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1-Methyl-4-imidazoline-2-thione:* Structure, Comparison with Related Molecules and a Discussion of Coordination Characteristics

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(Received 20 September 1982; accepted 10 December 1982)

Abstract

$C_4H_6N_2S$, $M_r = 114.1$, triclinic, $P\bar{1}$, $a = 7.338$ (12), $b = 7.068$ (1), $c = 11.589$ (4) Å, $\alpha = 106.82$ (6), $\beta = 99.79$ (2), $\gamma = 93.21$ (5)°, $U = 563.5$ Å³, $Z = 4$, $D_m = 1.35$ (1), $D_x = 1.35$ Mg m⁻³, $\mu(Cu K\alpha) = 3.874$ mm⁻¹, $F(000) = 240.0$; final $R = 0.0562$ for 1687 counter reflections. The asymmetric unit consists of two molecules linked *via* N–H...S bonds [N(32)...S(21) = 3.315 (5); N(31)...S(22) = 3.363 (5) Å]. Average distances for the two independent molecules are C(2)–S(2) = 1.685 (2); C(2)–N(1) = 1.351 (4); C(2)–N(3) = 1.345 (3); N(3)–C(4) = 1.387 (4); N(1)–C(5) = 1.374 (3); C(4)–C(5) = 1.333 (5); and N(1)–C(1) = 1.464 (4) Å. These results are compared with those of related molecules. Coordination of mimt produces a

lengthening of the C(2)–S(2) bond as well as ‘twisting’ and ‘tilting’ of the molecule in order to facilitate metal–ligand π interactions.

Introduction

The imidazolethione system is known to possess wide-ranging pharmacological activity including central nervous system depressant and acticonvulsant properties (Kohn, Kohn, Steenberg & Buckley, 1977), as well as bacteriostatic (Foye & Ho, 1972) and thyrostatic activity (Jemec, 1970). The search for carcinostatic compounds has been extended to the nucleosides (Gosselin, Imbach, Townsend & Panzica, 1979) and metal complexes (Dehand, Jordanov & Beck, 1975) of imidazolethiones.

Prominent among this group of compounds is 1-methyl-4-imidazoline-2-thione (mimt) which is known primarily for its thyrotoxic activity and is commer-

* Also known as 1-methyl-2(3*H*)-imidazolinethione.

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cially available as methimazole (*Martindale Extra Pharmacopoeia*, 1977), thycapzol (Jemec, 1970) and tapazole (Gosselin *et al.*, 1979). In addition to its pharmaceutical activity mimt is also an effective inhibitor of metallic corrosion (Donnelly, Downie, Grzeskowiak, Hamburg & Short, 1978).

The diverse properties of imidazolethione molecules may be related to the coordinating ability of the heterocyclic $RN-C(S)-NR'$ thioamide system and to the fact that the molecules are capable of coordinating to metals both at metal surfaces and in living systems.

4-Imidazoline-2-thione (imt), the parent molecule of the series, is capable of S,N chelation (Raper & Crackett, 1981) and monodentate S donation (Raper, O'Neill & Daniels, 1980a). The N(1)-methyl derivative (mimt) is capable of S,N bridging (Park, 1978; Bult & Rakhorst, 1976), and monodentate S donation with a variety of metals (Raper & Brooks, 1977; Raper & Nowell, 1980; Raper, O'Neill & Daniels, 1980b). The N(1),N(3)-dimethyl derivative (dmimt) is an exclusive monodentate S donor (O'Neill, Raper & Daniels, 1981; Kheddar, Protas, Le Baccon, Guglielmetti & Guerchais, 1976).

Several reports dealing with the crystal structures of the metal complexes of mimt have already appeared (Raper & Nowell, 1979, 1980; Nowell, Cox & Raper, 1979; O'Neill, Raper, Nowell & Daniels, 1981; O'Neill, Raper, Daniels & Nowell, 1982; Agnus, Louis & Weiss, 1980).

We now report the crystal structure of mimt and discuss the effect of coordination upon the bond lengths in the molecule.

Experimental

Pale-amber crystals of the compound were obtained from absolute ethanol. Cell constants obtained initially from Weissenberg and precession photographs were refined from the centred settings of 25 reflections on an Enraf-Nonius CAD-4 diffractometer at the Data Collection (SERC) Centre, Queen Mary College, University of London. Intensity data were collected from a crystal $0.4 \times 0.2 \times 0.1$ mm in the θ range 8.5 to 64.5° using monochromated Cu $K\alpha$ radiation and $\theta-2\theta$ scans; of the 1918 unique reflections collected, 1987 had $I > 2\sigma(I)$ and were considered observed. The data were corrected for Lorentz, polarization and absorption effects.

