that other favoured orientations of the ammonium ion may be present in this structure. In any case it seems reasonable to conclude that the rotation of the ammonium ion is not completely free, the distribution of oxygen atoms around the nitrogen atom imposing a certain number of preferential orientations, as that described above.

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The Crystal Structure of *trans*-1-Amino-1,3-dicarboxycyclopentane

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trans-1-Amino-1,3-dicarboxycyclopentane crystallizes with acetic acid of crystallization in the space group $Pca2_1$, with $Z=4$, $a=9\cdot122$ (5), $b=13\cdot964$ (9), $c=8\cdot667$ (5) Å, $V=1104$ (1) Å^3. $D_x=1\cdot40$ and $D_m=1\cdot39$ g cm^{-3}. Diffractometer data, collected with monochromatic Cu $K\alpha$ radiation, consisted of 1104 independent reflections of which 190 were less than $2\cdot33\sigma(I)$. The structure was solved by direct methods and refined by a full-matrix least-squares procedure to the final residual $R=0\cdot065$. All hydrogen atoms were located and were refined isotropically. There is an intramolecular hydrogen bond between the 1-amino group and the 3-carboxyl group and the crystal packing is dominated by hydrogen-bond formation. The conformation of the cyclopentane ring is intermediate between that of an envelope and of a half-chair.

Introduction

It has been shown that 1-amino-1,3-dicarboxycyclopentane, an analogue of glutamate, is a substrate for glutamine synthetase (Stephani, Rowe, Gass & Meister, 1972). The enzyme interacts with one isomer of the racemic *cis* form of the analogue, but not with the *trans* form. A crystallographic study of the *trans* analogue has been undertaken as part of a study of the conformations of both isomers.

Experimental

A mixture of the *cis* and *trans* isomers was separated by the procedure of Stephani, Rowe, Gass & Meister (1972). The crystal data are given in Table 1. Since the crystals, which grew as colorless needles in glacial acetic acid, formed in a noncentrosymmetric space group, it appears that the racemic mixture was resolved into its optical isomers on crystallization. Three-dimensional data were collected on a Syntex automated diffractometer equipped with a graphite monochromator and Cu $K\alpha$ radiation using the θ–2θ scan tech-

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nique. Intensities were measured for 1104 unique reflections in the range $\sin \theta / \lambda = 0$ to 0.61 Å^{-1}. Values for $\sigma(I)$ were derived from counting statistics. There were 190 reflections for which the measured intensities were less than $2.33 \, \sigma(I)$. 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. Values of $\sigma(F)$ were determined as $\sigma(F) = (F/2)\{\sigma^2(I)/I^2 + \delta^2\}^{1/2}$ where δ is a measured instrumental uncertainty, determined from the variation of the intensities of the three periodically monitored check reflections ($\delta = 0.0290$). No absorption correction was applied.

Structure determination and refinement

The structure was solved by direct methods with the multiple-solution program *MULTAN* (Germain, Main & Woolfson, 1971) using 361 reflections with $E > 1.40$. The first E map gave the position of all the heavy atoms except the ring atom C(4) and the acetic acid of crystallization. The resulting structure-factor calculation using all reflections had a value of $R = \sum |\Delta F| / \sum |F_o|$ of 0.405. Two Fourier maps revealed the position of the remainder of the heavy atoms; a structure-factor calculation for the complete structure yielded an R of 0.25. Three cycles of isotropic full-matrix least-squares refinement reduced R to 0.157, and subsequent full-matrix least-squares anisotropic refinements gave $R = 0.087$. Positions of all of the hydrogen atoms were derived from a difference electron-density map. Refinement of all atomic parameters was continued with the temperature factors of hydrogen atoms treated isotropically and of all other atoms
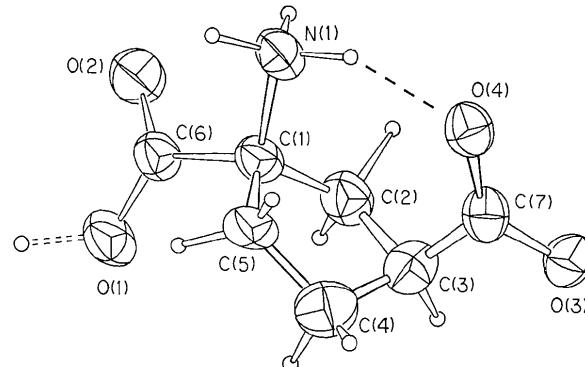

Fig. 1. View of molecule with thermal ellipsoids, drawn with the aid of program *ELLIPS* (Carrell & Stodola, 1974).

