Crystal and Molecular Structure of *trans*-4-Aminocrotonic Acid

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Crystals of the title compound are monoclinic, space group $P2_1/c$, a = 8.863(3), b = 7.870(2), c = 14.971(5) Å, β = 115.37(3)°, Z = 8. The structure was solved by direct methods and refined by least-squares procedure to a value R 0.048 for 1 834 observed diffraction maxima. The location of all hydrogen atoms (difference-Fourier synthesis) shows that the molecules are zwitterions linked by a three-dimensional network of hydrogen bonds.

γ-AMINOBUTYRIC acid (I) is considered to be an inhibitory transmitter substance in mammalian brain.[1,2] As part of a study of the correlation of molecular structure and physiological activity of (I) and of its analogues, we undertook the crystal structure determination of *trans*-4-aminocrotonic acid (II) which has similar physiological affects.[3]

EXPERIMENTAL

Crystals of (II) were recrystallised from aqueous solution by a slow evaporation of the solvent, as needles, elongated along b.

Crystal Data.—$C_4H_7NO_2$, M = 101.1, Monoclinic, a = 8.863(3), b = 7.870(2), c = 14.971(5) Å, β = 115.37(3)°, U = 940.8 Å^3, D_c = 1.426 g cm^{-3}, Z = 8, D_m = 1.43(1) g cm^{-3}. Space group $P2_1/c$ (No. 14, C^5_{2h}); Mo-K_α radiation, λ = 0.7107 Å; μ(Mo-K_α) = 1.1 cm^{-1}.

Intensity Measurements.—Three dimensional X-ray diffraction data from a single crystal *ca.* 0.30 × 0.35 × 0.30 mm were measured on a computer-controlled[4] four-circle diffractometer by use of graphite monochromatised (002) Mo-K_α radiation. A coupled θ—2θ step scan with $\Delta 2\theta$ 0.04°, counting time of 3 s per step, and peakwidth of 1.6° were used. In the range 2θ 5—60°, 1 834 diffraction maxima of a possible 2 944 in a quadrant of reciprocal space (h, k, $\pm l$) had $I \geqslant 3\sigma(I)$ and were considered observed. Data were corrected for Lorentz and polarization effects but not for absorption or extinction.

Structure Solution and Refinement.—Normalized structure factors $|E|$ were calculated from the observed structure factors by the K curve method[5,6] normalizing (h, k, $\pm l$; l even) and (h, k, $\pm l$; l odd) separately to achieve the condition $\langle |E|^2 \rangle_{av}$ = 1.0.

An initial set of phases for 179 reflections with $|E| \geqslant 1.5$ was obtained using the multiple-solution technique and cyclic refinement by the tangent formula.[7,8] An E map calculated with the phases derived from the most consistent solution revealed the positions of all non-hydrogen atoms in the unit cell.

Refinement of the scale factor and overall temperature

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[1] E. Roberts and E. Eidelberg, *Internat. Rev. Neurobiol.*, 1960, **2**, 479.

[2] D. R. Curtis and J. C. Watkins, *Pharmacol. Rev.*, 1965, **17**, 347.

[3] P. M. Beart, G. A. R. Johnston, and M. L. Uhr, *J. Neurochem.*, 1972, **19**, 1855.

[4] W. R. Busing, R. D. Ellison, H. A. Levy, S. P. King, and P. T. Roseberry, *U.S. Atomic Energy Commission Report* ORNL, 4143, 1968.

[5] J. Karle and H. Hauptman, *Acta Cryst.*, 1953, **6**, 131.

[6] J. Karle and H. Hauptman, *Acta Cryst.*, 1956, **9**, 635.

[7] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1970, **B26**, 274.

[8] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

factor on these atoms gave $R = 0.306$. Three cycles of full-matrix least-squares refinement of the positional parameters reduced R to 0.123, at which point the individual isotropic thermal parameters were allowed to refine for two cycles reducing R to 0.113. A further three cycles of anisotropic refinement reduced R to 0.074. A difference-Fourier synthesis at this stage clearly indicated all hydrogen atom positions. The final cycles of refinement, including the hydrogen-atom positions, by full-matrix least-squares were continued until all parameter shifts were $\leqslant 0.1\sigma$. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1$ for all reflections.