The positions of all non-H atoms were obtained by direct methods (Sheldrick, 1976) and were refined by full-matrix least-squares methods with anisotropic temperature factors. The positions of the two imido H atoms [H(31), H(32)] were obtained by difference Fourier maps but were not refined; their isotropic temperature factors were refined collectively to a final $U = 0.160$ (18) \AA^2 . Methyl H-atom coordinates were

refined as a rigid group (C-H = 1.08 \AA) with an overall isotropic temperature factor which refined to a final $U = 0.185$ (12) \AA^2 . The coordinates of the olefinic H atoms were fixed (C-H = 1.08 \AA) and an overall isotropic temperature factor was refined to a final $U = 0.093$ (6) \AA^2 .

Scattering factors were calculated from an analytical approximation (*International Tables for X-ray Crystallography*, 1974). Full-matrix refinement with the weighting scheme $w = 1/[\sigma^2(F_o) + 0.029054 (F_o)^2]$ gave a final $R = 0.0562$ and $R_w = 0.0674$. Final

Table 1. Final fractional coordinates ($\times 10^4$) and B_{eq} defined according to Willis & Pryor (1975), with e.s.d.'s in parentheses

	x	y	z	B_{eq} (\AA^2)
S(21)	-3328 (1)	2261 (1)	5598 (1)	4.63 (3)
C(21)	-1014 (3)	2887 (3)	6062 (2)	3.27 (7)
N(11)	279 (3)	2736 (3)	5358 (2)	3.56 (6)
C(11)	-134 (5)	2017 (5)	4010 (3)	4.80 (8)
N(31)	-64 (3)	3585 (3)	7236 (2)	3.77 (7)
C(41)	1818 (4)	3859 (5)	7243 (3)	4.52 (9)
C(51)	2011 (4)	3348 (5)	6083 (3)	4.31 (9)
S(22)	-2165 (1)	3281 (1)	9549 (1)	5.16 (4)
C(22)	-2956 (3)	858 (4)	8872 (2)	3.46 (8)
N(32)	-3672 (3)	-42 (3)	7683 (2)	3.95 (7)
N(12)	-2923 (3)	-610 (3)	9414 (2)	3.89 (7)
C(12)	-2234 (5)	-310 (6)	10720 (3)	3.77 (12)
C(42)	-4083 (4)	-2082 (4)	7450 (3)	3.88 (4)
C(52)	-3599 (5)	-2409 (4)	8543 (3)	5.01 (11)

Table 2. Bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

(a) Non-H-atom values			
S(21)-C(21)	1.684 (2)	S(22)-C(22)	1.686 (2)
C(21)-N(31)	1.352 (3)	C(22)-N(32)	1.337 (3)
C(21)-N(11)	1.342 (4)	C(22)-N(12)	1.360 (4)
N(31)-C(41)	1.382 (4)	N(32)-C(42)	1.393 (4)
C(41)-C(51)	1.322 (5)	C(42)-C(52)	1.344 (5)
C(51)-N(11)	1.369 (3)	C(52)-N(12)	1.378 (3)
N(11)-C(11)	1.467 (4)	N(12)-C(12)	1.460 (4)
C(21)-N(11)-C(51)	110.0 (2)	C(22)-N(12)-C(52)	109.6 (2)
N(11)-C(51)-C(41)	107.9 (3)	N(12)-C(52)-C(42)	108.2 (3)
C(51)-C(41)-N(31)	106.9 (2)	C(52)-C(42)-N(32)	105.5 (2)
C(41)-N(31)-C(21)	109.6 (2)	C(42)-N(32)-C(22)	111.2 (3)
N(31)-C(21)-N(11)	105.6 (2)	N(32)-C(22)-N(12)	105.5 (2)
S(21)-C(21)-N(11)	127.7 (2)	S(22)-C(22)-N(12)	127.0 (2)
S(21)-C(21)-N(31)	126.7 (2)	S(22)-C(22)-N(32)	127.5 (2)
C(21)-N(11)-C(11)	124.3 (2)	C(22)-N(12)-C(12)	124.6 (2)
C(11)-N(11)-C(51)	125.8 (3)	C(12)-N(12)-C(52)	125.7 (3)
(b) H-atom values			
N(31)-H(31)	1.11	N(32)-H(32)	1.075
C-H	1.08		
C(2)-N(3)-H(3)	117.8*	N(1)-C(5)-H(5)	126.1*
C(4)-N(3)-H(3)	126.6*	C(5)-C(4)-H(4)	127.2*
N(3)-C(4)-H(4)	126.6*	C(4)-C(5)-H(5)	125.9*
(c) Hydrogen-bond distances and angles			
N(32)-H(32)...S(21)	3.315	(H...S)	2.242
N(31)-H(31)...S(22)	3.363	(H...S)	2.269
C(22)-S(22)-H(31)	89.9	C(21)-S(21)-H(32)	92.8