Table 1. *Crystal data for trans-1-amino-1,3-dicarboxycyclopentane*

$C_7H_{11}NO_4 . C_2H_4O_2$ F.W. 233·20
Crystal system: orthorhombic   Space group: $Pca2_1$
$a = 9.122 (5)$ Å   Systematic absences: $h00$ with h odd
$b = 13.964 (9)$ $0k0$ with k odd
$c = 8.667 (5)$ $00l$ with l odd
$V = 1104 (1)$ Å^3 $h0l$ with h odd
     $Z = 4$ $0kl$ with l odd

$D_x = 1.40$ g cm^{-3} $F(000) = 496$
$D_m = 1.39$ g cm^{-3} (in trichloroethylene and 1,1-dichloroethane)

Crystal size: $0.10 \times 0.15 \times 0.40$ mm

Table 2. *Final atomic parameters*

Positional parameters are given as fractional cell coordinates $\times 10^4$ ($\times 10^3$ for hydrogen atoms). Anisotropic temperature factor parameters 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_{ij} and B values given in Å^2. The standard deviations for each parameter, determined from the inverted full matrix, are given in parentheses and apply to the last specified digits. The z value for N(1) was constrained during refinement.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	−1746 (6)	2116 (3)	5710 (0)	5·70 (26)	3·03 (16)	3·03 (19)	−0·12 (17)	−0·44 (23)	−0·24 (18)
O(1)	−18 (6)	3341 (3)	8821 (5)	9·33 (31)	4·12 (17)	3·07 (18)	−1·01 (22)	−0·75 (21)	0·00 (16)
O(2)	−777 (5)	1833 (3)	8525 (6)	6·78 (24)	3·42 (15)	3·64 (18)	−0·23 (19)	−0·79 (20)	0·63 (15)
O(3)	786 (6)	3606 (3)	1557 (6)	7·43 (28)	4·96 (19)	3·47 (18)	−1·96 (22)	0·31 (20)	0·78 (17)
O(4)	−1021 (6)	2801 (3)	2696 (6)	5·89 (22)	6·22 (22)	3·35 (18)	−1·54 (20)	−0·03 (19)	−0·37 (20)
O(5)	878(6)	1356 (3)	905 (7)	9·48 (31)	2·44 (13)	5·64 (23)	0·39 (18)	−2·03 (28)	0·37 (18)
O(6)	667 (6)	−197 (3)	485 (6)	8·37 (31)	2·90 (15)	4·87 (24)	0·01 (18)	−0·49 (23)	0·21 (17)
C(1)	−650 (7)	2824 (4)	6287 (7)	5·16 (31)	2·50 (19)	2·64 (23)	−0·20 (22)	−0·40 (24)	0·02 (17)
C(2)	824 (8)	2668 (4)	5477 (8)	5·50 (36)	4·08 (24)	2·97 (25)	0·19 (27)	0·03 (24)	0·09 (22)
C(3)	956 (9)	3468 (6)	4260 (11)	5·89 (41)	5·37 (34)	4·94 (35)	−0·58 (32)	1·22 (33)	0·55 (31)
C(4)	146 (11)	4273 (5)	5030 (12)	9·47 (56)	4·59 (34)	6·04 (43)	−0·35 (37)	1·18 (48)	0·63 (32)
C(5)	−1120 (8)	3856 (4)	5875 (9)	6·54 (37)	2·94 (20)	3·72 (28)	0·33 (25)	−0·40 (31)	0·20 (24)
C(6)	−480 (8)	2653 (4)	8043 (9)	5·22 (34)	2·88 (22)	3·08 (28)	0·24 (23)	−0·05 (26)	0·01 (22)
C(7)	153 (11)	3271 (6)	2751 (10)	6·94 (44)	5·76 (39)	2·98 (30)	−0·94 (37)	−0·14 (35)	0·19 (32)
C(8)	1167 (9)	453 (5)	1212 (9)	6·24 (38)	3·40 (23)	3·30 (30)	0·18 (27)	0·57 (29)	0·43 (23)
C(9)	2184 (10)	355 (5)	2541 (12)	8·10 (49)	3·98 (26)	5·26 (41)	0·17 (33)	−1·19 (41)	0·53 (28)

