KATRITSKY, A. R., NESBIT, M. R. MICHALSKI, J., TULIMOWSKI, Z. & ZWIERZAK, A. (1970). *J. Chem. Soc.* (*B*), pp. 140–147.

KIRBY, A. I. & WARREN, S. G. (1967). *The Organic Chemistry of Phosphorus*, Chap. 10. pp. 274–364. Amsterdam: Elsevier.

MCEWEN, W. E. (1965). *Topics in Phosphorus Chemistry*, Vol. 2, pp. 2–39. Edited by M. GRAYSON AND E. J. GRIFFITH. New York: John Wiley.

RAKOFF, H. & ROSE, N. C. (1966). *Organic Chemistry*, p. 640, New York: Macmillan.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, pp. 456–458. New York: Macmillan.

WADSWORTH, W. S. (1967). *J. Org. Chem.* **32**, 1603–1604.

WHITE, D. W., MCEWEN, G. K., BERTRAND, R. D. & VERKADE, J. G. (1971). *J. Chem. Soc.* (*B*), pp. 1454–1461.

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The Crystal and Molecular Structure of Glycocyamine

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Glycocyamine, $NH_2.NH.C(NH).CH_2COOH$, crystallizes in the monoclinic system with $a=5{\cdot}09$ (1), $b=6{\cdot}16$ (1), $c=17{\cdot}47$ (3) Å, $\beta=95{\cdot}2$ (2)°. The space group is $P2_1/n$. Three-dimensional intensities were collected by equi-inclination Weissenberg photography around **a** and **b** with Cu $K\alpha$ radiation and estimated visually. The structure was solved from Patterson projections down **a** and **b** and refined by the full-matrix least-squares method. Hydrogen atoms were located from a difference Fourier synthesis. The non-hydrogen atoms were assigned anisotropic and the hydrogen atoms isotropic temperature factors. The final R is 0·075 for 868 observed reflexions, or 0·082 if 108 unobserved reflexions are included. The average standard deviation for bonds between non-hydrogen atoms is 0·004 Å. Glycocyamine is a zwitterion, the two C–O bond lengths being 1·262 and 1·247 Å. The proton from the carboxyl group is attached to the guanidinium group. Both the carboxyl and guanidinium groups are planar. The double-bond orders of the C–N bonds in the guanidinium group are 0·29, 0·38, and 0·34. All the hydrogen atoms available for hydrogen-bond formation are satisfied.

Introduction

Glycocyamine or guanidinoacetic acid, $C_3H_7N_3O_2$, plays an important biological role in the formation of creatine. In the present paper the crystal and molecular structure of glycocyamine is reported.

Experimental

Glycocyamine crystallizes from aqueous solution as transparent prisms elongated along **a**. The crystals are stable under normal conditions of temperature and humidity. Rotation and Weissenberg photographs taken about **a** and **b** (λ for Cu $K\alpha=1{\cdot}542$ Å) showed that the crystals are monoclinic with $a=5{\cdot}09$ (1), $b=6{\cdot}16$ (1), $c=17{\cdot}47$ (3) Å, $\beta=95{\cdot}2$ (2)°. The only systematic absences are $0k0$ with k odd and $h0l$ with $(h+l)$ odd indicating that the space group is $P2_1/n$. The density measured by flotation is 1·44 while that calculated for 4 molecules of $C_3H_7N_3O_2$ per unit cell is 1·42 g cm^{-3}.

Intensities were collected for $0\text{–}4kl$ and $h,0\text{–}2,l$ using the multiple-film, equi-inclination Weissenberg technique with Cu $K\alpha$ radiation. Intensities were estimated by visual comparison with a calibrated strip. The crystals used for collecting data along **a** and **b** had cross sections $0{\cdot}30\times0{\cdot}35$ and $0{\cdot}40\times0{\cdot}30$ mm respectively. No absorption correction was applied. The intensities were corrected for Lorentz, polarization, and spot-size effects (Phillips, 1954, 1956), correlated through common reflexions, and put on an absolute scale by Wilson's (1942) method.

Structure determination

The dimensions of the end groups in glycocyamine are similar. Also, it is to be expected that these groups take part in hydrogen bonding. A model was constructed satisfying these conditions. From the projections of the model on (100) and (010), the interatomic vectors were calculated and shown to be in good agreement with the Patterson syntheses. The Patterson synthesis projected down **a** is shown in Fig. 1. R for the three-dimensional data using the above model was 0·42.

