $I_{\text{obs}} < 0.77\sigma(I_{\text{obs}})$ ,  $I_{\text{obs}}$  was set equal to  $0.77\sigma(I_{\text{obs}})$ . The intensity data were converted to structure amplitudes by application of Lorentz and polarization factors and placed on an absolute scale with a Wilson plot. No

absorption correction was applied. The intensity statistics indicated a non-centric structure.

Table 1. *Crystal data for 1-amino-3-methylcyclopentanecarboxylic acid*

Formula: $C_7H_{13}O_2N \frac{1}{2}H_2O$	F.W. 152.2
Crystal system: monoclinic	
$a = 13.618$ (3), $b = 6.093$ (1), $c = 10.217$ (2) Å, $\beta = 95.93$ (2)°	
(from 15 reflections measured on a diffractometer with Cu $K\alpha_1/K\alpha_2$ peaks resolved. Cu $K\alpha_1$ radiation, $\lambda = 1.5405$ Å).	
$V = 843.2$ Å <sup>3</sup>	$F(000) = 332$
$D_x = 1.20$ g cm <sup>-3</sup>	$Z = 4$
$D_m = 1.21$ g cm <sup>-3</sup> (in a mixture of 1,1-dichloroethane and 1,2-dibromoethane)	
$\mu$ (Cu $K\alpha$ ) = 6.7 cm <sup>-1</sup>	
Space group: $A2$	Systematic absences: $hkl$ with $k+l$ odd
General positions: $(0, 0, 0; 0, \frac{1}{2}, \frac{1}{2}) + x, y, z$ $-x, y, -z$	
872 unique data measured, 589 with $I \geq 2\sigma(I)$	
Maximum $\sin \theta/\lambda = 0.606$	
Statistics on $E$ values:	
$ E  = 0.872$ , $ \bar{E}_2  = 1.000$ , $ \bar{E}_2 - \bar{1}  = 0.794$ indicating a non-centric structure.	

### Structure determination and refinement

The structure was solved by direct methods with a multiple-solution program (Main, Woolfson & Germain, 1971) using 164 reflections with  $E > 1.25$ . The first solution tried was the correct one. The first  $E$  map gave the position of all heavy atoms except the methyl carbon atom. The resulting structure-factor calculation had a value of  $R = \sum |\Delta F| / \sum |F_o|$  (for reflections with non-zero weights) of 0.25. The  $R$  value for the complete structure, determined from another Fourier map was 0.20. After 3 cycles of isotropic and 2 cycles of anisotropic full-matrix least-squares refinement, the  $R$

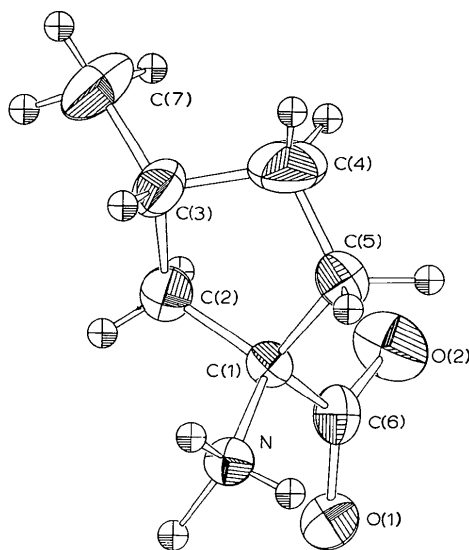


Fig. 1. View of molecule with thermal ellipsoids.

value was 0.104. The positions of the hydrogen atoms were derived from difference Fourier syntheses. These were included in two further least-squares cycles which resulted in  $R = 0.064$ , and a weighted  $R$  value of 0.048. All shifts were less than one estimated standard deviation. The weights used in the refinement were  $1/[\sigma^2(F_o)]$ ; those data with  $I_{obs} < 2\sigma(I)$  were assigned zero weight. The quantity minimized was  $\sum w[|F_o| - |F_c|]^2$ .