Table 2 (cont.)

	x	y	z	B
H(1N)	−269 (9)	232 (4)	634 (8)	9 (2)
H(2N)	−168 (8)	220 (5)	454 (10)	5 (2)
H(3N)	−129 (7)	150 (4)	594 (10)	6 (2)
H(3A)	59 (17)	318 (11)	90 (22)	13 (4)*
H(3B)	−44 (25)	359 (15)	1002 (31)	14 (6)*
H(21)	171 (7)	271 (4)	630 (9)	4 (2)
H(22)	74 (8)	193 (5)	495 (9)	8 (2)
H(31)	197 (7)	363 (5)	413 (9)	5 (2)
H(41)	−18 (9)	487 (5)	429 (9)	7 (2)
H(42)	92 (7)	456 (5)	586 (12)	12 (2)
H(51)	−107 (8)	399 (5)	702 (11)	6 (2)
H(52)	−190 (7)	389 (5)	518 (10)	3 (2)
H(O5)	14 (8)	148 (5)	0 (11)	7 (2)
H(91)	242 (9)	−25 (4)	269 (9)	8 (2)
H(92)	264 (9)	84 (5)	272 (10)	12 (2)
H(93)	162 (9)	46 (6)	361 (11)	10 (2)

* 50% occupancy.

anisotropically. The weights used in the refinement were $1/[\sigma^2(F_o)]$ with reflections below 2·33 $\sigma(I)$ assigned zero weight. The quantity minimized was $\sum w\{|F_o|-|F_c|\}^2$. The final refinement converged with $R=0·065$ and weighted $R=0·068$.

The atomic scattering factor parameters used for oxygen, nitrogen and carbon atoms are those listed by Cromer & Mann (1968), and for hydrogen atoms the scattering factors of Stewart, Davidson & Simpson (1965). Computer programs used in this determination were the X-RAY 72 System (Stewart, 1972), *UCLALS4* (full-matrix least-squares) (Gantzel, Sparks, Long & Trueblood, 1969), modified by H. L. Carrell, and the CRYSNET package (Bernstein *et al.*, 1974).

The final atomic parameters are presented in Table 2. Fig. 1 is a view of the molecule representing probability surfaces for non-hydrogen atoms (Carrell &

Table 3. *Hydrogen-bond system*

D–H···A	D···A (Å)	D–H (Å)	H···A (Å)	∠D–H···A (°)	∠H–D···A (°)
N(1)–H(1N)···O(4^i)	2·834 (6)	1·06 (10)	1·79 (7)	166 (6)	9 (4)
N(1)–H(2N)···O(4)	2·859 (5)	1·02 (15)	1·90 (8)	154 (6)	17 (4)
N(1)–H(3N)···O(6^ii)	2·861 (6)	0·98 (7)	1·94 (6)	155 (7)	17 (5)
O(3)–H(3A)···O(1^iii)	2·509 (7)	0·84 (17)	1·90 (19)	128 (14)	37 (12)
O(1)–H(3B)···O(3^iv)	2·509 (7)	1·16 (26)	1·74 (25)	119 (17)	38 (11)
O(5)–H(O5)···O(2^iii)	2·642 (7)	1·05 (9)	1·60 (9)	168 (7)	7 (4)