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Table 1. *Positional coordinates and temperature factors with estimated standard deviations*

Anisotropic temperature factors are in the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$, and are multiplied by 10^4.

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	0·6512 (5)	0·2000 (4)	0·5655 (1)	354 (11)	238 (7)	32 (1)	186 (7)	53 (3)	25 (2)
O(2)	0·6187 (4)	0·0464 (3)	0·6790 (1)	269 (10)	229 (7)	32 (1)	102 (6)	58 (3)	14 (2)
C(1)	0·7039 (6)	0·0517 (5)	0·6143 (2)	188 (12)	152 (7)	27 (1)	56 (7)	22 (3)	12 (2)
C(2)	0·9090 (6)	−0·1102 (5)	0·5906 (2)	230 (11)	151 (8)	24 (1)	80 (7)	23 (3)	18 (2)
N(1)	0·9602 (5)	−0·2853 (4)	0·6477 (1)	237 (9)	146 (6)	20 (1)	88 (6)	23 (2)	7 (2)
C(3)	1·1421 (6)	−0·4424 (5)	0·6387 (2)	161 (11)	153 (7)	20 (1)	35 (7)	2 (3)	0 (2)
N(2)	1·2854 (6)	−0·4471 (4)	0·5781 (2)	286 (12)	173 (7)	27 (1)	111 (7)	38 (3)	10 (2)
N(3)	1·1917 (6)	−0·5968 (5)	0·6927 (2)	325 (12)	219 (8)	23 (1)	120 (7)	25 (3)	12 (2)

Table 1 (*cont.*)

Positional and thermal parameters of the hydrogen atoms.

	x/a	y/b	z/c	B (Å^2)
H(1)	0·835 (10)	−0·170 (8)	0·541 (3)	2·1 (0·9)
H(2)	1·088 (10)	−0·097 (7)	0·574 (3)	0·9 (0·8)
H(3)	0·864 (10)	−0·227 (7)	0·690 (3)	1·0 (0·8)
H(4)	1·189 (10)	−0·459 (8)	0·521 (3)	2·0 (0·9)
H(5)	1·460 (11)	−0·487 (8)	0·587 (3)	1·0 (0·9)
H(6)	1·037 (10)	−0·666 (9)	0·717 (3)	1·4 (1·0)
H(7)	1·382 (11)	−0·682 (8)	0·690 (3)	1·1 (0·9)

Refinement was carried out by the full-matrix least-squares method on a CDC 3600 computer using a modified version of the Busing, Martin & Levy (1962) *ORFLS* program. The function minimized was $\sum w(F_o-F_c)^2$, where $w=1/\sigma^2$ and σ is the standard deviation of a reflection: $\sigma=0{\cdot}30\ F_o$ for $F_o<2{\cdot}5$; $\sigma=0{\cdot}075F_o$ for $35{\cdot}0>F_o>2{\cdot}5$; and $\sigma=0{\cdot}15F_o$ for $F_o>35{\cdot}0$. The scattering factors for O,N,C, and H were taken from *International Tables for X-ray Crystallography* (1962).

As there was some confusion in identifying the carboxyl and guanidinium groups, all terminal atoms were initially assigned the scattering factor of nitrogen. Three cycles of refinement with isotropic temperature factors reduced R to 0·19. Inspection of the dimensions of the molecule at this stage helped to identify the end groups. Two more cycles with correct scattering factors reduced R to 0·14. Three cycles with anisotropic temperature factors gave $R=0{\cdot}091$. A difference Fourier synthesis revealed all the hydrogen atoms with peak heights varying from 0·17 to 0·32 e Å^{-3}. Contributions of the hydrogen atoms were included in the structure-factor calculations and R dropped to 0·078. After two more cycles with anisotropic temperature factors for C, N, and O and isotropic for H, R converged to 0·075 for 868 observed reflexions, or 0·082 if 108 unobserved reflexions were included.

The final positional and thermal parameters with their e.s.d.'s are given in Table 1, and the observed and calculated structure factors in Table 2.

