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The Crystal and Molecular Structure of L-α,γ-Diaminobutyric Acid Hydrochloride*

By P. S. Naganathan and K. Venkatesan

Centre of Advanced Study in Physics, University of Madras, Madras-25, India

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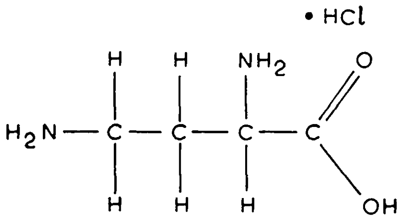
The crystal structure of L-α,γ-diaminobutyric acid hydrochloride, $C_4H_{10}N_2O_2.HCl$, has been determined using three-dimensional photographic data. The crystals are monoclinic, space group $P2_1$, with cell dimensions $a=5{\cdot}36$, $b=8{\cdot}33$, $c=8{\cdot}27$ Å and $\beta=107{\cdot}7°$. Refinement was carried out with full-matrix least-squares methods, including anisotropic thermal parameters for all non-hydrogen atoms to a final R index of 0·099 for 724 observed reflexions. The crystal structure is stabilized by a three-dimensional network of hydrogen bonds. The backbone and side group conformations of the diaminobutyric acid molecule have been studied.

Introduction

Diaminobutyric acid is a neurotoxic amino acid (O'Neal, Chen, Reynalds, Meghal & Koeppe, 1968) present in the free state in many plants (Ressler, Redstone & Erenberg, 1961; Bell, 1962; Bell & Trimanna, 1965). This amino acid is also of interest because of its presence in antibiotic substances such as polymyxin and aerosporin. The crystal structures of DL-α-amino-n-butyric acid (Ichikawa & Iitaka, 1968), aminoisobutyric acid (Hirokawa, Kuribayashi & Nitta, 1952) and butyric acid (Streiter & Templeton, 1962) have been studied by X-ray methods. The molecular features and conformations of L-α,γ-diaminobutyric acid hydrochloride (I) are presented in this paper. The crystals were kindly provided by Dr D. Rajagopal Rao, Central Food Technological Research Institute, Mysore, India.



(I)

Experimental

Rotation, Weissenberg and precession photographs were taken using Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å) and crystal data as obtained from Weissenberg and precession photographs are:

Crystal system	Monoclinic
Cell dimensions	$a=5.36\pm0{\cdot}02$ Å $b=8{\cdot}33\pm0{\cdot}02$ $c=8.27\pm0{\cdot}02$ $\beta=107{\cdot}7\pm0{\cdot}2°$
Space group	$P2_1$ ($0k0$, $k=2n+1$ absent)
Number of molecules in cell:	$Z=2$
Molecular formula	$C_4N_2O_2H_{11}Cl$
F.W.	153·6
D_M	1·467 g.cm^{-3}
D_C	1·452 g.cm^{-3}
μ(Cu $K\alpha$)	43 cm^{-1}.

The other possible space group, $P2_1/m$, is not compatible with the optical activity of the compound. The density of the crystal was determined by the flotation method using a mixture of bromoform and benzene.

The intensity data were collected with Cu $K\alpha$ radiation for layers hKl, $K=0$ to 7 and Hkl, $H=0$ and 1, by mounting the crystal about the b and a axes, respectively, using the equi-inclination Weissenberg technique for higher layers. The specimen for the data collection had a cross section of about 0·10 × 0·10 mm about the b axis and about 0·10 × 0·20 mm about the a axis. The intensities were estimated visually with the aid of a set of graded intensities recorded for the same specimen. Correction for elongation of spots was applied by the method of Phillips (1962). No absorption correction was applied as it was not considered necessary. The two sets of data about the b and a axes were then correlated by the method of Rollett & Sparks (1960). There were 180 common reflexions. The discrepancy factor between the two sets of data as defined by

$$\sum||F_H^{(b)}|-|F_H^{(a)}||/\sum\tfrac{1}{2}(|F_H^{(b)}|+|F_H^{(a)}|)=0{\cdot}105\,.$$

Out of 811 reflexions accessible within the copper sphere, 724 independent ones were observed and included in the refinement.

Structure determination and refinement

An unsharpened three-dimensional Harker section at $V=\frac{1}{2}$ was computed and the position of the chlorine atom was uniquely located. Since the choice of the

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origin along y is arbitrary in space group $P2_1$, the y coordinate of chlorine was fixed at 0·2500. The starting coordinates of the chlorine atom were x = 0·05, y = 0·25, z = 0·05. A structure-factor calculation with the chlorine contribution alone gave an R index of 0·44. All eight light atoms were located from a chlorine-phased electron density map. The R index for the trial structure was 0·33.

The structure was refined in the initial stages using successive three-dimensional difference electron density maps. Three such maps were computed and the R index at this stage was 0·195.

Four cycles of full-matrix least-squares refinement were carried out on a CDC 3600 computer using the program of Gantzel, Sparks & Trueblood (1961). The quantity minimized was $\sum w(|F_o|-|F_c|)^2$, where w is the weight of the observation. The analysis of an $|F_o|$ *vs.* $\sum|\Delta F|^2$ plot, obtained with common reflexions collected about the b and a axes, suggested the weighting function of the following form:

$$1/(1{\cdot}5+|F_o|+0{\cdot}07|F_o|^2)$$

(Cruickshank, Lowell & Truter, 1961) for use in the structure refinement. The above weighting function was used from the start of the least-squares refinement. Refinement of positional coordinates, individual isotropic vibration parameters and the overall scale factor reduced the R index to 0·125. A difference electron density map computed at this stage showed peaks where hydrogen atoms were expected to occur, at heights ranging from 0·2 to 0·5 e.Å^{-3}. Two more cycles of isotropic refinement resulted in an R index of 0·11. Hydrogen atoms were not refined, but were included in the structure-factor calculations with the isotropic temperature factors of the heavy atoms to which they are bonded. A further three cycles of refinement with anisotropic thermal parameters for chlorine, and the eight lighter atoms, reduced the R index to 0·099. In the last cycle, the maximum parameter shift was less than one tenth of the corresponding estimated standard deviation. The final positional and thermal parameters for the non-hydrogen atoms are given in Table 1(a) and (b); those for hydrogen atoms in Table 2. The final electron density distribution is presented in Fig. 1. Observed and calculated structure factors are recorded in Table 3.