Code
(i) $\frac{1}{2}-x$, y, $\frac{1}{2}+z$;   (iii) $x, y, z-1$
(ii) $-x$, $-y$, $\frac{1}{2}+z$;   (iv) $x, y, z+1$

∠C(6)C(1)C(5) 113.6 (5)
∠N(1)C(1)C(2) 109.8 (4)
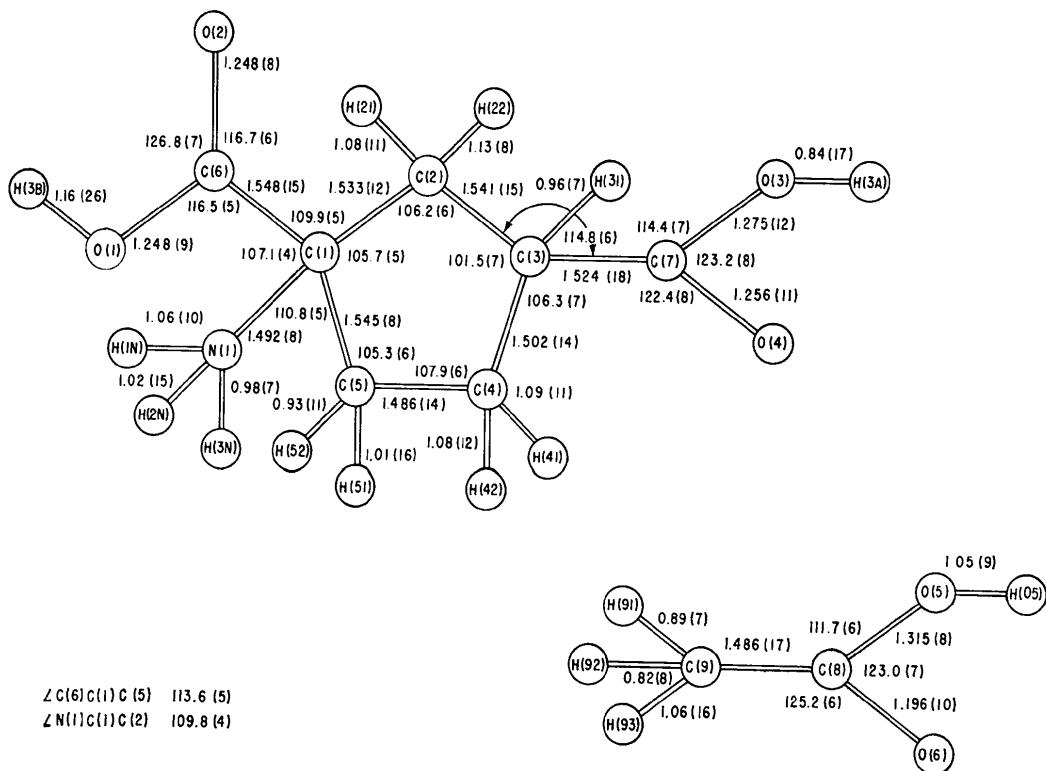
Fig. 2. Distances (Å) and angles (°) with estimated standard deviations.

Stodola, 1974). Some angles and distances in the cyclopentane derivative and in the acetic acid of crystallization (with their estimated standard deviations) are given in Fig. 2.

Discussion of the structure

The cyclopentane derivative crystallized as a zwitterion with a positive charge on the amino group and partial negative charges on both carboxyl groups. C–O distances in these carboxyl groups lie in the range 1·24–1·27 Å, and a hydrogen atom is disordered between O(3) and O(1) of different molecules (see Table 3). An intramolecular hydrogen bond between the 1-amino group and the 3-carboxyl group is shown in Fig. 1. Such an interaction between an amino group and a carboxyl group has been suggested to occur in some conformations of certain dipeptides in solution (Nakon & Angelici, 1974).

The carboxyl groups are coplanar with the α-carbon atom, within experimental error. The nitrogen atom N(1) lies 0·58 Å from the plane through O(1)–O(2)–C(6)–C(1), and 0·20 Å from the plane of the group O(3)–O(4)–C(7)–C(3) to which it is hydrogen bonded. The angle between the planes O(1)–O(2)–C(1)–C(6) and N–C(1)–C(6) is 24·1°.