The atomic scattering factors used for oxygen, nitrogen and carbon atoms were those in *International Tables for X-ray Crystallography* (1962) and for hydrogen atoms those of Stewart, Davidson & Simpson (1965). Computer programs used in this determination were *MULTAN* (Main *et al.*, 1971), the X-RAY 70 System (Stewart, Kundell & Baldwin, 1970), and *UCLALS4* (full-matrix least-squares) (Gantzel, Sparks, Long & Trueblood, 1969), modified by H. L. Carrell.

The final atomic parameters are listed in Table 2. Fig. 1 is a view of the molecule with thermal ellipsoids (Johnson, 1965) and angles and distances in the compound with their estimated standard deviations are

Table 2. *Final atomic parameters*

Positional parameters are given as fractions of cell edges. Anisotropic temperature factors are expressed as:

$$\exp - [ \frac{1}{4}(h^2 a^{*2} B_{11} + k^2 b^{*2} B_{22} + l^2 c^{*2} B_{33} + 2hka^* b^* B_{12} + 2hla^* c^* B_{13} + 2klb^* c^* B_{23}) ],$$

and isotropic temperature factors as  $\exp -(B \sin^2 \theta/\lambda^2)$  with  $B$  values given in Å<sup>2</sup>. The standard deviations for each parameter, determined from the inverted full matrix, are given in parentheses and apply to the last specified digits. Positional parameters for hydrogen atoms are  $\times 10^3$ , for other atoms  $\times 10^4$ . Anisotropic temperature parameters are  $\times 10^2$ .

	$x$	$y$	$z$	$B$
O(W1)	5000 (0)	5000 (0)	5000 (0)	
O(1)	4627 (2)	1855 (8)	3028 (3)	
O(2)	3157 (3)	751 (9)	3541 (4)	
N	3958 (3)	3783 (10)	839 (4)	
C(1)	3183 (3)	3043 (12)	1686 (5)	
C(2)	2628 (4)	5029 (13)	2142 (5)	
C(3)	1660 (4)	5210 (14)	1273 (6)	
C(4)	1439 (4)	2770 (17)	1020 (9)	
C(5)	2387 (4)	1688 (14)	837 (5)	
C(6)	3700 (4)	1749 (12)	2855 (5)	
C(7)	844 (5)	6410 (20)	1863 (10)	
H(1W)	488 (5)	438 (10)	437 (5)	4 (2)
H(21)	251 (2)	479 (7)	304 (4)	1 (1)
H(22)	298 (4)	623 (13)	218 (6)	8 (2)
H(31)	175 (3)	588 (9)	35 (4)	3 (1)
H(41)	93 (4)	269 (14)	53 (6)	9 (2)
H(42)	108 (5)	201 (16)	188 (8)	11 (3)
H(51)	240 (3)	3 (10)	112 (4)	4 (1)
H(52)	257 (3)	155 (10)	0 (5)	5 (1)
H(71)	76 (4)	537 (15)	287 (6)	9 (2)
H(72)	29 (5)	716 (14)	142 (7)	12 (3)
H(73)	108 (5)	779 (13)	228 (7)	8 (2)
H(N1)	463 (3)	482 (11)	130 (5)	5 (2)
H(N2)	369 (4)	451 (12)	-3 (6)	7 (2)
H(N3)	421 (4)	261 (10)	59 (5)	3 (1)
C(5a)	1382 (11)	2574 (33)	1278 (18)	3.8 (4)
C(7a)	754 (13)	6467 (44)	1692 (19)	3.5 (5)
C(5b)	1471 (15)	2995 (44)	779 (21)	4.4 (5)
C(7b)	933 (17)	6416 (53)	2212 (25)	6.1 (7)

Table 2 (cont.)

	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
O(W1)	529 (27)	254 (29)	257 (25)	0 (0)	16 (41)	0 (0)
O(1)	338 (15)	377 (21)	266 (17)	42 (38)	-86 (25)	84 (38)
O(2)	534 (20)	626 (30)	306 (20)	-82 (48)	-6 (31)	283 (43)
N	252 (17)	278 (23)	192 (19)	7 (38)	-1 (27)	31 (41)
C(1)	239 (19)	245 (28)	140 (22)	-19 (46)	42 (33)	7 (47)
C(2)	355 (24)	310 (33)	273 (26)	9 (56)	89 (42)	20 (59)
C(3)	386 (27)	316 (34)	483 (35)	106 (68)	74 (50)	71 (72)
C(4)	276 (30)	715 (60)	1053 (60)	0 (75)	-100 (67)	-311 (141)
C(5)	371 (24)	321 (31)	219 (25)	-62 (63)	-6 (39)	-72 (58)
C(6)	406 (24)	248 (29)	195 (24)	-7 (62)	14 (41)	-64 (55)
C(7)	554 (35)	568 (56)	1247 (69)	285 (88)	260 (84)	25 (145)