* Averaged values.

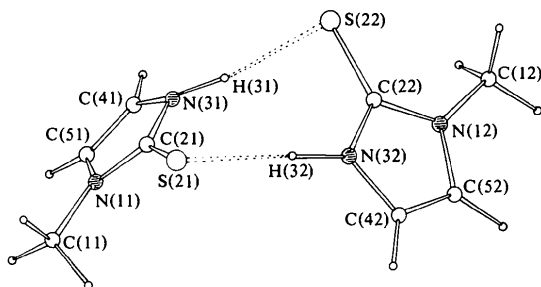


Fig. 1. Perspective view of the asymmetric unit showing labelling of the atoms and H-bonded interactions.

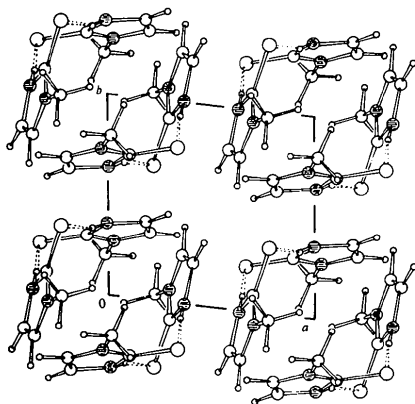


Fig. 2. Unit-cell contents viewed along c^* .

atomic parameters are given in Table 1,* and relevant distances and angles are in Table 2. Fig. 1 shows the atom numbering and Fig. 2 the unit-cell contents.

Description and discussion of the structure

The asymmetric unit contains two crystallographically unique and essentially planar mimt molecules. These independent molecules are linked in pairs by hydrogen bonds between the S and neighbouring imide H atoms (Fig. 1). The overall $N(3) \cdots S(2)$ distances (3.315 and 3.363 Å) are typical of H-bonded thione systems (Form, Raper & Downie, 1976). The $H \cdots S$ distances (2.242 and 2.269 Å) are significantly shorter than the sum of the corresponding van der Waals radii (2.85 ± 0.2 Å) (Pauling, 1960) and according to Donohue's (1968) criteria must be regarded as strongly H-bonded. Furthermore, the $C-S \cdots H$ angles (92.8 and 89.9°) are unusual and suggest that each S atom uses an orbital which is essentially 'p' in character in the H-bond formation.

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and the results of mean-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38276 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The $C(2)-S(2)$ distances of 1.684 (2) and 1.686 (2) Å and the attachment of the labile H atom at the N(3) position confirm the presence of the thione tautomer (form II, Fig. 3) in both independent molecules. A similar conclusion has been derived from the 1H NMR spectrum in solution where the chemical shift for the labile proton (δ 11.72 p.p.m.) is more typical of N-H (δ 10–12 p.p.m.) than S-H (δ 3–5 p.p.m.) (Raper *et al.*, 1980a). In addition, the solid-state infrared spectrum of mimt shows the four 'thioamide' bands typical of many heterocyclic thione molecules (Raper & Brooks, 1977).

Of the three types of C–N distance in mimt the exocyclic $C(1)-N(1)$ bonds are clearly the longest [1.460 (4) and 1.467 (4) Å] and correspond to essentially σ -bonded contacts (Wheatley, 1955). The C–N distances within the heterocycle are significantly shorter with the $N(3)-C(4)$ and $N(1)-C(5)$ distances occurring in the range 1.369 (3) to 1.393 (4) Å and the $N(1)-C(2)$ and $N(3)-C(2)$ distances ranging from 1.337 (3) to 1.360 (4) Å. Although the greatest π -electron density appears to be concentrated in the 'thioamide' portion of the molecule all the bond lengths, including those of the $C(4)-C(5)$ atoms, exhibit some bond shortening (Sutton, 1965) and consequently all the atoms appear to contribute to the π -electron ring current.

