O1	0.3649 (5)	0.69750 (10)	−0.1139 (3)	0.0703 (7)
Cl1	0.54992 (9)	0.46160 (3)	0.27423 (7)	0.0419 (2)
Cl2	0.41012 (10)	0.67899 (3)	0.24778 (7)	0.0455 (2)
N1	0.0764 (3)	0.47686 (7)	0.3810 (2)	0.0262 (4)
N2	0.2776 (3)	0.37380 (8)	0.4059 (2)	0.0303 (4)
N3	0.1771 (3)	0.54476 (8)	0.1627 (2)	0.0301 (4)

Table 2. *Selected geometric parameters (Å, °)*

C1—N1	1.337 (3)	C5—C6	1.382 (3)
C1—C2^{i}	1.408 (3)	C6—C7	1.378 (3)
C1—C3	1.498 (3)	C7—N2	1.352 (3)
C2—N1	1.344 (3)	C8—N3	1.352 (3)
C2—C1^{i}	1.408 (3)	C8—C9	1.380 (3)
C2—C8	1.487 (3)	C9—C10	1.391 (3)
C3—N2	1.351 (3)	C10—C11	1.383 (3)
C3—C4	1.380 (3)	C11—C12	1.372 (3)
C4—C5	1.398 (3)	C12—N3	1.340 (3)
N1—C1—C2^{i}	119.5 (2)	N2—C7—C6	120.6 (2)
N1—C1—C3	113.8 (2)	N3—C8—C9	119.7 (2)
C2^{i}—C1—C3	126.5 (2)	N3—C8—C2	114.8 (2)
N1—C2—C1^{i}	120.6 (2)	C9—C8—C2	125.2 (2)
N1—C2—C8	114.0 (2)	C8—C9—C10	119.1 (2)
C1^{i}—C2—C8	125.3 (2)	C11—C10—C9	119.8 (2)
N2—C3—C4	118.8 (2)	C12—C11—C10	119.1 (2)
N2—C3—C1	114.9 (2)	N3—C12—C11	120.5 (2)
C4—C3—C1	125.8 (2)	C1—N1—C2	119.9 (2)
C3—C4—C5	119.7 (2)	C3—N2—C7	122.3 (2)
C6—C5—C4	120.2 (2)	C12—N3—C8	121.7 (2)
C7—C6—C5	118.4 (2)		

Symmetry code: (i) $-x, 1-y, 1-z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···Cl1	0.94 (3)	2.15 (3)	3.071 (2)	165 (2)
N3—H3···Cl1	0.90 (3)	2.18 (3)	3.061 (2)	166 (2)
O1—H1A···Cl2	0.80 (4)	2.46 (4)	3.251 (3)	171 (3)
O1—H1B···Cl2^{i}	0.87 (4)	2.35 (4)	3.197 (3)	166 (4)

Symmetry code: (i) $x, \frac{3}{2}-y, z-\frac{1}{2}$.

Table 4. *Comparison of dihedral angles (°)*

	tppz-H4^{a}	tppz-H2^{b}	tppz-I^{b}	tppz-II^{c}
A^B	60.5(1)	60.0	62.4	60.4
A^C	41.3(1)	16.6	48.9	59.0
B^C	38.5(1)	59.6	51.7	46.4

References: (*a*) this work; (*b*) Bock, Vaupel *et al.* (1992); (*c*) Greaves & Stoeckli-Evans (1992).

The pyridinium and water H atoms were located from difference maps and refined isotropically. The aromatic H atoms were included in calculated positions as riding atoms with *SHELXL*93 default parameters (Sheldrick, 1993).

Data collection: *DIF*4 (Stoe & Cie, 1993*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1993*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLUTON*, *PLATON* (Spek, 1993). Software used to prepare material for publication: *SHELXL*93.

We wish to thank the Swiss National Science Foundation for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1156). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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γ-Aminobutyric Acid: a Novel Tetragonal Phase

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Abstract

In the tetragonal phase of γ-aminobutyric acid, $C_4H_9NO_2$, the single type of molecule adopts a partially folded zwitterionic form. Whereas in the previously characterized monoclinic phase the partially folded zwitterionic molecules exhibit a *gauche* conformation with respect to the C2—C3 bond, in this phase the molecules exhibit a *trans* conformation. The altered pattern of intramolecular N···O distances may be of significance with respect to the neurotransmission behavior of this substance. In addition to three strong hydrogen bonds involving the three H atoms bound to the N atom, as in the monoclinic phase, there is a fourth weaker one which results in a two-center bifurcated bond. There is also evidence suggestive of an intramolecular bridging

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hydrogen bond involving the N atom, an O atom and a methylene H atom, as previously proposed as a stabilizing factor for the *gauche* conformation observed in the monoclinic phase.