Discussion

The interatomic distances and angles are given in Table 3 and Fig. 2. The glycocyamine molecule is a zwitterion, the difference between the two C–O lengths [1·262 (4) and 1·247 (4) Å] being not highly significant. The proton from the carboxyl group is transferred to the guanidinium group as in L-arginine dihydrate (Karle & Karle, 1964). The carboxyl group is substantially planar. The least-squares plane passing through O(1),

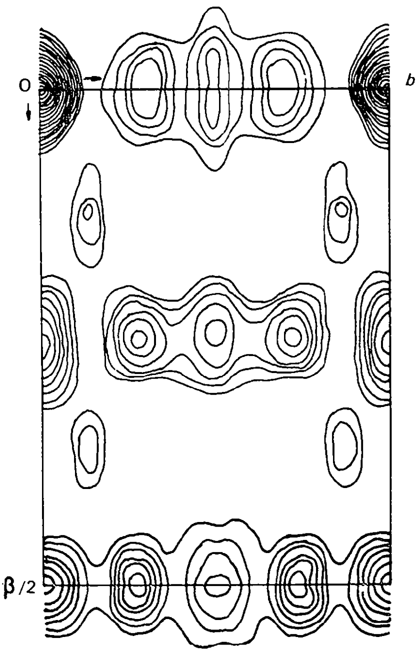
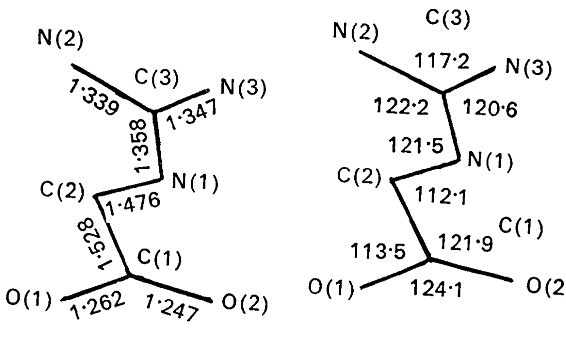


Fig. 1. Patterson synthesis projected down **a**.

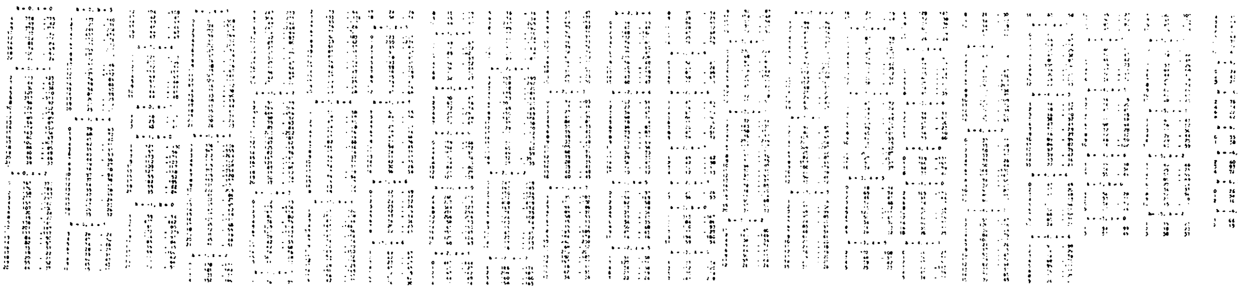


(*a*) (*b*)

Fig. 2. (*a*) Bond distances. (*b*) Bond angles.

Table 2. *Observed and calculated structure factors*

Within each group, the columns reading from left to right contain the values of l, $10F_o$, and $10F_c$. Unobserved reflexions are not included.



O(2), C(1), and C(2) is

$$0{\cdot}6922X'+0{\cdot}5499Y'+0{\cdot}3861Z'=6{\cdot}1409$$

where X', Y', Z' are coordinates in Å referred to a set of orthogonal axes with $X'=X+Z\cos\beta$, $Y'=Y$, $Z'=Z\sin\beta$. The deviations from this plane of the atoms O(1), O(2), C(1), C(2), and N(1) are 0·010, 0·013, −0·032, 0·009, and −0·083 Å respectively.