Table 2. *Positional and thermal parameters of hydrogen atoms*

Atom	Bonded to	x	y	z	B(Å^2)
H(1)	N(1)	0·883	+0·017	0·767	3·21
H(2)	N(1)	1·067	−0·050	0·667	3·21
H(3)	N(1)	0·783	−0·133	0·650	3·21
H(4)	C(2)	0·733	+0·150	0·517	2·65
H(5)	C(3)	0·800	−0·100	0·350	3·12
H(6)	C(3)	0·550	−0·133	0·333	3·12
H(7)	C(4)	0·750	+0·167	0·200	3·51
H(8)	C(4)	0·383	+0·133	0·200	3·51
H(9)	N(2)	0·483	+0·017	−0·067	3·22
H(10)	N(2)	0·733	−0·100	0·050	3·22
H(11)	N(2)	0·400	−0·117	0·050	3·22

Atomic scattering factors used for Cl$^-$, O, N, C and H are those listed in *International Tables for X-ray Crystallography* (1962). The real part of the anomalous dispersion corrections for chlorine ($\Delta f'$ = 0·3 for Cu $K\alpha$) was taken into account.

Note that the imaginary component of the anomalous dispersion corrections for the chloride ion was not incorporated in the refinements ($\Delta f''$ = 0·6 for Cu $K\alpha$). The neglect of $\Delta f''$ in the refinements of non-centric

Table 1. *Positional parameters* (a) *and thermal parameters* (b) *of non-hydrogen atoms*

(a) Standard deviations (in parentheses) are multiplied by 10^4.

	x	y	z
Cl	0·0519 (4)	−0·2500 (−)	0·0586 (2)
C(1)	0·4106 (16)	+0·0572 (12)	0·5444 (10)
C(2)	0·6816 (15)	+0·0469 (13)	0·5155 (10)
C(3)	0·6658 (18)	−0·0399 (13)	0·3480 (11)
C(4)	0·5847 (19)	+0·0691 (14)	0·1982 (11)
N(1)	0·8683 (14)	−0·0388 (11)	0·6604 (9)
N(2)	0·5455 (14)	−0·0301 (10)	0·0431 (8)
O(1)	0·2372 (12)	+0·1308 (10)	0·4409 (8)
O(2)	0·3878 (12)	−0·0112 (11)	0·6742 (9)

(b) The temperature factor is of the form: exp $-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cl	376 (8)	125 (3)	150 (3)	+5 (10)	169 (7)	−2 (6)
C(1)	270 (29)	118 (15)	106 (12)	+17 (33)	98 (28)	−23 (20)
C(2)	246 (28)	124 (16)	109 (12)	−48 (34)	138 (28)	−1 (21)
C(3)	330 (33)	105 (15)	112 (13)	−20 (36)	139 (33)	−23 (24)
C(4)	449 (40)	117 (16)	116 (13)	−6 (40)	169 (38)	+4 (25)
N(1)	318 (27)	145 (14)	135 (11)	0 (34)	120 (28)	0 (23)
N(2)	387 (32)	138 (15)	117 (12)	−6 (33)	165 (31)	+17 (20)
O(1)	330 (24)	130 (13)	157 (11)	+23 (28)	180 (26)	+33 (19)
O(2)	274 (23)	182 (16)	150 (11)	+66 (31)	179 (25)	+40 (21)

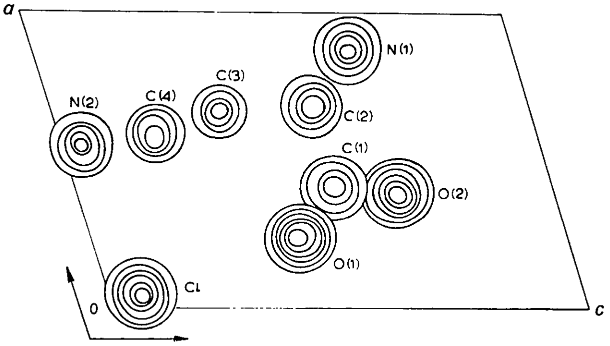

Fig. 1. Composite diagram of final electron density distribution. Contours are drawn at intervals of 2 e.Å^{-3}, starting from 1 e.Å^{-3}, while near chlorine the interval is 5 e.Å^{-3}.

structures could give rise to positional errors (Ueki, Zalkin & Templeton, 1966; Cruickshank & McDonald, 1967). Consequently, in the present case where most of the data were obtained from photographs recorded about the *b* axis, standard deviations of the *y* coordinates of the light atoms recorded in Table 1 are expected to be slightly underestimated.

Description of the structure

Crystal packing and hydrogen bonding

The packing of the diaminobutyric acid molecules is characterized by a three-dimensional network of hydrogen bonds. Fig. 2 illustrates the packing of the molecules in the crystal lattice. Six protons are available for hydrogen bonding and all of them are involved in intermolecular hydrogen bonding. Hydrogen-bond distances and angles are listed in Table 4. Each nitrogen atom is a donor in the structure, N(1) and N(2) each for three hydrogen bonds. However, atom N(2) has four near neighbours: Cl(I), Cl(II), O(2)(III), Cl*(VI), at distances 3·25, 3·25, 2·91 and 3·45 Å, respectively (Table 4). From consideration of the various angles and distances involving N(2), H(9), O(2)(III) and Cl*(VI) (Table 4), apparently N(2)···Cl*(VI) is an ionic contact. To determine the nature of the contact, the position of the hydrogen atoms of the $N(2)H_3^+$ group were fixed from geometrical considerations using (i) the bond length N–H = 1·0 Å, (ii) the tetrahedral disposition of the hydrogen atoms at the nitrogen atom and (iii) the staggered disposition of the N–H bonds. The pertinent bond lengths and angles involving atoms N(2), H(9),