Comment

This structural study of a novel tetragonal phase of γ-aminobutyric acid (GABA), is one of a continuing series on hydrogen bonding in carboxylic acids. The structure of GABA and especially its likely molecular conformations are of interest in connection with the development of a detailed understanding of its role in vertebrate central-nervous-system neurotransmission [see, for example, Davidson (1976)]. The structure of a monoclinic phase of GABA analyzed in space group No. 14 has been studied extensively by X-ray diffraction (room temperature: Tomita, Higashi & Fujiwara, 1973; 138 K: Steward, Player & Warner, 1973; 122 K: Craven & Weber, 1983) and neutron diffraction (122 K: Weber, Craven & McMullan, 1983) with results which are, overall, highly concordant (some atom relabeling is necessary). In that phase, the molecules occur as partially folded zwitterions.

GABA

In the tetragonal phase of GABA, the zwitterionic form of the molecule is again observed (Fig. 1). Thus, the hydrogen bonding involves the three H atoms bonded to the N atom, H1*A*, H1*B* and H1*C*, and potential acceptors O1 and O2. As in the monoclinic phase, three strong hydrogen bonds are formed, O1 accepting one and O2 accepting two; however, there is now a fourth, weaker hydrogen bond involving O1 as an acceptor (see Table 3) and H1*A* is involved in a two-center bifurcated hydrogen bond. The hydrogen-bonding pattern in this structure is shown in Fig. 2. As in the monoclinic structure, the N—H and N···O_a distances and N—H···O_a angles for the three strong hydrogen bonds are all very similar. Moreover, as in the monoclinic structure there are infinite chains of hydrogen-bonded molecules running in one direction which are crosslinked into a three-dimensional network by the remaining hydrogen bonds.

A major difference between the monoclinic and tetragonal structures occurs with respect to the molecular conformation about the C2—C3 bond: in the monoclinic phase the conformation is *gauche* with a torsion angle of ±72.6 (1)° (Weber *et al.*, 1983) whereas in this structure the conformation is *trans* with a torsion angle of ±174.6 (3)°. Thus, while in both structures a partially folded zwitterionic form of the molecule occurs, the pattern of intramolecular N···O distances is different: for monoclinic GABA, 4.238 (7) and 5.612 (6) Å (Tomita *et al.*, 1973); for tetragonal GABA, 4.975 (3) and 5.321 (3) Å. [For the fully extended molecule determined in GABA.HCl, these distances are 5.05 (2) and

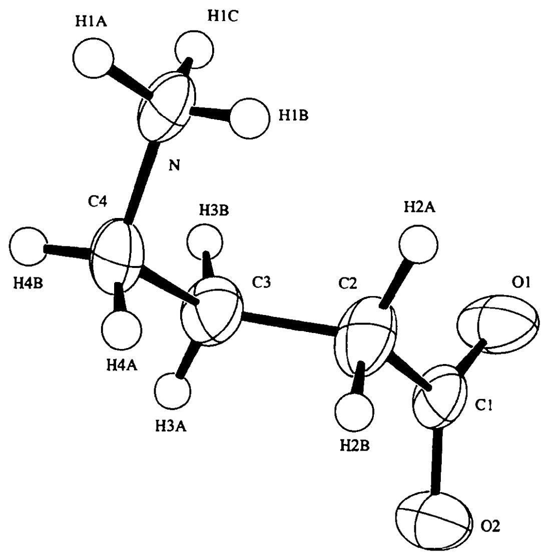

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of γ-aminobutyric acid showing our numbering scheme. Displacement ellipsoids are drawn at 50% probability for all atoms except H atoms for which they have been set artificially small.