given in Fig. 2. Calculated and observed structure factors are available.\*

### Discussion of the structure

In a study of analogues of methionine as substrates and inhibitors of the methionine adenosyltransferase reaction (ATP: L-methionine *S*-adenosyltransferase, E.C. 2.5.1.6) it was found that one of the four isomers of 1-amino-3-methylcyclopentanecarboxylic acid is a moderately powerful inhibitor (Lombardini, Coulter & Talalay, 1970) whereas the other three isomers were considerably less active. This study was undertaken in order to determine the relative configuration of the compound so that its spatial relationship to the substrate L-methionine could be determined. The compound is an analogue of 1-aminocyclopentanecarboxylic acid (cycloleucine). The latter is also an inhibitor of the adenosyltransferase reaction (Lombardini *et al.*, 1970) and is currently being studied as an antitumor

agent (Berlinguet, Begin & Sarkar, 1962; Carter, 1970).

The distances and angles shown in Fig. 2, the fact that the two C-O distances in the carboxyl group are nearly equal, together with the locations of hydrogen atoms, imply that in this structure the amino acid exists as a zwitterion. As illustrated in Fig. 3, the carboxyl group and the methyl group lie on the same side of the cyclopentane ring in the zwitterion, *i.e.* the isomer is 1*R*:3*R* or 1*S*:3*S*. However, since the compound was prepared from a 3*R* ketone (Lombardini *et al.*, 1970), it is assumed that the active inhibitor is the 1*R*:3*R* isomer.

The angles in the cyclopentane ring vary between 104.6 and 107.9° except for the angle at the site of methyl substitution, C(2)-C(3)-C(4), which is 99.9°. The external angles C(2)-C(3)-C(7) and C(4)-C(3)-C(7) are 115.7 and 113.4° respectively, with the sum of these three angles equal to the sum of three tetrahedral angles.

In the cyclopentane ring system the temperature factor for C(5) is high, with the maximum motion perpendicular to the ring system. This is a common situation in cyclopentane derivatives and, in the case of the unmethylated compound (Mallikarjunan, Chacko &

\* This table has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30158 (10 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Torsion angles and pseudorotation parameters

	Ordered model	Disordered model	
		<i>a</i>	<i>b</i>
C(5)-C(1)-C(2)-C(3)	$\varphi_0$	-17.0 (-12.4, -23.5°)	-17.0°
C(1)-C(2)-C(3)-C(4)	$\varphi_1$	33.9 (32.4, 38.0)	43.6
C(2)-C(3)-C(4)-C(5)	$\varphi_2$	-39.5 (-40.0, -38.0)	-52.6
C(1)-C(5)-C(4)-C(3)	$\varphi_3$	30.0 (32.4, 23.5)	44.1
C(2)-C(1)-C(5)-C(4)	$\varphi_4$	-7.9 (-12.4, 0.00)	-19.0
O(1)-C(6)-C(1)-N		11.8°	
O(2)-C(6)-C(1)-N		-169.7	
O(1)-C(6)-C(1)-C(2)		-109.1	
O(1)-C(6)-C(1)-C(5)		133.0	
O(2)-C(6)-C(1)-C(2)		69.5	
O(2)-C(6)-C(1)-C(5)		-48.5	
C(6)-C(1)-C(2)-C(3)		-140.1	
C(6)-C(1)-C(5)-C(4)		114.1	
C(1)-C(2)-C(3)-C(7)		156.0	158.5

Equation (Altona, Geise & Romers, 1968)

$$\varphi_j = \varphi_m \cos(\Delta/2 + 144j)$$

Assuming  $\varphi_0 = \text{C}(5)\text{-C}(1)\text{-C}(2)\text{-C}(3)$

Ordered model  $\varphi_m = 40.0^\circ$ ,  $\Delta = 481.4^\circ$

(Values in parentheses are calculated values for the half-chair and envelope models, respectively.)