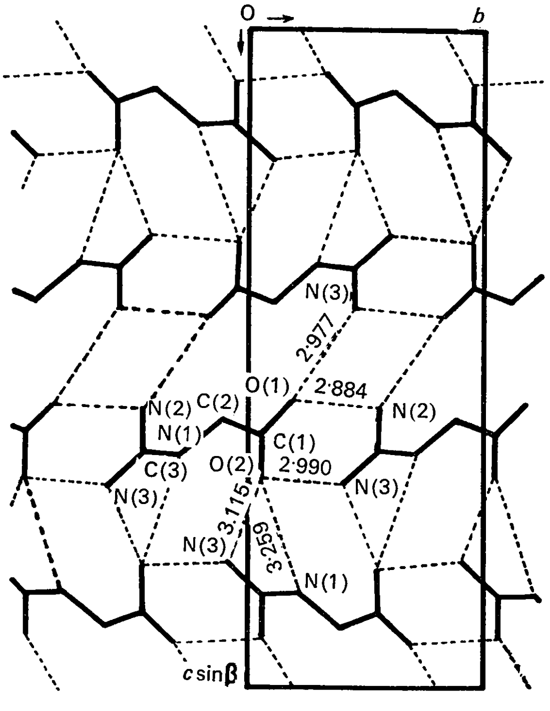


Fig. 3. Packing of the molecules projected down **a**.

Table 3. *Interatomic distances and angles*

C(1)–O(1)	1·262 (4) Å	C(2)–H(1)	0·98 (5) Å
C(1)–O(2)	1·247 (4)	C(2)–H(2)	0·98 (5)
C(1)–C(2)	1·528 (4)	N(1)–H(3)	0·98 (5)
C(2)–N(1)	1·476 (4)	N(2)–H(4)	1·07 (5)
N(1)–C(3)	1·358 (4)	N(2)–H(5)	0·92 (5)
C(3)–N(2)	1·339 (4)	N(3)–H(6)	1·02 (5)
C(3)–N(3)	1·347 (4)	N(3)–H(7)	1·11 (5)
O(1)–C(1)–O(2)	124·1 (3)°	N(1)–C(2)–H(2)	98 (3)°
O(1)–C(1)–C(2)	113·5 (3)	H(1)–C(2)–H(2)	94 (4)
O(2)–C(1)–C(2)	121·9 (3)	C(2)–N(1)–H(3)	100 (3)
C(1)–C(2)–N(1)	112·1 (2)	C(3)–N(1)–H(3)	137 (3)
C(2)–N(1)–C(3)	121·5 (2)	C(3)–N(2)–H(4)	120 (3)
N(1)–C(3)–N(2)	122·2 (3)	C(3)–N(2)–H(5)	117 (3)
N(1)–C(3)–N(3)	120·6 (3)	H(4)–N(2)–H(5)	120 (4)
N(2)–C(3)–N(3)	117·2 (3)	C(3)–N(3)–H(6)	119 (3)
C(1)–C(2)–H(1)	105 (4)	C(3)–N(3)–H(7)	114 (3)
N(1)–C(2)–H(1)	111 (3)	H(6)–N(3)–H(7)	122 (4)
C(1)–C(2)–H(2)	134 (3)		

Table 4. *Intermolecular distances and angles*

N(2)···O(1$^{\mathrm{i}}$)	2·884 (4) Å	H(6)···O(2$^{\mathrm{iii}}$)	2·43 (5) Å
H(5)···O(1$^{\mathrm{i}}$)	2·21 (5)	N(3)···O(2$^{\mathrm{i}}$)	3·115 (4)
N(2)···O(1$^{\mathrm{ii}}$)	2·977 (4)	H(7)···O(2$^{\mathrm{i}}$)	2·08 (5)
H(4)···O(1$^{\mathrm{ii}}$)	2·39 (5)	N(1)···O(2$^{\mathrm{iii}}$)	3·259 (3)
N(3)···O(2$^{\mathrm{iii}}$)	2·990 (4)	H(3)···O(2$^{\mathrm{iii}}$)	2·68 (5)
C(2)–N(2)···O(1$^{\mathrm{i}}$)	118·6 (2)°	N(2)–H(5)···O(1$^{\mathrm{i}}$)	129·8 (4·0)°
H(5)–N(2)···O(1$^{\mathrm{i}}$)	36·0 (3·1)	C(3)–N(2)···O(1$^{\mathrm{ii}}$)	139·8 (2)
N(2)–H(4)···O(1$^{\mathrm{ii}}$)	113·0 (3·3)	H(4)–N(2)···O(1$^{\mathrm{ii}}$)	47·7 (2·6)
C(3)–N(3)···O(2$^{\mathrm{iii}}$)	103·8 (2)	N(3)–H(6)···O(2$^{\mathrm{iii}}$)	113·5 (3·5)
H(6)–N(3)···O(2$^{\mathrm{iii}}$)	48·3 (2·8)	C(3)–N(3)···O(2$^{\mathrm{i}}$)	122·2 (2)
O(2$^{\mathrm{i}}$)–H(7)···O(2$^{\mathrm{i}}$)	154·3 (3·9)	H(7)–N(3)···O(2$^{\mathrm{i}}$)	16·8 (2·6)
C(2)–N(1)···O(2$^{\mathrm{iii}}$)	146·2 (2)	N(1)–H(3)···O(2$^{\mathrm{iii}}$)	118·0 (3·5)
H(3)–N(1)···O(2$^{\mathrm{iii}}$)	46·6 (2·8)	C(3)–N(1)···O(2$^{\mathrm{iii}}$)	84·9 (2)