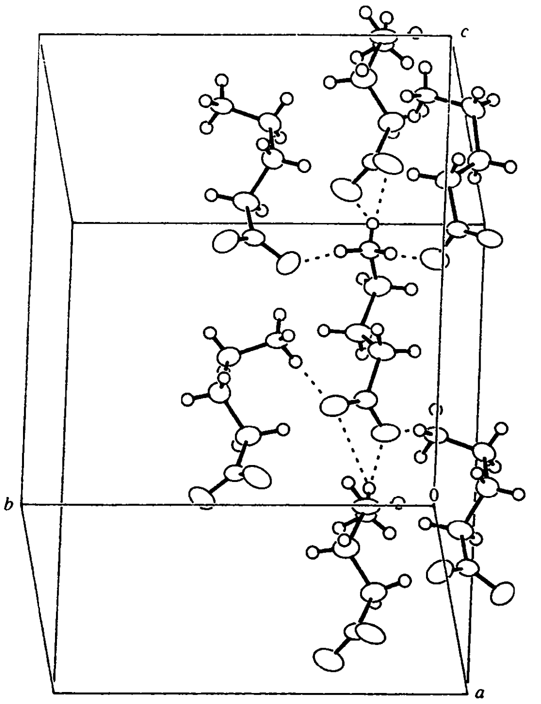

Fig. 2. *ORTEP*II (Johnson,1976) drawing of a central γ-aminobutyric acid molecule and the six neighbors to which it is directly hydrogen bonded. Displacement ellipsoids are drawn at 50% probability for all atoms except H atoms for which they have been set artificially small. Hydrogen bonds are shown as dashed lines.

6.11 (2) Å (cited in Tomita *et al.*, 1973).] This pattern of distances may be of significance with respect to details of the neurotransmission behavior of GABA as presented by Davidson (1976). At the very least, the occurrence of the *trans* conformation in this solid phase supports the possible occurrence of the *trans* conformation in solution or in the vertebrate central nervous system.

In this structure as in the monoclinic structure, C1, C2, O1 and O2 lie in a plane; here their average deviation from the best-fit plane is <0.001 (2) Å. However, now C1, C2, C3 and C4 (rather than C2, C3, C4 and N) lie in a second plane such that their average deviation from the best-fit plane is 0.033 (3) Å. The dihedral angle between these two planes is 85.2 (3)°; the related dihedral angle in the monoclinic structure is 79.1° (Tomita *et al.*, 1973).

In examining the monoclinic structure, Craven & Weber (1983) found that one of the methylene-H atoms was considerably more positively charged than the others and that this same H atom was closer to both the negatively charged N and O1 atoms than the corresponding sums of van der Waals radii. They concluded that this H atom forms an intramolecular hydrogen bridge N···H···O1 and that this stabilizes the *gauche* conformation. Accordingly, it is of interest to consider whether a similar interaction may occur in the *trans* conformer observed in the tetragonal structure. We find that H2*A* (Fig. 1) is the methylene H atom best situated geometrically to form an intramolecular bridge bond (N···H2*A*···O1) in the *trans* conformation. The N···H2*A* distance is 2.75 (5) Å, just equal to the Bondi (1964) radius sum, while the H2*A*···O1 distance is 2.56 (4) Å, 0.14 Å less than the Bondi radius sum; the N···H2*A*···O1 angle is 139 (2)°, the corresponding angle in the *gauche* form being 109° (Craven & Weber, 1983). In the absence of information about the charge on H2*A*, the present data do not establish that bridge bonding occurs in the *trans* conformer, but they suggest it is plausible.

Individual bond distances and angles are on the whole quite similar to those determined for the molecule in the monoclinic phase. If the room temperature X-ray data for that phase (Tomita *et al.*, 1973) are used for comparison, we find that the largest difference in bond lengths is for C3—C4, for which Tomita *et al.* report 1.502 (5) Å *versus* 1.529 (4) Å in this study, and the largest difference in bond angles is for C1—C2—C3 which Tomita *et al.* report to be 114.5 (4)° *versus* 112.0 (2)° in this study.

The refined final C—H bond distances ranged from 0.88 (4) to 1.04 (4) Å with a mean value of 0.98 (4) Å; the refined final N—H bond distances were 0.87 (4), 0.89 (4) and 0.93 (3) Å. Excepting pairs of atoms both of which are directly involved in hydrogen bonding, the closest intermolecular approaches are between the carboxylic-C atom, C1, and the three H atoms which are hydrogen bonded to the carboxylic-O atoms, H1*A*^{i}, H1*B*^{ii} and H1*C*^{iii} [(i) = $x, -y, -\frac{1}{2}+z$; (ii) = $\frac{1}{2}+y, 1-x, -\frac{1}{4}+z$; (iii) = $1-y, \frac{1}{2}-x, -\frac{1}{4}+z$]. These distances fall short of the Bondi (1964) radius sum by 0.30, 0.07 and 0.11 Å, respectively. All other intermolecular distances exceed the corresponding radius sums.

Experimental

γ-Aminobutyric acid was obtained from Pfaltz & Bauer, Inc. Slow evaporation of an aqueous solution of this material produced crystals of suitable size and quality. One of these was cut to provide the experimental sample.