Atomic scattering factors for neutral carbon, nitrogen, and oxygen were taken from ref. 9, and for hydrogen from ref. 10. The final R is 0.048. Final positional and thermal parameters for non-hydrogen atoms are in Table 1, hydrogen atom positions in Table 2, and bond distances and angles in Tables 3 and 4, torsion angles in Table 5. Observed and calculated structure factors have been deposited as Supplementary Publication, No. SUP 21243 (4 pp., 1 microfiche).*

TABLE 1

Fractional co-ordinates and thermal motion parameters ($\times 10^4$) * derived from least-squares refinement, with estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2 264(3)	4 135(3)	1 137(2)	326(7)	197(6)	357(5)	33(6)	13(6)	4(6)
C(2)	2 740(3)	2 332(3)	1 458(2)	293(7)	221(6)	284(4)	12(6)	92(6)	29(6)
C(3)	2 048(3)	1 003(3)	902(2)	262(7)	217(6)	257(4)	25(5)	82(6)	26(5)
C(4)	2 641(3)	−781(3)	1 194(2)	254(6)	210(6)	290(4)	1(6)	114(5)	31(6)
O(1)	2 053(2)	−1 891(2)	525(1)	516(6)	229(5)	316(3)	43(5)	71(3)	−16(3)
O(2)	3 700(2)	−1 090(2)	2 057(1)	468(6)	295(5)	305(3)	21(5)	30(3)	65(3)
N(1)	3 719(3)	5 085(3)	1 140(2)	308(6)	155(5)	281(3)	4(4)	98(3)	17(4)
C(11)	3 143(3)	6 627(3)	3 695(2)	357(7)	232(6)	313(3)	−75(5)	97(5)	20(4)
C(12)	3 234(3)	4 727(3)	3 808(2)	271(7)	255(6)	260(4)	14(4)	92(4)	17(4)
C(13)	1 971(3)	3 669(3)	3 607(2)	266(6)	182(5)	253(4)	18(4)	61(4)	23(4)
C(14)	2 195(3)	1 768(3)	3 728(2)	308(6)	189(5)	222(3)	21(4)	119(4)	26(3)
O(11)	914(2)	881(2)	3 220(1)	348(6)	203(5)	380(3)	−27(3)	51(3)	15(3)
O(12)	3 572(2)	1 178(2)	4 308(1)	335(5)	286(5)	328(3)	98(4)	64(3)	68(3)
N(11)	1 485(3)	7 324(2)	3 538(2)	328(6)	124(5)	249(4)	−9(4)	29(4)	−4(3)

* The Debye–Waller factor is defined as $T = \exp[-2\pi^2\Sigma\Sigma a_i^* a_j^* h_i h_j U_{ij}]$ with U in Å^2.

TABLE 2

Fractional co-ordinates ($\times 10^3$) for hydrogen atoms derived from least-squares refinement, with estimated standard deviations in parentheses

Atom	x	y	z
H(1)	389(4)	472(5)	59(3)
H(2)	467(5)	496(5)	166(3)
H(3)	342(4)	623(5)	95(3)
H(4)	131(4)	419(4)	41(3)
H(5)	172(4)	472(4)	158(2)
H(6)	359(4)	217(5)	211(3)
H(7)	119(4)	116(4)	21(2)
H(11)	124(4)	709(4)	416(3)
H(12)	61(4)	682(5)	299(3)
H(13)	132(4)	853(5)	349(3)
H(14)	402(4)	716(4)	426(3)
H(15)	339(4)	695(4)	310(2)
H(16)	434(4)	428(4)	400(2)
H(17)	77(4)	404(4)	340(2)

All hydrogen atoms have $U = 0.032$ Å^2.

TABLE 3

Interatomic distances (Å) and angles (°) for nonhydrogen atoms, with estimated standard deviations in parentheses

(*a*) Distances

C(2)–C(1)	1.500(3)	C(12)–C(11)	1.503(3)
C(3)–C(2)	1.314(3)	C(13)–C(12)	1.322(3)
C(4)–C(3)	1.497(3)	C(14)–C(13)	1.510(3)
O(1)–C(4)	1.262(3)	O(11)–C(14)	1.270(3)
O(2)–C(4)	1.253(3)	O(12)–C(14)	1.246(3)
N(1)–C(1)	1.489(3)	N(11)–C(11)	1.490(3)

(*b*) Angles

N(1)–C(1)–C(2)	110.5(2)	N(11)–C(11)–C(12)	112.7(2)
C(1)–C(2)–C(3)	124.0(2)	C(11)–C(12)–C(13)	127.0(2)
C(3)–C(4)–O(1)	116.3(2)	C(13)–C(14)–O(11)	115.8(2)
C(3)–C(4)–O(2)	119.8(2)	C(13)–C(14)–O(12)	119.5(2)
O(1)–C(4)–O(2)	123.8(2)	O(11)–C(14)–O(12)	124.7(2)
C(2)–(C)3)–C(4)	124.0(2)	C(12)–C(13)–C(14)	122.8(2)

TABLE 4

Interatomic distances (Å) and angles (°) involving hydrogen atoms, with estimated standard deviations in parentheses