The bond angles within mimt are similar to those reported for 1,3-dimethyl-4-imidazoline-2-thione (Ansell, 1972), with the largest internal angles in both molecules occurring at the N atoms. Thione substitution at C(2) produces significant changes in the angles around that atom relative to the corresponding values in imidazole. The $N(1)-C(2)-N(3)$ angle in the imidazole molecule (Craven, McMullan, Bell & Freeman, 1977) is $112.0 (1)^\circ$ and the $H(2)-C(2)-N(1,3)$ angles are $123.7 (6)^\circ$ and $124.3 (6)^\circ$ respectively. In mimt the average $N(1)-C(2)-N(3)$ angle (Table 2) is $105.6 (2)^\circ$ and the external $S(2)-C(2)-N(1,3)$ angles range from $126.7 (2)$ to $127.7 (2)^\circ$.

Thioketonic distances in reported imidazolethione molecules range from 1.624 to 1.708 Å (Table 3) with the corresponding π characters extending from 75.0 to

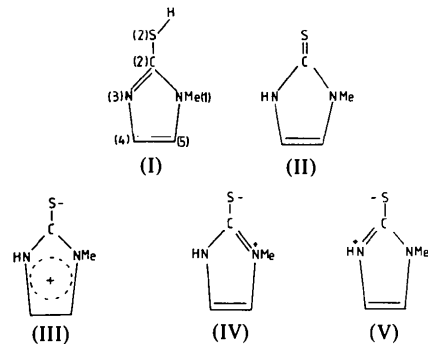


Fig. 3. Tautomeric and canonical forms of mimt.

Table 3. Comparison of bond lengths (Å) from related molecules

Compound and reference	2-Imidazolidinethione (II)			4-Imidazoline-2-thione (III)		
	C(2)—S(2)	N(1)—C(2)	N(3)—C(2)	N(3)—C(4)	N(1)—C(5)	C(4)—C(5)
(I)						
Imidazole (I)						
Imidazole at 123 K (Martínez-Carrera, 1966)	—	1.349	1.326	1.378	1.369	1.358
Imidazole at 293 K (Craven <i>et al.</i> , 1977)	—	1.337 (3)	1.316 (2)	1.367 (2)	1.362 (2)	1.357 (2)
(II)						
2-Imidazolidinethione (Wheatley, 1953)	1.708	1.322*	1.322*	1.471*	1.471*	1.536
2-Thioxo-4-imidazolidinone (Walker, Folting & Merritt, 1969)	1.642 (3)	1.393 (3)	1.322 (4)	1.448 (3)	1.349 (3)	1.508 (3)
1-Thiocarbamoyl-2-imidazolidinethione (Valle, Cojazzi, Busetti & Mammi, 1970)	1.673 (4)	1.306 (6)	1.408 (5)	1.473 (5)	1.464 (5)	1.507 (7)
1-Methyl-4,5-(D-glucofurano)imidazolidine-2-thione (Jiménez-Garay, López-Castro & Márquez, 1974)	1.685 (2)	1.351 (4)	1.345 (4)	1.387 (4)	1.374 (3)	1.333 (5)
4-Amino-1,3-dimethyl-2-thioxo-5-imidazolidinone (Sato, Kinoshita, Hata & Tamura, 1976)	1.624 (8)	1.360 (8)	1.385 (8)	1.368 (8)	1.375 (8)	1.488 (8)
(III)						
L-Ergothioneine dihydrate (Sugihara, Uemura, Matsuura, Tanaka, Tamaichi & Kakudo, 1976)	1.691 (3)	1.351 (4)	1.344 (4)	1.384 (4)	1.384 (4)	1.349 (4)
1-p-Tolyl-4-(α -D-erythrofuranosyl)-4-imidazoline-2-thione (Barragán, López-Castro & Márquez, 1977)	1.68 (1)	1.36 (1)	1.36 (1)	1.40 (1)	1.39 (1)	1.32 (1)
4-Formyl-4-imidazoline-2-thione (Conde, Moreno & Márquez, 1977)	1.672 (4)	1.368 (4)	1.349 (4)	1.388 (5)	1.353 (5)	1.364 (4)
2-Benzimidazolethione (Form <i>et al.</i> , 1976)	1.671 (8)	1.362 (6)*	1.362 (6)*	1.383 (8)*	1.383 (8)*	1.400 (7)
1,3-Dimethyl-4-imidazoline-2-thione (Ansell, 1972)	1.696 (5)	1.349 (6)*	1.349 (6)*	1.392 (4)*	1.392 (4)*	1.325 (5)
1-Methyl-4-imidazoline-2-thione (average values) (this study)	1.685 (2)	1.351 (4)	1.345 (4)	1.387 (4)	1.374 (3)	1.333 (5)

* Molecules are required to have 2/m symmetry.