Table 3. *Observed and calculated structure factors*

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
0	0	1	9.1	6.8
0	0	2	30.6	33.4
0	0	3	20.4	22.4
0	0	4	3.9	3.6
0	0	5	6.8	6.3
0	0	6	5.6	4.3
0	0	7	12.8	12.3
0	0	8	11.9	11.0
0	0	10	4.7	5.3
1	0	-10	3.7	3.2
1	0	-9	4.2	4.4
1	0	-8	1.5	1.6
1	0	-7	4.7	3.6
1	0	-6	14.2	13.3
1	0	-5	7.8	7.8
1	0	-4	10.5	10.7
1	0	-3	24.9	24.0
1	0	-2	11.4	10.4
1	0	-1	20.5	18.8
1	0	0	11.5	10.8
1	0	1	27.1	26.1
1	0	2	6.7	7.4
1	0	3	4.3	3.4
1	0	4	0.9	1.1
1	0	5	12.8	10.8
1	0	6	4.7	4.9
1	0	7	3.9	3.3
1	0	9	3.1	3.5
2	0	-9	6.2	6.0
2	0	-8	11.8	10.9
2	0	-7	5.2	5.2
2	0	-6	4.6	3.2
2	0	-4	23.4	21.5
2	0	-3	28.3	28.3
2	0	-2	2.3	2.3
2	0	-1	67.8	72.8
2	0	0	14.5	13.2
2	0	1	3.1	3.1
2	0	2	13.2	12.1
2	0	3	0.9	0.7
2	0	4	9.0	10.1
2	0	6	8.2	8.0
2	0	7	8.4	10.0
2	0	8	1.1	1.4
3	0	-10	3.1	3.0
3	0	-9	2.7	2.6
3	0	-8	1.6	1.6
3	0	-7	9.8	10.7
3	0	-6	9.5	9.5
3	0	-5	5.5	5.3
3	0	-4	19.2	17.6
3	0	-3	2.2	2.2
3	0	-2	18.9	20.5
3	0	-1	6.2	5.7
3	0	0	11.5	13.0
3	0	1	5.4	4.9
3	0	2	5.8	5.5
3	0	3	1.5	1.6
3	0	4	8.4	8.5
3	0	5	3.1	3.2
3	0	6	4.2	3.8
3	0	7	1.1	0.9
4	0	-10	2.8	3.0
4	0	-9	3.3	3.8
4	0	-7	11.3	10.5
4	0	-6	2.1	3.1
4	0	-5	16.7	17.3
4	0	-4	10.8	11.7
4	0	-3	4.5	4.1
4	0	-2	19.3	19.5
4	0	-1	13.2	10.9
4	0	0	4.5	3.8
4	0	3	8.3	8.9
4	0	4	1.9	1.6
4	0	5	4.5	5.3
4	0	6	3.6	3.0
5	0	-9	0.9	0.9
5	0	-8	3.9	3.3
5	0	-7	3.4	3.7
5	0	-6	1.5	1.7
5	0	-5	6.6	5.9
5	0	-4	3.0	4.8
5	0	-3	6.7	6.1
5	0	-1	1.6	1.1
5	0	0	2.2	1.8
5	0	1	3.1	2.9
5	0	2	2.0	2.2
5	0	3	3.8	4.0
5	0	4	2.0	2.4
6	0	-7	1.7	1.0
6	0	-6	7.1	7.0
6	0	-5	5.4	5.7
6	0	-4	1.6	1.7
6	0	-3	4.3	5.5
6	0	-2	4.0	3.9
6	0	-1	1.8	1.7
6	0	0	3.1	2.7
0	1	1	4.1	3.8
0	1	2	31.1	31.3
0	1	3	20.7	20.6
0	1	4	24.6	23.8
0	1	5	12.5	13.8
0	1	6	12.3	12.6
0	1	7	4.3	4.2
0	1	8	4.1	4.2
0	1	10	2.9	2.2
1	1	-10	3.1	2.4
1	1	-9	1.6	2.0
1	1	-8	1.8	2.5
1	1	-7	10.8	11.4
1	1	-6	11.6	10.7
1	1	-5	11.5	12.9
1	1	-4	12.3	11.4
1	1	-3	11.7	13.8
1	1	-2	23.2	26.5
1	1	-1	11.8	12.7
1	1	0	11.7	12.9
1	1	1	24.1	28.6
1	1	2	18.2	19.7
1	1	3	11.6	10.7
1	1	4	12.3	13.8
1	1	5	5.3	7.1
1	1	6	14.8	15.2
1	1	7	5.0	5.1
1	1	8	3.1	3.3
1	1	9	3.8	3.8
2	1	-10	3.1	2.8
2	1	-9	5.4	4.8
2	1	-8	5.4	4.9
2	1	-7	7.6	9.2
2	1	-6	12.3	12.0
2	1	-5	15.9	17.4
2	1	-4	7.4	7.9
2	1	-3	16.2	16.4
2	1	-2	6.5	6.6
2	1	-1	13.8	14.0
2	1	0	9.4	10.7
2	1	1	17.0	20.1
2	1	2	18.9	20.2
2	1	3	18.8	19.6
2	1	4	8.4	9.2
2	1	5	8.3	8.6
2	1	6	2.5	1.9
2	1	7	2.2	1.5
2	1	8	3.0	2.6
3	1	-9	3.6	3.3
3	1	-8	7.3	6.7
3	1	-7	7.5	7.9
3	1	-6	9.6	9.3
3	1	-5	5.5	6.0
3	1	-4	6.3	5.7
3	1	-3	5.9	6.1
3	1	-2	8.7	7.1
3	1	-1	11.4	9.2
3	1	0	15.1	14.1
3	1	1	11.0	11.9
3	1	2	8.1	9.1
3	1	3	7.3	7.6
3	1	4	3.7	4.3
3	1	5	7.3	7.7
4	1	-10	3.4	2.9
4	1	-9	4.1	4.1
4	1	-8	5.5	5.6
4	1	-7	6.0	6.7
4	1	-6	7.5	8.4
4	1	-5	4.2	4.6
4	1	-4	4.9	5.3
4	1	-3	4.0	4.4
4	1	-2	8.0	7.8
4	1	-1	5.5	6.8
4	1	0	12.5	11.3
4	1	1	14.9	14.9
4	1	2	12.7	12.0
4	1	3	3.3	4.0
4	1	4	3.2	4.1
4	1	5	3.0	3.2
5	1	-8	2.9	3.4
5	1	-7	3.6	4.9
5	1	-6	1.8	1.6
5	1	-5	2.5	2.7
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5	1	-2	3.8	3.2
5	1	-1	10.0	9.5
5	1	0	4.2	5.3
5	1	1	7.2	7.6
5	1	2	2.2	2.8
5	1	3	2.7	2.4
5	1	4	2.5	1.7
6	1	-7	2.6	3.2
6	1	-6	2.5	2.9
6	1	-4	3.0	3.3
6	1	-3	3.5	4.5
6	1	-2	4.1	4.6
6	1	-1	3.9	4.5
6	1	0	4.3	5.5
6	1	1	3.2	3.4
0	2	0	33.4	36.3
0	2	1	48.9	44.0
0	2	2	19.2	19.7
0	2	3	23.3	26.9
0	2	4	8.9	9.3
0	2	5	3.0	2.8
0	2	6	14.7	15.4
0	2	7	2.9	2.4
0	2	8	2.5	3.3
0	2	9	6.5	5.9
1	2	-10	3.0	3.2
1	2	-8	8.8	8.7
1	2	-7	4.9	4.8
1	2	-6	4.6	4.3
1	2	-5	4.8	3.9
1	2	-4	14.7	15.7
1	2	-3	27.5	26.1
1	2	-2	27.8	26.0
1	2	-1	39.6	38.1
1	2	0	52.4	51.6
1	2	1	11.6	11.5
1	2	2	23.1	22.0
1	2	3	2.0	2.4
1	2	4	2.4	2.1
1	2	5	8.1	6.6
1	2	6	7.0	5.5
1	2	7	9.9	8.5
1	2	8	7.5	6.1
1	2	9	3.1	2.7
2	2	-10	3.9	4.8
2	2	-9	4.7	4.5
2	2	-8	2.9	2.8
2	2	-7	12.8	10.9
2	2	-5	11.9	9.1
2	2	-4	12.7	12.1
2	2	-3	10.5	11.3
2	2	-2	31.8	29.2
2	2	-1	11.2	11.2
2	2	0	12.1	11.7
2	2	1	22.5	22.0