Disordered model (a)  $\varphi_m = 53.9^\circ$ ,  $\Delta = 504.7^\circ$

(b)  $\varphi_m = 24.4^\circ$ ,  $\Delta = 450.2^\circ$

Zand, 1972) the comparable atom was found to be best represented by two positions with 50% occupancy. Therefore, in order to test whether there is a similar situation in this methylated compound, the two atoms C(5) and C(7) were each split into two half atoms which were refined isotropically by full-matrix least-squares methods. The  $R$  value increased to 0.081, and the half atoms refined to positions 0.59 Å apart for C(5a) and C(5b) and 0.56 Å apart for C(7a) and C(7b) with very similar isotropic temperature factors (see Table 2). However, neither bond lengths nor bond angles were improved and, in view of the increased  $R$  value, the value of this refinement is questionable.

The puckered forms of a cyclopentane ring are favored over the planar conformation by approximately 4 kcal mole<sup>-1</sup> (Kilpatrick, Pitzer & Spitzer, 1947). There are two symmetrical puckered forms designated the 'half-chair' and the 'envelope', and all possible intermediates between these with constant energies and bond angles (thus excluding the planar form) are possible. Therefore, since there is a continuum of possible conformations as a result of pseudo-rotation (*i.e.* the puckering can move around the rings), it is necessary to have a mathematical designation for the shape of a ring system with respect to the total pseudo-

rotation pathway (Altona, Geise & Romers, 1968). The observed puckering may be described in terms of the torsion angles, listed for this compound in Table 3, and these torsion angles,  $\varphi_j$ , may be fit to a formula  $\varphi_j = \varphi_m \cos(\Delta/2 + 144j)$  where  $j$  is an integer (0–4) and  $\varphi_m$  is a maximum possible value for the torsion angles. The term  $\Delta$ , which can vary from 0–720°, is referred to as the phase angle, and when it is an even multiple of 36° the ring is in the half-chair ( $C_2$ ) conformation; when it is an odd multiple the ring is in the envelope ( $C_s$ ) conformation. In order to consider the disordered and ordered molecules in an equivalent manner we have arbitrarily chosen  $\varphi_0$  to be the torsion angle C(5)–C(1)–C(2)–C(3). The value found for  $\Delta$  was 481.4° for the ordered molecule, and values of 504.7 and 450.2° respectively were found for the disordered molecules *a* and *b*. (The nearest value for a half-chair would be 504.0°, while for an envelope the nearest values would be 468.0 or 540.0°.) Thus molecule *a* has a half-chair conformation in the cyclopentane ring while molecule *b* has more nearly an envelope conformation and the ordered molecule lies nearer to a half-chair than an envelope conformation. Table 4 gives deviations of the atoms from the least-squares plane through the ring.

