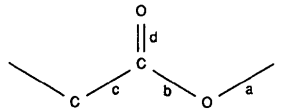
C(3*a*)	0.0373 (3)	0.1747 (1)	0.5471 (2)	0.046 (1)
O(4*a*)	−0.0157 (2)	0.1099 (1)	0.5961 (1)	0.051 (1)
C(5*a*)	−0.0614 (3)	0.1028 (1)	0.7067 (2)	0.041 (1)
O(5*a*)	−0.1248 (2)	0.0491 (1)	0.7307 (1)	0.064 (1)
C(6*a*)	−0.0419 (3)	0.1627 (1)	0.7964 (2)	0.038 (1)
C(31*a*)	0.2282 (3)	0.1641 (2)	0.5257 (3)	0.071 (1)
C(61*a*)	0.0906 (3)	0.1519 (1)	0.9246 (2)	0.044 (1)
C(62*a*)	0.0780 (4)	0.2150 (1)	1.0061 (2)	0.070 (1)
C(63*a*)	0.0412 (4)	0.0875 (1)	0.9901 (2)	0.061 (1)
C(64*a*)	0.2859 (3)	0.1469 (1)	0.9087 (2)	0.053 (1)
O(65*a*)	0.3033 (2)	0.0916 (1)	0.8292 (1)	0.054 (1)
C(66*a*)	0.4859 (3)	0.0820 (2)	0.8188 (3)	0.077 (1)
C(1′*a*)	−0.1041 (3)	0.1890 (1)	0.4251 (2)	0.048 (1)
C(2′*a*)	−0.3014 (3)	0.1941 (1)	0.4377 (2)	0.054 (1)
C(3′*a*)	−0.4108 (3)	0.1820 (1)	0.3064 (2)	0.060 (1)
O(3′*a*)	−0.5691 (3)	0.1972 (1)	0.2680 (2)	0.098 (1)
C(4′*a*)	−0.2914 (4)	0.1474 (2)	0.2319 (2)	0.073 (1)
C(5′*a*)	−0.1118 (4)	0.1331 (1)	0.3243 (2)	0.066 (1)

Table 2. *Selected bond lengths* (Å), *bond angles* (°) *and dihedral angles* (°)

	(1)	(2)	(3)	(4) Molecule 1	(4) Molecule 2
O(1)—C(2)	1.343 (4)	1.329 (3)	1.325 (2)	1.333 (3)	1.313 (3)
C(2)—C(3)	1.515 (5)	1.510 (4)	1.514 (2)	1.512 (3)	1.515 (3)
C(3)—O(4)	1.453 (4)	1.453 (3)	1.453 (2)	1.459 (3)	1.453 (3)
O(4)—C(5)	1.326 (4)	1.337 (3)	1.344 (2)	1.326 (2)	1.337 (3)
C(5)—C(6)	1.503 (5)	1.502 (4)	1.518 (2)	1.510 (3)	1.504 (3)
C(6)—O(1)	1.447 (4)	1.450 (3)	1.449 (2)	1.440 (2)	1.441 (2)
C(2)—O(2)	1.196 (4)	1.209 (3)	1.206 (2)	1.199 (3)	1.196 (3)
C(5)—O(5)	1.203 (4)	1.200 (3)	1.189 (2)	1.195 (3)	1.195 (3)
O(1)—C(2)—C(3)	116.4 (3)	120.5 (2)	120.2 (1)	119.9 (2)	121.4 (2)
C(2)—C(3)—O(4)	111.4 (3)	112.0 (2)	110.0 (1)	113.1 (2)	113.6 (2)
C(3)—O(4)—C(5)	118.6 (3)	121.1 (2)	121.3 (1)	125.2 (2)	124.8 (2)
O(4)—C(5)—C(6)	117.7 (3)	118.6 (2)	118.3 (1)	120.0 (2)	120.4 (2)
C(5)—C(6)—O(1)	112.0 (3)	114.0 (2)	112.6 (1)	114.1 (2)	114.5 (2)
C(6)—O(1)—C(2)	119.2 (3)	123.7 (2)	123.5 (1)	123.2 (2)	125.0 (2)
O(1)—C(2)—C(3)—O(4)	35.3 (4)	10.5 (3)	19.3 (2)	−11.9 (3)	0.5 (3)
C(2)—C(3)—O(4)—C(5)	−43.5 (4)	−34.2 (3)	−41.3 (2)	−5.1 (3)	2.0 (3)
C(3)—O(4)—C(5)—C(6)	9.6 (4)	34.7 (3)	30.6 (2)	8.6 (3)	−6.4 (3)
O(4)—C(5)—C(6)—O(1)	32.4 (4)	−10.5 (3)	2.9 (2)	3.8 (2)	7.9 (3)
C(5)—C(6)—O(1)—C(2)	−40.4 (4)	−12.6 (3)	−24.2 (2)	−21.3 (2)	−5.8 (3)
C(6)—O(1)—C(2)—C(3)	6.3 (4)	11.7 (3)	12.3 (2)	25.8 (3)	1.9 (3)