2	2	3	2.4	2.9
2	2	4	2.7	4.0
2	2	5	10.9	11.3
2	2	6	2.9	3.6
2	2	7	1.8	1.6
2	2	8	3.6	3.5
3	2	-10	4.1	3.4
3	2	-9	4.5	4.1
3	2	-8	4.7	5.2
3	2	-7	7.0	7.7
3	2	-6	4.8	5.1
3	2	-5	14.1	14.5
3	2	-4	15.7	15.8
3	2	-3	17.6	17.8
3	2	-2	16.4	14.2
3	2	-1	29.9	25.5
3	2	0	5.8	4.0
3	2	1	6.3	5.3
3	2	2	2.7	2.1
3	2	3	5.2	4.3
3	2	4	6.9	6.3
3	2	5	5.1	5.5
3	2	6	6.1	5.7
3	2	7	5.2	4.4
4	2	-10	2.0	3.5
4	2	-9	3.6	2.4
4	2	-8	4.4	4.0
4	2	-7	4.8	4.6
4	2	-6	8.8	10.1
4	2	-4	8.5	7.6
4	2	-3	12.1	11.7
4	2	-2	2.7	2.3
4	2	-1	2.7	3.2
4	2	0	12.5	11.5
4	2	1	7.0	6.8
4	2	2	4.0	4.4
4	2	3	2.7	1.7
4	2	4	5.6	6.6
4	2	5	2.2	2.1
5	2	-8	5.2	4.0
5	2	-7	2.6	3.0
5	2	-6	5.5	5.4
5	2	-5	10.0	8.9
5	2	-4	7.0	6.3
5	2	-3	7.3	6.7
5	2	-2	7.3	7.1
5	2	-1	2.9	2.5
5	2	0	2.9	2.6
5	2	1	2.7	2.5
5	2	2	2.6	2.7
5	2	3	5.0	4.3
5	2	4	3.1	2.6
6	2	-6	2.0	1.0
6	2	-5	4.1	3.2
6	2	-4	4.0	4.7
6	2	-3	2.1	2.1
6	2	-2	3.1	2.5
6	2	-1	4.0	3.3
6	2	0	2.2	2.5
0	3	1	20.0	20.7
0	3	2	20.4	20.7
0	3	3	7.1	8.9
0	3	4	8.5	9.8
0	3	5	6.4	5.8
0	3	6	12.3	11.0
0	3	7	4.0	3.8
0	3	8	3.6	3.3
0	3	9	3.5	4.0
1	3	-10	1.9	2.2
1	3	-9	1.6	1.4
1	3	-8	4.0	3.7
1	3	-7	7.8	6.9
1	3	-6	9.7	9.9
1	3	-5	11.9	13.8
1	3	-4	19.8	22.1
1	3	-3	12.5	15.0
1	3	-2	5.1	4.8
1	3	-1	13.7	12.5
1	3	0	23.3	21.2
1	3	1	10.0	9.3
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1	3	3	24.5	27.0
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1	3	5	10.5	10.7
1	3	6	5.1	5.0
1	3	7	4.1	4.6
1	3	8	3.1	2.6
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2	3	-8	2.2	3.2
2	3	-7	9.0	9.1
2	3	-6	6.9	7.4
2	3	-5	6.3	6.3
2	3	-4	11.1	12.8
2	3	-3	13.5	12.3
2	3	-2	12.4	9.8
2	3	-1	6.8	6.7
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2	3	1	14.5	12.9
2	3	2	12.8	11.7
2	3	3	6.4	5.5
2	3	4	7.5	7.3
2	3	5	5.8	5.8
2	3	6	5.3	4.6
2	3	7	2.7	2.4
2	3	8	2.2	2.7
3	3	-10	2.3	3.4
3	3	-9	2.6	3.2
3	3	-8	6.9	6.5
3	3	-7	7.4	7.0
3	3	-6	7.4	7.9
3	3	-5	10.5	12.9
3	3	-4	4.8	5.1
3	3	-3	2.4	2.7
3	3	-2	6.5	3.3
3	3	-1	14.2	13.8
3	3	0	11.9	10.2
3	3	1	11.5	9.8
3	3	2	17.7	15.7
3	3	3	7.1	7.2
3	3	4	4.3	5.0
3	3	5	3.7	3.5
3	3	6	1.6	1.0
3	3	7	1.5	1.9
4	3	-9	3.8	3.6
4	3	-8	4.2	4.7
4	3	-7	4.8	6.1
4	3	-6	4.2	3.7
4	3	-5	7.8	7.3
4	3	-4	6.6	5.6
4	3	-3	2.3	2.0
4	3	-2	3.1	3.4
4	3	-1	13.5	11.4
4	3	0	7.1	5.0
4	3	1	10.8	10.6
4	3	2	6.4	6.6
4	3	3	1.6	1.2
4	3	4	3.5	3.5
4	3	5	2.7	2.9
5	3	-9	2.3	3.9
5	3	-8	3.0	3.9
5	3	-7	1.8	2.6
5	3	-6	3.8	5.4
5	3	-5	2.3	1.9
5	3	-4	2.5	3.7
5	3	-3	2.3	1.9
5	3	-2	9.9	9.7
5	3	-1	4.2	3.4
5	3	0	7.7	6.3
5	3	1	5.8	5.0
5	3	2	6.0	5.7
6	3	-6	2.7	3.1
6	3	-5	1.6	1.5
6	3	-4	2.4	2.1
6	3	-3	1.3	1.2
6	3	-2	4.1	4.6
6	3	-1	2.0	4.0
6	3	0	2.7	3.5
0	4	0	27.5	27.6
0	4	1	16.6	19.1
0	4	2	7.2	8.1
0	4	3	26.1	26.2
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0	4	6	2.0	2.2
0	4	7	8.6	8.6
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1	4	-8	4.1	3.1
1	4	-7	6.8	5.9
1	4	-6	1.4	1.7
1	4	-5	1.4	1.4
1	4	-4	5.6	5.9
1	4	-3	9.0	8.9
1	4	-2	18.3	18.6
1	4	-1	12.6	13.6
1	4	0	10.6	10.1
1	4	1	19.1	19.3
1	4	2	3.4	2.9
1	4	3	5.8	6.4
1	4	4	5.3	5.8
1	4	5	1.4	1.7
1	4	6	8.7	7.5
1	4	7	4.1	3.2
1	4	8	3.7	3.0
2	4	-9	3.5	2.6
2	4	-8	7.9	7.3
2	4	-7	2.6	3.2
2	4	-6	1.4	1.7
2	4	-5	6.2	6.6
2	4	-4	19.2	20.3
2	4	-3	13.4	12.5
2	4	-2	14.0	13.3
2	4	-1	21.1	20.9
2	4	0	18.9	18.2
2	4	1	1.6	2.2
2	4	2	13.2	14.0
2	4	3	1.3	2.1
2	4	4	9.0	10.0
2	4	5	2.0	2.8
2	4	6	7.7	7.0
2	4	7	4.1	4.3
3	4	-9	2.8	2.1
3	4	-8	4.4	3.7
3	4	-7	3.4	2.9
3	4	-6	2.7	3.0
3	4	-5	6.8	5.7
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3	4	2	1.9	2.1
3	4	3	4.7	5.1
3	4	4	1.4	1.6
3	4	5	5.8	5.8
3	4	6	2.6	3.1
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4	4	-8	5.1	3.6
4	4	-7	2.4	2.9
4	4	-6	1.4	1.5
4	4	-5	10.2	10.1
4	4	-4	12.0	11.5
4	4	-3	8.8	9.1
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5	4	0	1.2	1.8
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5	4	2	2.9	3.9
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6	4	-4	3.9	3.6