(*a*) Distances

H(1)–N(1)	0.95(4)	H(11)–N(11)	1.06(4)
H(2)–N(1)	0.88(4)	H(12)–N(11)	0.94(3)
H(3)–N(1)	0.95(4)	H(13)–N(11)	0.96(4)
H(4)–C(1)	1.05(3)	H(14)–C(11)	0.93(3)
H(5)–C(1)	1.07(3)	H(15)–C(11)	1.03(3)
H(6)–C(2)	0.95(3)	H(16)–C(12)	0.96(3)
H(7)–C(3)	1.00(3)	H(17)–C(13)	1.02(3)

(*b*) Angles

H(1)–N(1)–C(1)	108(2)	H(11)–N(11)–C(11)	111(2)
H(2)–N(1)–C(1)	117(2)	H(12)–N(11)–C(11)	112(2)
H(3)–N(1)–C(1)	110(2)	H(13)–N(11)–C(11)	119(2)
H(4)–C(1)–C(2)	111(2)	H(14)–C(11)–C(12)	110(2)
H(5)–C(1)–C(2)	110(2)	H(15)–C(11)–C(12)	109(2)
H(6)–C(2)–C(3)	120(2)	H(16)–C(12)–C(13)	120(2)
H(7)–C(3)–C(4)	120(2)	H(17)–C(13)–C(14)	113(2)

TABLE 5

Torsion angles (deg.) for non-hydrogen atoms, with estimated standard deviations in parentheses

N(1)–C(1)–C(2)–C(3)	−118.8(3)
C(1)–C(2)–C(3)–C(4)	174.1(2)
C(2)–C(3)–C(4)–O(1)	−168.3(2)
C(2)–C(3)–C(4)–O(2)	9.9(4)
N(11)–C(11)–C(12)–C(13)	13.1(4)
C(11)–C(12)–C(13)–C(14)	178.7(3)
C(12)–C(13)–C(14)–O(11)	−157.4(2)
C(12)–C(13)–C(14)–O(12)	23.4(4)

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

[9] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[10] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

DISCUSSION

The atom numbering scheme for both independent molecules is shown in Figure 1, the planes containing C(2)—(4) for both molecules being coincident with the plane of the paper. Molecular packing and hydrogen bonding are shown in Figures 2 and 3 which are viewed in the direction of —a*.

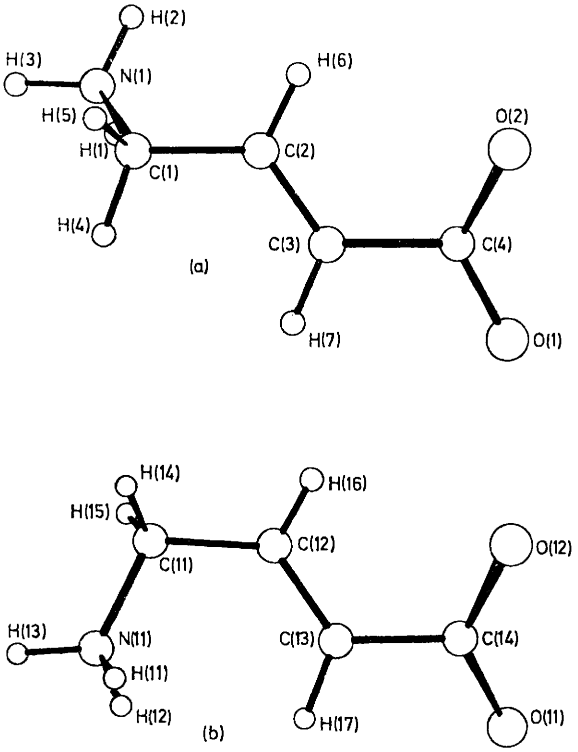

FIGURE 1 Atomic numbering for both independent molecules; (a) molecule (A), (b) molecule (B)

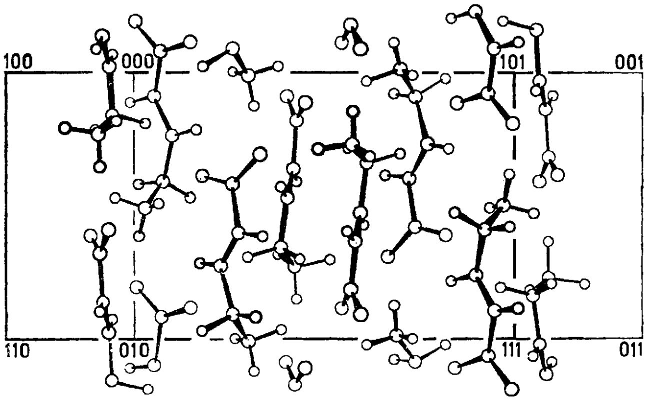

FIGURE 2 Molecular packing viewed in the direction of —a*

The location in the difference-Fourier map of three hydrogen atoms tetrahedrally surrounding each nitrogen atom confirmed the existence of a zwitterionic structure. These hydrogen atoms are suitably placed to form hydrogen bonds with adjacent molecules *via* the carboxylate oxygen atoms, resulting in a three-dimensional network of hydrogen bonds. Atoms O(2) and O(12) are each involved in one hydrogen bond whereas O(1) and O(11) are involved in two, the H ··· O ··· H angles being 102 and 125°, respectively. The lengths of the N–H ··· O bonds are given in Table 6. A close contact [O(12) ··· N(1$^{\mathrm{II}}$) 2.74 Å; O(12) ··· N(1)–C(1) 163°] also exists in the crystal.