43.0% (Trinajstić, 1968). The C—N distances involving the C(2) atoms range from 1.306 to 1.408 Å while those which involve the ethylenic C atoms [C(4) and C(5)] range from 1.349 to 1.493 Å. The general effect is one of concentration of π -electron density in the 'thioamide' portion of the molecules even among the saturated (imidazolidine) molecules. In the unsaturated 4-imidazoline-2-thione molecules the thioketonic C(2)—S(2) distances range from 1.671 to 1.696 Å. In addition, the C(2)—N(3) and C(2)—N(1) distances are generally shorter than the corresponding N(3)—C(4) and N(1)—C(5) values which suggests that the electron distribution in the 'thioamide' portion of these molecules may be rationalized by a combination of the canonical forms (II–V) in Fig. 3 (Johnson & Paul, 1970). In mimt, the presence of 52% π -character (Trinajstić, 1968) in the C(2)—S(2) bond requires almost equal contributions from forms (II) and (III); 35% π character (Wheatley, 1955) in the C(2)—N(1) and C(2)—N(3) bonds requires further contributions from forms (IV) and (V) (Fig. 3).

The effect of methyl substitution at the N(1) and N(3) positions among the imidazolinethione molecules may be expected to produce an increase in the corresponding C(2)—S(2) distances. There is an indica-

tion that a slight increase in the C(2)—S(2) distances occurs within the molecules. The values range from 1.671 (7) Å in 2-benzimidazolethione (Form *et al.*, 1976) to an averaged value of 1.685 (2) Å in mimt (this study) and 1.696 (5) Å in 1,3-dimethyl-4-imidazoline-2-thione (Ansell, 1972).

In coordinated mimt molecules the C(2)—S(2) bond length has an average value of 1.718 (7) Å for tetrahedral complexes and 1.716 (11) Å for square-planar environments (Table 4). These distances correspond to about 39% π character (Trinajstić, 1968). This is consistent with a reduction in the π character of the C(2)—S(2) bond of the order of 13% upon coordination. The remaining bond lengths of the mimt molecule remain essentially unaffected by coordination. In addition to the shortening of the C(2)—S(2) distance other significant features of the coordinated mimt molecules are the dihedral angles formed between the molecules and the M —S(2)—C(2) planes ('twisting') and the MS_4 square-planar arrangement ('tilting') (Table 4). Twisting of the molecule is fairly uniform in tetrahedral complexes while both twisting and tilting of the molecules is significantly varied in square-planar environments. Among the factors contributing to these angular effects is the possibility of a π interaction

Table 4. Averaged bond lengths (Å) and dihedral angles (°) in *mimt* and its coordination compounds

Compound and reference	N(1)—C(1)	N(1)—C(2)	C(2)—S(2)	C(2)—N(3)	N(3)—C(4)	C(4)—C(5)	C(5)—N(1)	Twisting*	Tilting†
<i>mimt</i> (this study)	1.464 (4)	1.351 (4)	1.685 (2)	1.345 (4)	1.387 (4)	1.333 (5)	1.374 (3)		
Co(<i>mimt</i>) ₂ (ClO ₄) ₂ (Raper & Nowell, 1979)	1.474 (7)	1.339 (3)	1.717 (4)	1.330 (6)	1.358 (8)	1.337 (9)	1.387 (7)	68.3	—
Zn(<i>mimt</i>) ₂ (NO ₃) ₂ ·2H ₂ O (Nowell <i>et al.</i> , 1979)	1.463 (8)	1.339 (7)	1.708 (6)	1.345 (8)	1.367 (11)	1.328 (11)	1.384 (9)	66.2–77.2	—
Co(<i>mimt</i>) ₂ (NO ₃) ₂ ·2H ₂ O (Raper & Nowell, 1980)	1.440 (17)	1.347 (15)	1.731 (12)	1.356 (15)	1.382 (19)	1.376 (20)	1.390 (18)	63.9–74.7	—
Ni(<i>mimt</i>) ₂ (ClO ₄) ₂ (O'Neill, Raper, Nowell & Daniels, 1981)	1.451 (22)	1.342 (14)	1.713 (11)	1.324 (18)	1.377 (23)	1.318 (28)	1.375 (20)	13.6–84.2	72.6–87.8
Pt(<i>mimt</i>) ₂ Cl ₂ ·2H ₂ O (O'Neill <i>et al.</i> , 1982)	1.490 (24)	1.333 (20)	1.718 (12)	1.357 (17)	1.357 (19)	1.335 (23)	1.397 (19)	22.4–35.2	58.3–75.3