6	4	-3	1.8	1.9
6	4	-2	5.4	4.2
6	4	-1	3.1	2.8
0	5	1	7.6	7.1
0	5	2	7.9	9.2
0	5	3	20.0	19.9
0	5	4	6.4	5.1
0	5	5	14.7	16.0
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0	5	7	6.5	5.3
0	5	8	0.9	1.2
1	5	-9	2.6	1.6
1	5	-8	4.9	3.4
1	5	-6	10.7	8.6
1	5	-5	7.3	6.4
1	5	-4	2.7	2.0
1	5	-3	12.4	11.4
1	5	-2	7.8	6.5
1	5	-1	2.5	2.3
1	5	0	7.0	6.5
1	5	1	6.6	5.9
1	5	2	19.8	17.2
1	5	3	2.1	2.6
1	5	4	11.0	8.9
1	5	5	5.9	4.5
1	5	6	3.6	2.8
1	5	7	1.0	0.4
2	5	-9	3.6	2.3
2	5	-8	7.0	5.8
2	5	-7	3.0	2.7
2	5	-6	13.5	11.7
2	5	-5	7.9	8.0
2	5	-4	12.4	11.3
2	5	-3	7.0	6.6
2	5	-2	4.4	5.5
2	5	-1	8.5	7.8
2	5	0	6.3	6.4
2	5	1	9.5	7.3
2	5	2	16.2	16.7
2	5	3	7.9	8.3
2	5	4	8.1	8.3
2	5	5	6.7	5.2
2	5	6	1.0	1.4
2	5	7	1.1	1.1
3	5	-9	4.9	4.7
3	5	-8	0.9	0.7
3	5	-7	8.6	7.8
3	5	-6	4.2	4.5
3	5	-5	1.2	1.4
3	5	-4	6.1	5.5
3	5	-3	1.1	1.7
3	5	-2	1.1	0.7
3	5	-1	8.1	7.4
3	5	0	3.6	2.9
3	5	1	15.3	13.8
3	5	2	4.3	2.9
3	5	3	5.6	5.5
3	5	4	5.5	2.7
4	5	-8	4.5	3.0
4	5	-7	7.0	5.4
4	5	-6	6.4	3.2
4	5	-5	6.8	5.6
4	5	-4	3.1	2.8
4	5	-3	2.4	1.9
4	5	-2	11.2	9.9
4	5	-1	2.4	2.3
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4	5	1	7.6	6.8
4	5	2	7.2	7.2
4	5	3	2.5	2.0
4	5	4	4.6	4.1
5	5	-7	4.1	2.6
5	5	-6	0.9	1.0
5	5	-5	1.0	1.2
5	5	-4	1.0	0.9
5	5	-3	2.4	2.4
5	5	-2	4.0	3.5
5	5	-1	3.6	3.7
5	5	0	5.8	5.0
5	5	1	2.2	2.0
6	5	-2	2.6	1.9
0	6	0	13.3	12.2
0	6	1	9.2	10.7
0	6	2	8.2	8.3
0	6	3	11.2	11.7
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0	6	5	1.0	1.0
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0	6	8	3.7	3.1
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1	6	-1	15.6	12.3
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1	6	3	8.0	8.1
1	6	4	7.5	7.0
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1	6	6	5.1	4.0
1	6	7	3.1	3.1
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2	6	-7	2.4	2.1
2	6	-6	3.1	2.7
2	6	-5	8.5	6.8
2	6	-4	8.5	8.0
2	6	-3	8.7	5.8
2	6	-2	13.8	11.8
2	6	-1	11.7	11.2
2	6	0	8.2	7.9
2	6	1	5.5	3.9
2	6	2	5.8	4.9
2	6	3	2.7	3.1
2	6	4	2.8	2.6
2	6	5	5.1	4.6
2	6	6	4.0	3.7
3	6	-8	1.2	1.7
3	6	-5	4.0	3.7
3	6	-4	11.1	11.2
3	6	-3	8.3	7.1
3	6	-2	7.9	7.9
3	6	-1	7.9	6.8
3	6	0	6.1	4.9
3	6	1	2.8	1.8
3	6	2	4.2	3.3
3	6	3	5.2	4.6
3	6	4	5.3	5.1
3	6	5	3.5	2.9
4	6	-3	9.8	9.2
4	6	-2	8.5	7.0
4	6	-1	4.9	4.4
4	6	-4	5.7	5.3
4	6	-5	3.8	4.0
4	6	-6	3.6	3.3
4	6	-7	2.0	1.9
4	6	1	2.6	1.6
4	6	2	3.8	3.2
4	6	3	2.2	2.2
5	6	-6	3.0	3.2
5	6	-5	4.1	4.7
5	6	-4	4.5	5.4
5	6	-3	1.3	1.8
5	6	-2	4.2	3.6
5	6	0	1.0	0.5
5	6	1	0.8	1.1
0	7	1	3.6	3.7
0	7	2	6.0	5.8
0	7	3	4.7	5.3
0	7	4	8.8	8.7
0	7	5	3.4	4.2
0	7	6	4.5	4.9
1	7	-7	4.7	5.8
1	7	-6	3.1	4.6
1	7	-5	6.7	6.8
1	7	-4	10.2	10.2
1	7	-3	4.7	4.1
1	7	-2	5.0	4.1
1	7	-1	5.6	3.5
1	7	0	5.4	3.9
1	7	1	8.8	8.6
1	7	2	3.2	3.3
1	7	3	12.6	12.9
1	7	4	4.2	4.9
1	7	5	4.6	5.4
1	7	6	3.2	4.0
1	7	7	1.6	1.5
2	7	-7	4.7	4.7
2	7	-6	3.1	3.1
2	7	-5	5.8	5.8
2	7	-4	3.8	3.6
2	7	-3	3.8	3.4
2	7	-2	2.4	2.2
2	7	0	4.8	5.0
2	7	1	5.8	5.5
2	7	2	3.5	4.2
2	7	3	4.2	5.3
2	7	4	2.6	3.2
2	7	6	1.2	1.4
3	7	-7	3.0	3.2
3	7	-6	4.2	3.3
3	7	-5	4.7	6.0
3	7	-4	1.2	1.5
3	7	-3	1.7	1.9
3	7	-2	6.2	5.4
3	7	-1	5.9	4.9
3	7	0	10.3	8.2
3	7	1	2.3	3.0
3	7	2	9.6	9.6
3	7	3	3.5	3.5
3	7	4	3.0	2.8
4	7	-6	2.6	2.5
4	7	-5	1.3	1.9
4	7	-4	1.4	2.0
4	7	-3	2.3	2.8
4	7	-2	2.7	2.9
4	7	-1	5.5	5.4
4	7	0	3.0	2.8
4	7	1	2.7	2.8
4	7	2	1.7	2.0
4	7	3	2.8	2.3
5	7	-4	2.3	1.6
5	7	-3	3.0	2.1
5	7	-2	4.0	3.5
5	7	-1	3.5	4.0
0	8	0	7.0	6.1
0	8	1	7.9	7.1
0	8	2	5.3	5.3
0	8	3	7.7	7.3
0	8	4	3.8	2.5
0	8	6	4.4	4.1
1	8	-5	2.1	3.0
1	8	-3	3.4	3.6
1	8	-2	6.3	6.4
1	8	-1	7.1	7.3
1	8	0	6.8	8.4
1	8	1	3.1	2.9
1	8	2	5.3	4.8
1	8	3	3.6	3.6
1	8	4	2.2	2.6
0	9	2	5.9	5.6
0	9	3	3.5	4.1
0	9	4	3.8	4.8
0	9	5	3.8	4.1
1	9	-5	3.3	4.4
1	9	-3	2.9	3.7
1	9	-1	3.5	3.9
1	9	0	2.8	3.3
1	9	1	2.2	2.4
1	9	2	3.8	4.0
1	9	3	2.3	2.7
1	9	4	3.3	3.7
0	10	0	8.2	8.2
0	10	2	4.0	4.4
1	10	-1	3.2	4.6
1	10	0	2.4	3.2
1	10	1	3.1	3.6