In the cyclopentane ring the angle C(2)–C(3)–C(4), at the site of substitution of the 3-carboxyl group, is smaller than expected (101·5°). The ring angle at carbon atom C(3) in 1-amino-3-methylcyclopentane-

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* The structure factor list has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30973 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1 NZ, England.
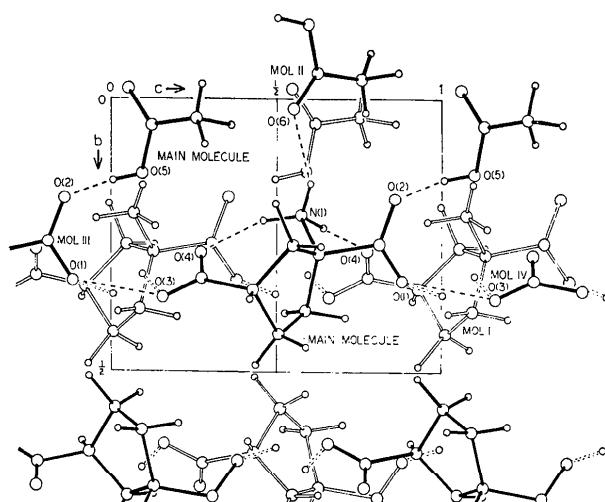

Fig. 3. Packing in the crystal. The cyclopentane amino acid and the acetic acid of crystallization are designated 'main molecule' in this diagram. Other molecules are designated according to the code in Table 3.

carboxylic acid (Carrell, Gallen & Glusker, 1973) is also small (99·9°). Other ring angles lie in the range of 105–108° with no reduction in the angle at the site of 1,1-amino acid substitution.

Important torsion angles (neglecting hydrogen atoms) are listed in Table 4 together with pseudorotation parameters. The torsion angles, φ_j, in Table 4 may be fitted to a formula $\varphi_j = \varphi_m \cos (\Delta/2 + 144j)$ where j is an integer (0 to 4) and φ_m is a maximum value for the torsion angles (Altona, Geise & Romers, 1968). If φ_4 were 0° then the cyclopentane ring would be in an envelope conformation ($\Delta = 468°$). If $\varphi_1 = \varphi_3$ and $\varphi_0 = \varphi_4$ then the ring would be in a half-chair conformation. In this structure the ring is intermediate between these situations ($\Delta = 488·5°$) with a maximum puckering at C(3) (which has a substituent carboxyl group). A similar conformation exists in 1-amino-3-methylcyclopentanecarboxylic acid (Carrell et al., 1973) ($\Delta = 481·4°$).

Table 4. *Torsion angles and pseudorotation parameters*

C(5)–C(1)–C(2)–C(3)	φ_0	−16·2 (9)°
C(1)–C(2)–C(3)–C(4)	φ_1	32·0 (9)
C(2)–C(3)–C(4)–C(5)	φ_2	−37·1 (10)
C(1)–C(5)–C(4)–C(3)	φ_3	27·7 (10)
C(2)–C(1)–C(5)–C(4)	φ_4	−6·4 (9)
O(1)–C(6)–C(1)–N		−156·9 (7)
O(2)–C(6)–C(1)–N		25·2 (9)
O(3)–C(7)–C(3)–C(2)		−145·9 (9)
O(4)–C(7)–C(3)–C(2)		32·9 (14)
O(3)–C(7)–C(3)–C(4)		102·8 (10)
O(4)–C(7)–C(3)–C(4)		−78·4 (12)
N—C(1)–C(2)–C(3)		103·4 (7)
N—C(1)–C(5)–C(4)		−125·3 (7)
C(6)–C(1)–C(2)–C(3)		−139·1 (7)
C(6)–C(1)–C(5)–C(4)		114·1 (8)
C(7)–C(3)–C(2)–C(1)		−82·1 (9)
C(7)–C(3)–C(4)–C(5)		83·2 (10)

Equation (Altona, Geise & Romers, 1968) $\varphi_j = \varphi_m \cos (\Delta/2 + 144j)$. It is assumed that $\varphi_0 = C(5)–C(1)–C(2)–C(3)$. $\tan (\Delta/2) = \{(\varphi_2 + \varphi_4) - (\varphi_1 + \varphi_3)\}/2\varphi_0(\sin 36° + \sin 72°)$ $\varphi_m = \varphi_0/\cos (\Delta/2)$. $\Delta = 488·5°$, $\varphi_m = +37·3°$.