* Twisting: dihedral angle between M—S(2)—C(2) and coordinated *mimt* molecules.† Tilting: dihedral angle between MS₂ square plane and coordinated *mimt* molecules.

between the metal 'd' orbitals and the 'thioamide' portion of the *mimt* molecules. Additional support for this interaction comes from the X-ray photoelectron spectra of Cu(*mimt*)₂Br, and *mimt*. These show a positive shift [162.9 to 164.9 eV (1 eV = 1.602 × 10⁻¹⁹ J)] in the electron-core binding energies of the sulphur (2p^{3/2}) electrons and a negative shift (404.5 to 400.5 eV) in the binding energies of the nitrogen (1s) electrons of the coordinated *mimt* molecules (Sherwood, 1982). The former is expected, in view of the S-donating character of *mimt*, and the latter is indicative of an increase in electron density at the N atoms of the molecule which is a likely consequence of a dπ–pπ, metal–thioamide interaction.

All calculations were performed on the NUMAC IBM 370/167 computer at the University of Newcastle upon Tyne, England.

We thank SERC and Dr M. B. Hursthouse, Queen Mary College, University of London, for the provision of X-ray intensity data.

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The Neutron Structure of and Thermal Motion in γ -Aminobutyric Acid (GABA) at 122 K

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(Received 7 July 1981; accepted 14 October 1982)

Abstract

At 122 K, γ -aminobutyric acid ($C_4H_9NO_2$) is monoclinic, space group $P2_1/a$, with $a = 8.214(2)$, $b = 10.000(2)$, $c = 7.208(2)$ Å, $\beta = 110.59(2)^\circ$. A structure refinement by full-matrix least squares based on 1686 neutron reflections ($\sin \theta/\lambda < 0.78$ Å $^{-1}$) has converged with $R_w(F^2) = 0.044$. Bond lengths and angles involving nuclear thermal centroids have e.s.d.'s less than 0.002 Å and 0.2° respectively, including those with H atoms. Because of marked anisotropy in atomic and molecular vibrations, thermal corrections to the bond lengths are important. These have been determined taking intramolecular modes of vibration into account. A novel aspect of the thermal-motion analysis is the inclusion of anharmonic thermal-motion corrections for the C–H bonds. They are found to be similar in magnitude and opposite to the harmonic corrections (~ 0.02 Å). The six C–H bond lengths before and after correction lie within the range 1.093–1.099 Å and 1.099–1.103 Å respectively. The C(trig.)–C(tetr.) bond may be longer (1.534 Å) than the C(tetr.)–C(tetr.) bonds (mean value 1.527 Å). There are three strong N–H \cdots O hydrogen bonds with similar geometries (H \cdots O distances: 1.69, 1.71, 1.74 Å; uncorrected).

Introduction

The detailed structure of γ -aminobutyric acid (GABA, Fig. 1) is of biological interest because this molecule is

believed to function as a neurotransmitter in the mammalian central nervous system (Davidson, 1976). We have carried out a neutron crystal structure determination at low temperature in conjunction with an X-ray study of the electronic charge density distribution in the molecule (Craven & Weber, 1983). The neutron structure is necessary for determining the nuclear positional and thermal parameters, including H atoms, without bias due to the electronic charge density distribution.

This crystal structure provides a good example of the importance of a detailed analysis of anisotropic thermal motion in order to derive corrected bond lengths and angles. The non-rigid behavior of the molecule was found to be highly significant. For the neutron C–H bond lengths, satisfactory agreement with spectro-

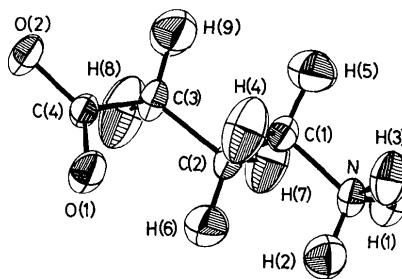


Fig. 1. γ -Aminobutyric acid. Atomic nomenclature and thermal ellipsoids at 90% probability (Johnson, 1976).