O(2)(III), Cl*(VI) are given in parentheses in Table 4. Values indicate that N(2)···Cl*(VI) is an ionic contact. However, N(2)···O(2)(III) is a non-linear hydrogen bond. Here is yet another example of four negatively charged atoms approaching a protonated amino group within distances of hydrogen bonds, while only three of them are hydrogen bonded. The chlorine ion accepts three hydrogen bonds. Deviation of the chlorine atom from the plane through N(1)(IV), N(2)(I) and N(2)(II) is 0·77 Å.

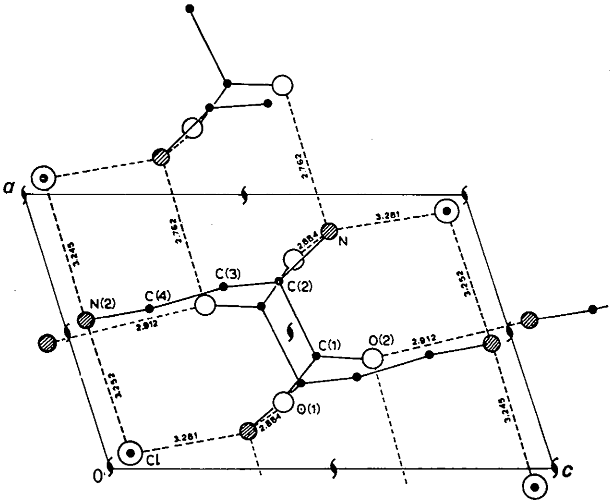


Fig. 2. Packing of the structure viewed down *b* axis.