The extensive network of hydrogen bonds which holds molecules together in the crystal is shown in Fig. 3. Hydrogen-bond lengths are tabulated in Table 3. There is a short hydrogen bond (2·509 Å) between the 1- and 3-carboxyl groups of different molecules with the hydrogen atom disordered between them. This type of disorder has been found in other carboxylic acids [for example see Glusker, Zacharias & Carrell (1975)]. The estimated standard deviations for these disordered hydrogen atoms, H(3A) and H(3B), from refinement with 50% occupancy, are high and values in Table 3 should be read taking these values into account. The amino group is involved in three hydrogen bonds, two to oxygen atoms of the 3-carboxyl group (one internal) and one to the acetic acid molecule. The acetic acid is the hydrogen-atom donor in a hydrogen bond to the 1-carboxyl group of the amino-cyclopentane diacid.

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Die Kristallstruktur von H.T.-GeS₂

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The high-temperature modification of GeS₂ crystallizes in the monoclinic space group $P2_1/c$ with $a = 6\cdot720$ (5), $b = 16\cdot101$ (5), $c = 11\cdot436$ (5) Å, $\beta = 90\cdot88$ (5)°, $Z = 16$. The structure was solved by a combination of superposition and direct methods and refined by least-squares techniques. The final R is $9\cdot0\%$. The structure is characterized by 'zweier-einfach' chains of GeS₄ tetrahedra running parallel to a. They are connected over vertices to layers perpendicular to c by double tetrahedra with a common edge.

Einführung

Vom GeS₂ sind bisher drei Modifikationen in der Literatur beschrieben. Von diesen ist die tetragonale Hochdruck/Hochtemperaturmodifikation (Prewitt & Young, 1965) mit einem R-Wert von 5,9 am besten gesichert. Für die *nadelförmige, säurelösliche Modifikation* liegen zwei Vorschläge vor – eine Raumnetzstruktur (Zachariasen, 1936) und eine deformierte CdJ₂-Struktur (Ch'ün-Hua, Pashinkin & Novoselova, 1963). Nach Arbeiten von Viaene & Moh (1970) existiert eine Hochtemperatur- und eine Tieftemperaturmodifikation von GeS₂. Von Rubenstein & Roland (1971) wurde die Hochtemperaturmodifikation, die offenbar schon früher von Pugh (1930) erhalten worden war, in Form von Einkristallen dargestellt, an denen Gitterkonstanten, Raumgruppe, Zellinhalt und Dichte bestimmt wurden. Auch für diese Modifikation diskutieren die

Autoren auf Grund der Zelldimensionen eine deformierte CdJ₂-Struktur. Da die vorgeschlagene Schichtstruktur mit oktaedrisch koordinierten Germaniumatomen aus kristallchemischen Gründen nicht wahrscheinlich erschien, wurde eine vollständige röntgenographische Strukturbestimmung durchgeführt.

Experimentelles

Es wurden Einkristalle von GeS₂ nach der von Rubenstein & Roland (1971) beschriebenen Methode aus den Elementen Ge und S in Quarzbomben bei 900°C dargestellt [Fig. 1(*a*)]. Die Dichte wurde nach der Pyknometermethode unter Xylol zu 2,89 g cm⁻³ bestimmt. Die Verbindung kristallisiert in Form von langgestreckten Plättchen, die sich bei mechanischer Beanspruchung sehr leicht plastisch verbiegen. Die Plättchenflächen sind (001) und (00Ī). Als weitere Begren-