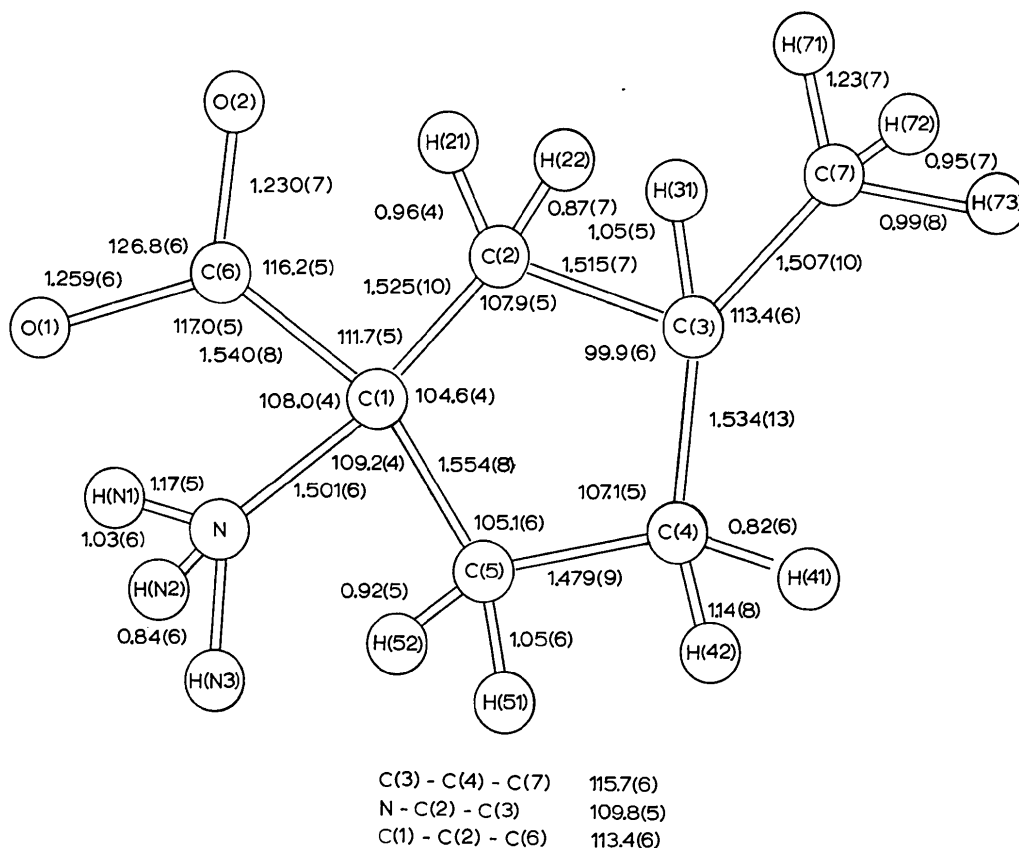


Fig. 2. Distances (Å) and angles (°) with estimated standard deviations.

Table 4. Deviations of atoms from the least-squares plane through the ring

C(1)*	-0.031 Å	H(N1)	-1.463 Å
C(2)*	0.160	H(N2)	-2.168
C(3)*	-0.234	H(N3)	-1.382
C(4)*	0.221	H(21)	1.089
C(5)*	-0.116	H(22)	-0.251
O(1)	0.816	H(31)	-1.275
O(2)	2.211	H(41)	0.026
N	-1.326	H(42)	1.341
C(6)	1.105	H(51)	0.531
C(7)	0.384	H(52)	-0.928
		H(71)	1.588
		H(72)	0.057
		H(73)	0.328

\* Used in calculation of the plane.

Several amino cycloalkanecarboxylic acid derivatives, particularly hydrohalides, have been studied. These include cyclopentane derivatives (Chandrasekharan, Mallikarjunan, Chandrasekharan & Zand, 1968; Mallikarjunan *et al.*, 1972), a cyclohexane derivative (Chacko, Srinivasan & Zand, 1971a), a cycloheptane derivative (Chacko, Srinivasan & Zand 1971b), and cyclooctane derivative (Srikrishnan, Srinivasan & Zand, 1971). In each of these compounds the carboxyl and amino groups lie almost in a plane perpendicular to the plane of the three carbon atoms C(2)C(1)C(5) of the ring system. Presumably the charges tend to keep these groups as far from the ring as possible as shown in Fig. 3. The puckering thus occurs at atoms C(3) and

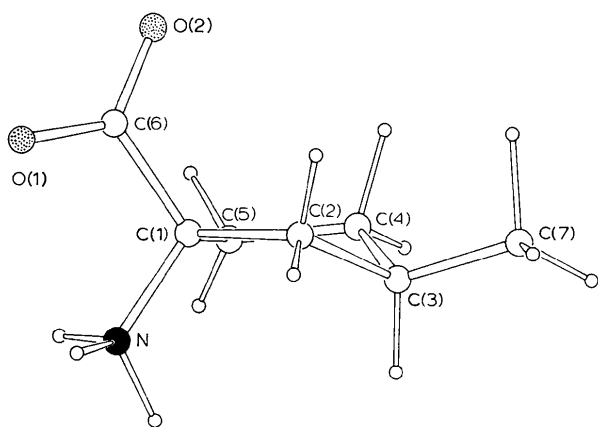


Fig. 3. View of the molecule showing the ring puckering.