Symmetry code:				
	i	$1+x$,	$-1+y$,	z
	ii	$2-x$,	$-y$,	$1-z$
	iii	$1{\cdot}5-x$,	$-0{\cdot}5+y$,	$1{\cdot}5-z$

There are four C–N bonds in the molecule. Of these C(2)–N(1) is a pure single bond [1·476 (4) Å]. The bond order of the three C–N bonds in the guanidyl group was calculated from the formula $x=\Delta/(0{\cdot}627-2\Delta)$, where x is the percentage double-bond character and Δ is the difference between the single-bond length (1·474 Å) and the observed length. The three bonds N(1)–C(3), N(2)–C(3), N(3)–C(3) have lengths of 1·358 (4), 1·339 (4) and 1·347 (4) Å, and double-bond orders of 0·29, 0·38 and 0·34 respectively. The guanidyl group is planar. The least-squares plane passing through N(1), C(3), N(2), and N(3) is

$$0{\cdot}6578X'+0{\cdot}5770Y'+0{\cdot}4841Z'=6{\cdot}9779.$$

The deviations of N(1), N(2), N(3), C(3), and C(2) from this plane are 0·004, 0·004, −0·004, −0·011 and 0·033 Å respectively.

The molecule is, therefore, defined in terms of two planes which intersect at an angle of 16°20′.

Intermolecular characteristics

The intermolecular lengths and angles are given in Table 4. The packing of the molecules viewed down **a** and **b** is shown in Figs. 3 and 4. There are five hydrogen atoms from the guanidinium group $-NHC(NH_2)_2^+$ available for hydrogen-bond formation. They are all satisfied by the carboxyl oxygens of different molecules. There are apparently two close neighbours to N(1), *viz.* $N(1)–O(2^{iii})=3{\cdot}259$ Å and $N(3)–N(1^{iv})=3{\cdot}371$ Å. In the former the distance $H(3)–O(2^{iii})=2{\cdot}68$ (5) Å which possibly indicates hydrogen bonding. In the latter all the N···H distances involved are much higher than the sum of the van der Waals radii. This site is, therefore, not involved in hydrogen bonding.

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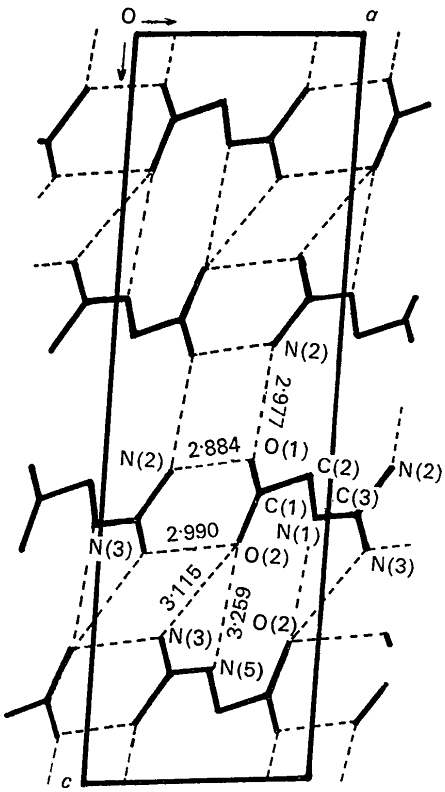

Fig. 4. Packing of the molecules projected down **b**.

References

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
Karle, I. L. & Karle, J. (1964). *Acta Cryst.* **17**, 835–841.
Phillips, D. C. (1954). *Acta Cryst.* **7**, 746–751.
Phillips, D. C. (1956). *Acta Cryst.* **9**, 819–821.
Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 151–152.