Table 3. *Geometrical parameters* (Å, °) *of the lactide heterocycle*



	Schweizer & Dunitz, 1982	All lactides	Without bridged lactides
a	1.447 (13)	1.449 (18)	1.450 (8)
b	1.340 (14)	1.344 (22)	1.335 (10)
c	1.495 (19)	1.510 (8)	1.508 (8)
d	1.195 (7)	1.193 (13)	1.197 (7)
ab	117 (2)	120 (4)	121 (3)
bd	123 (1)	119 (1)	119 (1)
bc	111 (1)	117 (4)	118 (2)
cd	125 (1)	124 (4)	123 (2)
ac		112 (3)	112 (2)

The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined with *SHELXTL* (Sheldrick, 1983). All H atoms were located by difference syntheses and refined with fixed individual displacement parameters using a riding model [except for the hydroxyl H atoms in (2) and (3), which were refined without constraints]. C and O atoms were refined anisotropically by blocked-cascade least-squares methods.

We thank Professor Schöllkopf (Universität Göttingen) for providing us with the samples and the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1070). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Cambridge Structural Database (1992). Version 4.6. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.
Clegg, W. (1981). *Acta Cryst.* A**37**, 22–28.
Coetzer, J. & Wiechers, A. (1973). *Acta Cryst.* B**29**, 917–919.
Hummel, G. J. van, Harkema, S., Kohn, F. E. & Feijen, J. (1982). *Acta Cryst.* B**38**, 1679–1681.
Lynch, V. M., Pojman, J., Whitesell, J. K. & Davis, B. E. (1990). *Acta Cryst.* C**46**, 1125–1127.
Mathieson, A. M. & Taylor, J. C. (1963). *Acta Cryst.* **16**, 524–530.
Schweizer, W. B. & Dunitz, J. D. (1982). *Helv. Chim. Acta*, **65**, 1547–1554.
Sheldrick, G. M. (1983). *SHELXTL User's Manual*. Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Acta Cryst. (1994). C**50**, 1721–1723

Heterocyclic Tautomerism. VI. A Redetermination and Reassignment of the Structure of 2-Aminothiazol-4(5*H*)-one (Pseudothiohydantoin)

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(*Received* 14 *March* 1994; *accepted* 3 *May* 1994)

Abstract

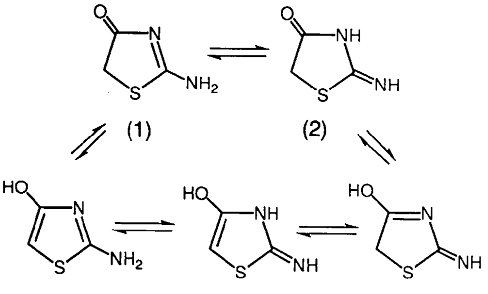
The structure of 2-aminothiazol-4(5*H*)-one, $C_3H_4N_2OS$, has been redetermined at 128 K. This compound is shown to exist as the amino tautomer rather than the previously reported imino tautomer [Amirthalingam & Muralidharan (1972). *Acta Cryst.* B**28**, 2421–2423; Ananthamurthy, Udupa & Murthy (1972). *Z. Kristallogr.* **137**, 316–317].

Comment

The title compound can exist as five possible tautomers, (1)–(5). In the solid state its infrared spectrum shows

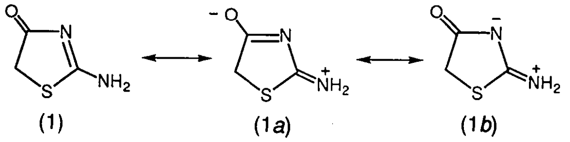
Acta Crystallographica Section C
ISSN 0108-2701 © 1994