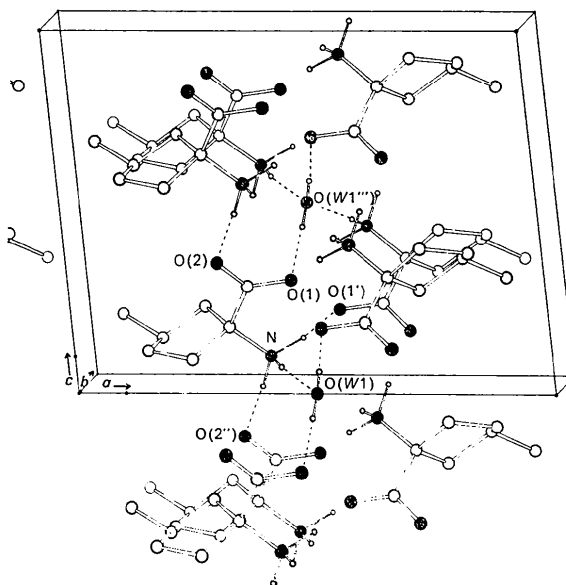


Fig. 4. Packing in the unit cell.

C(4). In this study in which there is a substituent on C(3) the reason for the type of puckering is not clear. There seem to be no close interactions between hydrogen atoms.

Angles and distances involved in the hydrogen bonds are given in Table 5. The  $-\text{NH}_3^+$  group forms three hydrogen bonds to O(1'), O(2'') and O(W1'') and the water molecule, O(W1''), forms two hydrogen bonds to two carboxylate oxygen atoms. A similar situation is found for 1-aminocyclopentanecarboxylic acid monohydrate (Mallikarjunan, Chacko & Zand, 1972). The packing in the unit cell is illustrated in Fig. 4.

The isomer of 1-amino-3-methylcyclopentanecarboxylic acid of this study inhibits the methionine adenosyltransferase reaction (ATP: L-methionine *S*-adenosyl transferase, EC 2.5.1.6) but, while it is no more active than the unsubstituted acid, it is more active as an inhibitor than any of the three other isomers (Lombardini *et al.*, 1970). L-Methionine is a substrate for this reaction, while methionine sulphoximine is inactive. The conformations of L-methionine ( $\alpha$ - and  $\beta$ -crystalline forms, Mathieson, 1952) and methionine sulphoximine (Christensen, Kjaer, Neidle & Rodgers, 1969) were compared with those of the aminocyclopentanecarboxylic acid here studied. If it is assumed that

Table 5. Hydrogen-bond system

D-H...A	D...A	D-H	H...A	$\angle \text{D-H}\cdots\text{A}$	$\angle \text{H-D}\cdots\text{A}$
O(W1)-H(O W1) ... O(1)	2.789 Å	0.75 Å	2.06 Å	162°	13°
N-H(N1) ... O(1')	2.846	1.17	1.70	165	9
N-H(N2) ... O(2'')	2.758	1.03	1.73	176	2
N-H(N3) ... O(W1'')	2.883	0.84	2.05	172	6
Code:	x	y	z		
'	1-x	$y+\frac{1}{2}$	$\frac{1}{2}-z$		
''	x	$y+\frac{1}{2}$	$-\frac{1}{2}+z$		
'''	x	$-\frac{1}{2}+y$	$-\frac{1}{2}+z$		

the zwitterion is held in the active site of the enzyme by the carboxyl and  $-\text{NH}_3^+$  groups then it is not possible to fit the cyclopentane derivative onto the crystallographically determined shapes for methionine. This may imply that the methionine molecule is not in an extended conformation in the active site of the enzyme (Lombardini *et al.*, 1970). Further studies of other inhibitors to the system are in progress.

We thank Mr Walter Orehowsky Jr for technical assistance. This research was supported by grants CA-10925, CA-06927 and RR-05539 from the National Institutes of Health, U.S. Public Health Service, and by an appropriation from the Commonwealth of Pennsylvania to the Institute for Cancer Research, and by Pharmacology-Toxicology Program Project Grant GM-16492 to the Johns Hopkins School of Medicine.