Crystal data

$C_4H_9NO_2$
$M_r = 103.12$
Tetragonal
$I4_1cd$
$a = 11.963\ (1)$ Å
$c = 15.282\ (2)$ Å
$V = 2187.0\ (6)$ Å^3
$Z = 16$
$D_x = 1.253$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15.4$–$17.3°$
$\mu = 0.093$ mm^{-1}
$T = 296$ K
Cut chunk
0.39 × 0.35 × 0.31 mm
Colorless

Data collection

AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1440 measured reflections
767 independent reflections
563 observed reflections [$I > \sigma(I)$]
$R_{\rm int} = 0.020$
$\theta_{\max} = 27.50°$

$h = 0 \rightarrow 15$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 19$
6 standard reflections monitored every 150 reflections intensity variation: ±1.6% (average maximum relative intensity)

Refinement

Refinement on *F*
$R = 0.033$
$wR = 0.037$
$S = 1.46$
563 reflections
100 parameters
All H-atom parameters refined
$w = 1/\sigma_F^2$
$(\Delta/\sigma)_{\max} = < 0.01$

$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.12$ e Å^{-3}
Extinction correction: Zachariasen (1963,1968)
Extinction coefficient: 1.7 (5) × 10^{-7}
Atomic scattering factors from Stewart, Davidson & Simpson (1965), (H), Cromer & Waber (1974), (C, N, O)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
O1	0.7053 (2)	0.0486 (2)	0.1422	0.0582 (6)
O2	0.8184 (2)	−0.0935 (2)	0.1417 (2)	0.0510 (6)
N	0.7802 (2)	0.0779 (2)	0.4616 (2)	0.0341 (6)
C1	0.7751 (2)	−0.0110 (2)	0.1786 (2)	0.0373 (6)

C2	0.8121 (3)	0.0137 (3)	0.2717 (2)	0.0476 (8)
C3	0.7479 (3)	−0.0540 (3)	0.3377 (2)	0.0444 (8)
C4	0.7911 (3)	−0.0387 (3)	0.4311 (2)	0.0465 (8)

Table 2. *Selected geometric parameters (Å, °)*

N—C4	1.477 (4)	C3—C4	1.529 (4)
C1—C2	1.519 (4)	C1—O1	1.231 (3)
C2—C3	1.505 (4)	C1—O2	1.248 (3)
C1—C2—C3	112.0 (2)	C2—C1—O1	120.5 (2)
C2—C3—C4	112.9 (3)	C2—C1—O2	117.1 (2)
C3—C4—N	112.2 (2)	O1—C1—O2	122.4 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N—H1A···O2^{i}	0.87 (4)	1.94 (4)	2.797 (3)	172 (3)
N—H1A···O1^{i}	0.87 (4)	2.63 (3)	3.274 (3)	131 (2)
N—H1B···O1^{ii}	0.89 (4)	1.88 (4)	2.764 (3)	178 (4)
N—H1C···O2^{iii}	0.93 (3)	1.85 (3)	2.769 (3)	169 (3)

Symmetry codes: (i) $x, -y, \frac{1}{2}+z$; (ii) $1-y, x-\frac{1}{2}, \frac{1}{4}+z$; (iii) $\frac{1}{2}-y, 1-x, \frac{1}{4}+z$.

Scan widths were $(1.52 + 0.30\tan\theta)°$ in ω, with a background/scan time ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment and systematic absences led to unique assignment of the space group as $I4_1cd$ (No. 110); since refinement proceeded well it was adopted. Fourier difference methods were used to locate the initial H-atom positions.

The maximum effect of extinction was 6.3% of F_o for 220. The maximum peak in the final difference map occurred ~0.9 Å from C2 and C3; the maximum negative peak occurred ~1.0 Å from H1C and ~1.2 Å from N.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FR1001). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Acetylbenzoic Acid: Phthalide Form

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Abstract

In the structure of the phthalide form of 2-acetylbenzoic acid, $C_9H_8O_3$, there is a single type of hydrogen bond. Each molecule donates one and accepts one hydrogen bond. The hydrogen-bonded molecules form sets of puckered ribbons running along the **c** direction which are not crosslinked to each other. The dihedral angle between the planes of adjacent molecules along a hydrogen-bonded ribbon is 77.4 (1)°.

Comment

This study of 2-acetylbenzoic acid is one of a continuing series on hydrogen bonding in carboxylic acids. As expected on the basis of the organic chemical literature, this acid crystallized in its phthalide form, (I). The only previous report on this structure (Gupta & Prasad, 1970) gave somewhat approximate cell parameters and a space-group assignment in agreement with the present results, but provided no atomic coordinates or structural analysis.

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