Bond distances and angles

Observed bond distances and angles in the molecule are given in Fig. 3. E.s.d.'s of bond lengths and angles among C, N, O atoms are 0·013 Å and 1°, respectively. Note that the angle at C^{β} [C(2)–C(3)–C(4)] (113°) is larger than the tetrahedral value. A similar observation has been made in the structures L-lysine hydrochloride dihydrate (Wright & Marsh, 1962), L-ornithine hydrochloride (Chiba, Ueki, Ashida, Sasada & Kakudo, 1967), DL-α-amino-n-butyric acid (Ichikawa & Iitaka, 1968) and in L-citrulline hydrochloride (Naganathan & Venkatesan, 1971). The $C^{\alpha}-C'$ [C(2)–C(1)] length of 1·544 (0·013) Å is larger than the weighted average distance of 1·527 (0·004) Å for the above distance (Marsh & Donohue, 1967; Sundaralingam & Putkey, 1970), but the difference cannot be considered significant. The values of 1·489 Å for the C(2)–N(1) bond and 1·486 Å for the C(4)–N(2) bond are in good agreement with the average value of C–N = 1·487 Å for accurately solved amino acid structures (Marsh & Donohue, 1967). While the value of 1·542 Å appears to be normal for the C(2)–C(3) bond, the value of 1·490 (0·013) Å for C(3)–C(4) is smaller than 1·526 (0·004) Å reported by Sundaralingam & Putkey (1970). The somewhat short C(3)–C(4) bond distance could be due to atom C(4) having relatively large displacements along the *a* and *b* axes. The root-mean-square displacements along the principal axes of the thermal ellipsoids are listed in Table 5. The maximum r.m.s. amplitude of thermal motion of various atoms ranges from 0·282 Å for O(2) to 0·215 Å for C(1); minimum amplitudes range from 0·074 Å for C(2) to 0·160 Å for N(1). Most atoms have their direction of maximum amplitudes almost along the *b* axis. Bond distances involving hydrogen atoms range from 0·87 to 1·15 Å.

The carboxyl group in this structure exists in the ionized form COO⁻. The protons associated with the COOH group as well as HCl have been accepted by atoms N(1) and N(2). There is a slight difference in the C–O distances within the COO⁻ group with C(1)–O(1) = 1·220 ± 0·012 Å and C(1)–O(2) = 1·252 ± 0·012 Å, the difference being significant only at about 2σ level; this difference, which is marginally significant, could be due to the influence of hydrogen bonding on the resonance in the carboxyl group (Donohue & Trueblood, 1952).

As seen in Table 6, the α,γ-diaminobutyric acid molecule is characterized by two planar groups, *viz.* (i) the carboxyl group and (ii) the group of atoms C(2)–C(3)–C(4)–N(2). The equation of the plane and the deviations are given in Table 6. The dihedral angle between planes I and II is 71·5°.

Table 4. *Hydrogen bond lengths and angles*

D–H···A	Length	C–$\hat{D}$···A	D–$\hat{\mathrm{H}}$···A	H–$\hat{D}$···A
N(1)–H(1)····Cl(IV)	3·281 Å	97·4°	153°	19°
N(1)–H(3)····O(1) (V)	2·882	101·5	146	23
N(1)–H(2)····O(2) (II)	2·762	114·6	164	10
N(2)–H(11)···Cl(I)	3·252	100·5	168	8
N(2)–H(10)···Cl(II)	3·245	112·5	174	4
N(2)–H(9)····O(2) (III)	2·912	142·5	148 (133)	22 (33)
N(2)–H(9)····Cl*(VI)	3·451	84	101 (108)	64 (56)

Symmetry code:	I	x	y	z
	II	$1+x$	y	z
	III	x	y	$z-1$
	IV	$-x$	$\frac{1}{2}+y$	$1-z$
	V	$-x$	$-\frac{1}{2}+y$	$-z$
	VI	$-x$	$\frac{1}{2}+y$	$-z$

Table 5. *R.m.s. displacements and directions of principal axes of thermal vibrations**

	j	$U(j)$	α_{1j}	α_{2j}	α_{3j}
Cl	1	0·141	142·0°	92·2°	52·1°
	2	0·210	52·2	87·2	37·9
	3	0·252	93·5	3·6	90·9
C(1)	1	0·130	134·3	135·7	89·5
	2	0·203	52·2	127·2	120·6
	3	0·215	111·7	69·5	149·4
C(2)	1	0·074	145·0	102·5	122·1
	2	0·200	58·2	130·6	123·2
	3	0·230	76·9	43·3	130·3
C(3)	1	0·121	134·2	112·0	52·4
	2	0·187	46·0	98·5	45·3
	3	0·235	100·0	23·8	68·7
C(4)	1	0·127	129·4	87·8	39·5
	2	0·203	39·8	94·6	50·6
	3	0·257	85·1	5·1	88·8
N(1)	1	0·160	144·4	90·0	54·4
	2	0·226	54·4	90·0	35·6
	3	0·226	90·0	0·0	90·0
N(2)	1	0·112	133·4	77·1	46·2
	2	0·222	45·1	91·1	45·0
	3	0·247	80·1	13·0	98·4
O(1)	1	0·115	144·8	69·9	62·4
	2	0·204	56·1	74·4	38·3
	3	0·262	81·6	25·9	114·3
O(2)	1	0·082	150·8	70·6	69·1
	2	0·213	61·0	48·2	55·5
	3	0·282	92·9	48·1	137·9

* The r.m.s. displacement U_j is directed along the jth axis of the ellipsoid, where α_{1j}, α_{2j}, α_{3j} are the angles between the th axis and a, c^* and b axes, respectively.

Table 6. *Least-squares planes*

Equation of the plane: $aX+bY+cZ=D$ with respect to crystallographic axes a, b, c^*, where X, Y, Z are expressed in Å units.