the presence of a carbonyl absorption and the absence of an hydroxyl absorption, thereby eliminating three of the possible tautomers, (3)–(5). Early studies of the tautomerism of this compound in the solid state concluded that it exists as the imino tautomer (2) (Comrie, 1964; Khovratovich & Chizhevskaya, 1967). In 1972 this was apparently confirmed by two X-ray crystal structure determinations (Amirthalingam & Muralidharan, 1972; Ananthamurthy, Udupa & Murthy, 1972). However, the validity of these results has since been questioned (Elguero, Marzin, Katritzky & Linda, 1976) and more recent infrared studies (Ramsh, Smorygo & Ginak, 1984; Ramsh, Smorygo & Khrabrova, 1985; Valls, Segarra, Alcalde, Marin & Elguero, 1985) have suggested that this compound exists in the solid state as the amino tautomer (1). In order to resolve this apparent contradiction, we have redetermined the crystal structure as part of a continuing study of the tautomerism of heterocyclic compounds (Steel, 1991). The structure determination was carried out at 128 K in order to locate the H atoms unambiguously.



The successful location and refinement of the H atoms clearly demonstrates that this compound exists as the amino tautomer (1) and not as the previously reported imino tautomer (2) (Amirthalingam & Muralidharan, 1972; Ananthamurthy, Udupa & Murthy, 1972). With the exception of the C(5) H atoms, the molecule is planar with an average deviation from the mean plane of 0.025 (1) Å.

In previous studies the H atoms were not located and the tautomeric structure was deduced from the length of the C(2)—N(2) bond and the hydrogen-bonding scheme. However, the relatively short C(2)—N(2) single bond [1.317 (1) Å], previously interpreted as the double bond of (2), is consistent with structure (1) in which there is a contribution from the polar resonance contributors (1*a*) and (1*b*). Short C—N bonds are found in enaminones for a similar reason (Greenhill, Chaaban & Steel, 1992). Furthermore, the intermolecular N—H···N hydrogen bonds about the centre of inversion, which were previously interpreted as N(3)—H···N(2) bonds (Amirthalingam & Muralidharan, 1972), are in fact N(2)—H···N(3) hydrogen bonds. As was noted previously, the other N(2) H atom is hydrogen bonded to the carbonyl O atom of a second molecule related to the original molecule by an *n* glide.



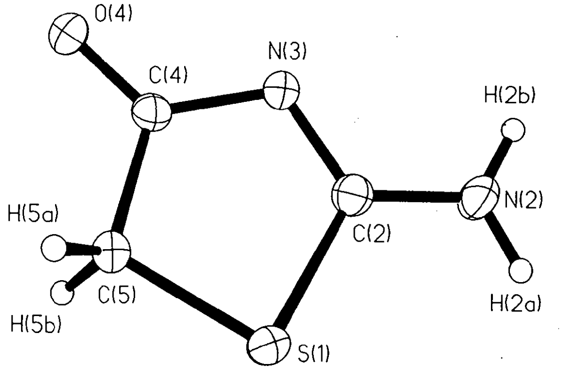


Fig. 1. Perspective view of the title compound showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 75% probability level.

Experimental

The title compound was prepared according to the method described in the literature (Allen & VanAllan, 1955) and was recrystallized from water.

Crystal data

$C_3H_4N_2OS$
$M_r = 116.14$
Monoclinic
$P2_1/n$
$a = 3.9400$ (2) Å
$b = 8.9766$ (4) Å
$c = 13.0269$ (8) Å
$\beta = 93.578$ (4)°
$V = 459.83$ (4) Å^3
$Z = 4$
$D_x = 1.678$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 42 reflections
$\theta = 12$–$17°$
$\mu = 0.557$ mm^{-1}
$T = 128$ (2) K
Needle
0.64 × 0.25 × 0.24 mm
Colourless

Data collection

Siemens *P*4*s* four-circle diffractometer
ω scans
Absorption correction: none
1396 measured reflections
1231 independent reflections
1157 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0096$
$\theta_{\rm max} = 28.99°$
$h = -5 \rightarrow 5$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 17$
3 standard reflections monitored every 97 reflections intensity variation: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0209$
$wR(F^2) = 0.0549$
$S = 1.132$
1231 reflections
81 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0220P)^2 + 0.2637P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.386$ e Å^{-3}
$\Delta\rho_{\min} = -0.264$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0345 (34)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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	$U_{\rm eq}$
S(1)	0.18274 (7)	0.11136 (3)	0.91024 (2)	0.01213 (10)
C(2)	0.3190 (3)	0.28744 (11)	0.95345 (8)	0.0112 (2)
N(2)	0.2736 (3)	0.32888 (11)	1.04858 (7)	0.0159 (2)
N(3)	0.4649 (2)	0.37589 (10)	0.88679 (7)	0.0115 (2)
C(4)	0.4930 (3)	0.30606 (11)	0.79469 (8)	0.0104 (2)
O(4)	0.6290 (2)	0.36192 (9)	0.72118 (6)	0.0146 (2)
C(5)	0.3437 (3)	0.14997 (12)	0.78708 (8)	0.0113 (2)