#### References

- ALTONA, C., GEISE, H. J. & ROMERS, C. (1968). *Tetrahedron*, **24**, 13–32.
- BERLINGUET, L., BEGIN, N. & SARKAR, N. K. (1962). *Nature, Lond.* **194**, 1082–1083.
- CARTER, S. K. (1970). *Chemotherapy Fact Sheet: 1-Aminocyclopentanecarboxylic acid (NSC-1026)*. Publications Section, Program Analysis Branch, Chemotherapy, National Cancer Institute, Bethesda, Md. 20014, U.S.A.
- CHACKO, K. K., SRINIVASAN, R. & ZAND, R. (1971a). *J. Cryst. Mol. Struct.* **1**, 261–269.
- CHACKO, K. K., SRINIVASAN, R. & ZAND, R. (1971b). *J. Cryst. Mol. Struct.* **1**, 213–224.
- CHANDRASEKHARAN, R., MALLIKARJUNAN, M., CHANDRASEKHARAN, G. & ZAND, R. (1968). *Curr. Sci.* **37**, 91–93.
- CHRISTENSEN, H. N., KJAER, A., NEIDLE, S. & RODGERS, D. (1969). *J. Chem. Soc. (D)*, pp. 169–170.
- GANTZEL, P. K., SPARKS, R. A., LONG, R. E. & TRUEBLOOD, K. N. (1969). UCLALS4 Program in Fortran IV. *International Tables for X-ray Crystallography* (1962). Vol. III, pp. 201–207. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). ORTEP. ORNL-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- KILPATRICK, J. E., PITZER, K. S. & SPITZER, R. (1947). *J. Amer. Chem. Soc.* **69**, 2483–2488.
- LOMBARDINI, J. B., COULTER, A. W. & TALALAY, P. (1970). *Mol. Pharmacol.* **6**, 481–499.
- MAIN, P., WOLFSON, M. M. & GERMAIN, G. (1971). MULTAN. A computer program for the automatic solution of crystal structures.
- MALLIKARJUNAN, M., CHACKO, K. K. & ZAND, R. (1972). *J. Cryst. Mol. Struct.* **2**, 53–66.
- MATHIESON, A. MCL. (1952). *Acta Cryst.* **5**, 332–341.
- SRIKRISHNAN, T., SRINIVASAN, R. & ZAND, R. (1971). *J. Cryst. Mol. Struct.* **1**, 199–212.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The X-RAY system of crystallographic programs. Version of July 1970, updated.
- ZELINSKY, N. & STODNIKOFF, G. (1906). *Chem. Ber.* **39**, 1722–1732.

*Acta Cryst.* (1973). **B29**, 2585

## The Crystallography of Nitramine–Solvent Complexes. IV.\* The Crystal Structure of the 1:1 Molecular Complex Formed by 1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane and 1,4-Dioxane

BY R. E. COBBLEDICK AND R. W. H. SMALL

*Chemistry Department, The University, Lancaster, England*

(Received 6 June 1973; accepted 8 June 1973)

The crystal structure of the 1:1 molecular complex formed by 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane and 1,4-dioxane (BSX–DOX) has been solved by direct methods with counter measured X-ray data. The crystals are monoclinic, space group  $P2_1/n$ , with  $a = 22.134$  (3),  $b = 13.828$  (4),  $c = 6.498$  (1) Å,  $\beta = 96.72$  (6)° and  $Z = 4$ . Least-squares refinement gave a final  $R$  of 0.0600. A feature of the structure is the presence of dimers of BSX in which the carbonyl oxygen atom of one BSX molecule interacts with the nitrogen atoms of two adjacent nitro groups in a BSX molecule related by a centre of symmetry. The  $\text{N} \cdots \text{O}$  distances are 3.033 and 3.105 Å. The dioxane molecules lie in channels between columns of BSX dimer units so that one oxygen atom of each molecule lies between two adjacent nitro groups. In this case the  $\text{N} \cdots \text{O}$  distances are 3.116 and 3.199 Å.

### Introduction

BSX is of interest because of the readiness with which it forms complexes with solvents. Usually simple re-

crystallization from the solvent will yield needles of the solvent complex. The complex crystals from different solvents may be divided into four groups (type A, B, C or D); within each group the cell dimensions are similar and the internal symmetry the same (Cobbledick & Small, 1973a). The crystal structure determina-

\* Part III: *Acta Cryst.* **B29**, 1659–1666.