	Deviations (Å)	Equation of the plane
(*a*) Carboxyl group:		
C(1)	−0·0011	$0{\cdot}1268X+0{\cdot}8409Y+0{\cdot}5261Z=2{\cdot}7640$
C(2)	0·0003	
O(1)	0·0004	
O(2)	0·0004	
N(1)†	0·0814	
(*b*) Plane through C(2), C(3), C(4), N(2):		
C(2)	−0·040	$0{\cdot}9810X+0{\cdot}1710Y+0{\cdot}0917Z=2{\cdot}7923$
C(3)	0·045	
C(4)	0·035	
N(2)	−0·042	
N(1)†	0·567	

† Not included in the calculation of the plane.

Molecular conformation

The conformation of the amino acid is best understood from a study of the sequence of partial conformations along the chain C(1)–C(2)–C(3)–C(4). Fig. 4(*a*) shows the conformation looking down the single bonds C(1)–C(2), C(2)–C(3) and C(4)–C(4). As in many other amino acids (Marsh & Donohue, 1967), the torsion angle N(1)–C(2)–C(1)–O(2) is small (−3°) which results from the electrostatic attraction between the positively charged nitrogen atom N(1) and the negatively charged

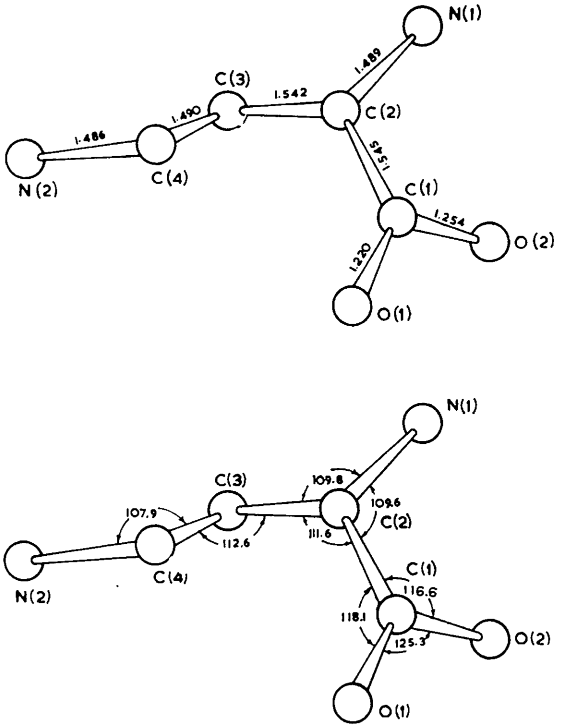
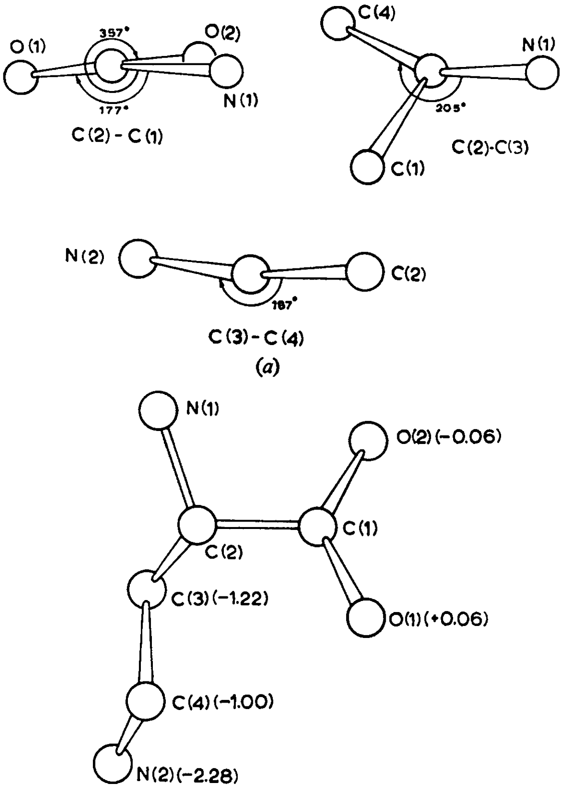


Fig. 3. Bond lengths and angles in the molecule.



(*a*)

(*b*)

Fig. 4. (*a*) Conformation about the various bonds, (*b*) projection of the side group onto the NC$^{\alpha}$C′ plane.

oxygen atom O(2). The location of the C^{γ} [C(4)] atom is in position II [*trans* to N(1)]. Orientation of the side group as a whole in relation to the backbone is shown in Fig. 4(*b*). This orientation is similar to that observed in DL-α-amino-n-butyric acid (Ichikawa & Iitaka, 1968) and L-ornithine hydrochloride (Chiba *et al.*, 1967).

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Crystal and Molecular Structure of [1]Benzothieno[2,3-*b*][1]benzothiophene ($C_{14}H_8S_2$)*

By I. Goldberg and U. Shmueli

Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel

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[1]Benzothieno[2,3-*b*][1]benzothiophene, $C_{14}H_8S_2$, crystallizes in the monoclinic space group $P2_1$ with two molecules in a unit cell of dimensions: $a = 9\cdot935 \pm 0\cdot003$, $b = 4\cdot027 \pm 0\cdot001$, $c = 13\cdot622 \pm 0\cdot004$ Å and $\beta = 97\cdot90 \pm 0\cdot03$°. The structure was determined from three-dimensional integrated precession data. The final R index, based on 960 observed reflexions, is 0·059. Distribution of the bond lengths in the thiophthene nucleus of the molecule indicates an extensive π delocalization which is probably due to the participation of the nonbonded electrons on the sulphur atoms in the conjugation. Results of a simple HMO calculation support this indication. The crystal consists of rigid, planar molecules stacked along the b axis. Results of a Shomaker–Trueblood type rigid-body motion analysis are consistent with the molecular arrangement.

Introduction

The chemistry of [1]benzothieno[2,3-*b*][1]benzothiophene (TNTN), as well as preliminary results of its structure, have been described recently (Dayagi, Goldberg & Shmueli, 1970). Following the results and implication of the chemical study, it was considered of interest to carry out a comparative structural investigation of TNTN and some of its oxidized derivatives. The main interest in such a study is to assess the influence of the two extreme oxidation states of sulphur on the detailed structures of the otherwise analogous heterocyclic molecules (Fig. 1). This assessment may be of value in estimating the effect of the electronic configuration of sulphur on the structure and chemistry of related compounds and in comparing experimental

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