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

S(1)—C(2)	1.7509 (11)	N(3)—C(4)	1.3642 (13)
S(1)—C(5)	1.7953 (10)	C(4)—O(4)	1.2329 (13)
C(2)—N(2)	1.3167 (13)	C(4)—C(5)	1.5206 (14)
C(2)—N(3)	1.3333 (13)		
C(2)—S(1)—C(5)	89.70 (5)	O(4)—C(4)—N(3)	124.01 (10)
N(2)—C(2)—N(3)	122.29 (10)	O(4)—C(4)—C(5)	120.62 (9)
N(2)—C(2)—S(1)	120.04 (8)	N(3)—C(4)—C(5)	115.37 (9)
N(3)—C(2)—S(1)	117.66 (8)	C(4)—C(5)—S(1)	106.05 (7)
C(2)—N(3)—C(4)	111.17 (9)		

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

D—H···A	H···A	D···A	D—H···A
N(2)—H(2A)···O(4$^{\rm i}$)	2.09 (2)	2.911 (1)	163 (1)
N(2)—H(2B)···N(3$^{\rm ii}$)	2.08 (2)	2.947 (1)	177 (1)

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

Data collection, cell refinement and data reduction: Siemens *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1121). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, C. F. H. & VanAllan, J. A. (1955). *Org. Synth. Coll.* Vol. III, pp. 751–752.
Amirthalingam, V. & Muralidharan, K. V. (1972). *Acta Cryst.* B**28**, 2421–2423.
Ananthamurthy, R. V., Udupa, M. R. & Murthy, B. V. R. (1972). *Z. Kristallogr.* **137**, 316–317.
Comrie, A. M. (1964). *J. Chem. Soc.* pp. 3478–3480.
Elguero, J., Marzin, C., Katritzky, A. R. & Linda, P. (1976). *The Tautomerism of Heterocycles. Adv. Heterocycl. Chem.* Suppl. **1**, p. 78.
Greenhill, J. V., Chaaban, I. & Steel, P. J. (1992). *J. Heterocycl. Chem.* **29**, 1375–1383.
Khovratovich, N. N. & Chizhevskaya, I. I. (1967). *Khim. Geterotsikl. Soedin.* pp. 637–641.
Ramsh, S. M., Smorygo, N. A. & Ginak, A. I. (1984). *Khim. Geterotsikl. Soedin.* pp. 1066–1070.
Ramsh, S. M., Smorygo, N. A. & Khrabrova, E. S. (1985). *Khim. Geterotsikl. Soedin.* pp. 32–37.
Sheldrick, G. M. (1990*a*). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1990*b*). *SHELXTL/PC User's Manual.* Siemens Analytical Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement.* Univ. of Göttingen, Germany.
Steel, P. J. (1991). *J. Heterocycl. Chem.* **28**, 1817–1818.
Valls, N., Segarra, V. M., Alcalde, E., Marin, A. & Elguero, J. (1985). *J. Prakt. Chem.* **327**, 251–260.

Acta Cryst. (1994). C**50**, 1723–1726

Anti-Inflammatory Drugs: 1-(2-Hydroxyethyl)pyrrolidinium Salt of Diclofenac

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(*Received* 17 *December* 1993; *accepted* 11 *April* 1994)

Abstract

In the solid-state structure of *N*-(2-hydroxyethyl)pyrrolidinium {2-[(2,6-dichlorophenyl)amino]phenyl}acetate, $C_6H_{14}NO^+.C_{14}H_{10}Cl_2NO_2^-$, the asymmetric unit contains two independent ion pairs differing mainly in the conformation of the cation. A complex network of inter- and intramolecular hydrogen bonds is present.

Comment

Non-steroidal anti-inflammatory drugs (NSAID's) have been receiving considerable attention during the last few decades. Their mechanism of action has been recognized (Vane, 1971) as inhibition of the activity of the cyclo-oxygenase enzyme. Different hypotheses have been made about the binding site, but all indicate that the carboxyl groups of the NSAID's are responsible for the interactions (Moser, Sallmann & Wiesenberg, 1990). Diclofenac, {2-[2,6-dichlorophenyl)amino]phenyl}acetic acid, is a potent and widely used anti-inflammatory agent and is usually

Acta Crystallographica Section C
ISSN 0108-2701 ©1994