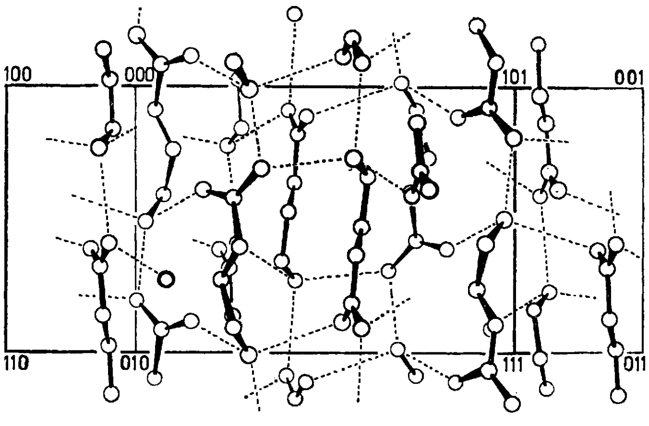

FIGURE 3 Crystal structure viewed in the direction of —a*; broken lines indicate hydrogen bonds

TABLE 6

Hydrogen-bond distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances

D ··· A *	
N(1) ··· O(1$^{\mathrm{I}}$)	2.744(3)
N(1) ··· O(2$^{\mathrm{II}}$)	2.843(3)
N(1) ··· O(12$^{\mathrm{III}}$)	2.929(3)
N(11) ··· O(1$^{\mathrm{IV}}$)	2.817(3)
N(11) ··· O(11$^{\mathrm{V}}$)	2.818(3)
N(11) ··· O(11$^{\mathrm{I}}$)	2.848(3)

(*b*) Angles

C(1)–N(1) ··· O(1$^{\mathrm{I}}$)	95.4(2)
C(1)–N(1) ··· O(2$^{\mathrm{II}}$)	100.6(2)
C(1)–N(1) ··· O(12$^{\mathrm{III}}$)	98.9(2)
C(11)–N(11) ··· O(1$^{\mathrm{IV}}$)	94.1(2)
C(11)–N(11) ··· O(11$^{\mathrm{V}}$)	107.3(2)
C(11)–N(11) ··· O(11$^{\mathrm{I}}$)	118.7(2)

* D = donor, A = acceptor. Roman numerals as superscripts denote the following transformations relative to the reference molecule at x, y, z:

I $x, 1 + y, z$
II $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
III $x, \frac{1}{2} - y, -\frac{1}{2} + z$
IV $x, \frac{1}{2} - y, \frac{1}{2} + z$
V $-x, \frac{1}{2} + y, \frac{1}{2} - z$

TABLE 7

Intramolecular N ··· O distances (Å) in (I) and (II), with estimated standard deviations in parentheses

(*a*) In (II) [a]			
N(1) ··· O(1)	5.657(3)	N(11) ··· O(11)	5.098(3)
N(1) ··· O(2)	5.052(3)	N(11) ··· O(12)	5.130(3)
(*b*) In (I) [b]			
N ··· O(1)	5.612(6)	N ··· O(2)	4.238(7)

[a] This work. [b] Ref. 13.

Molecule (A) is *anti*-clinal about the C(1)–C(2) bond whereas in (B) it is *syn*-periplanar, the respective torsion angles[11] being —118.8(3) and 13.1(4)°. Both molecules are *syn*-periplanar about the C(3)–C(4) bond, which is 1.497(3) in molecule (A) and 1.510(3) Å in molecule (B),

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[11] W. Klyne and V. Prelog, *Experientia*, 1960, **16**, 521.

close to the value (1.504 Å) suggested[12] for a C(sp^2)–C(sp^2) single bond.

The orientation of the charged amine group with respect to the carboxylate group is defined by the angle between the plane containing O(1), O(2), and C(4) and that containing N(1), C(1), and C(2). This angle is 69° in molecule (A), and 55° in molecule (B); these angles compare with 79° found in (I).[13]

Intramolecular N · · · O distances for (II) are given in Table 7 together with those for (I).

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[12] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, 233.

[13] K. Tomita, H. Higashi, and T. Fujiwara, *Bull. Chem. Soc. Japan*, 1973, **46**, 2199.