

Table 4. *Calculated (Hencsei & Párkányi, 1985) molecular parameters (Si←N), ΔSi, ΔN and α(NSiO) for the title compound compared with the corresponding experimental data*

	Calculated	Observed
Si←N	2.172 Å	2.134 (1) Å
ΔSi	0.178	0.209 (1)
ΔN	0.380	0.384 (1)
α(NSiO)	83.8°	82.8 (1)°

Si,O,C,N moiety are similar in dimensions and direction [ $\Delta C(4)$ : 0.380 (2),  $\Delta C(6)$ : 0.557 (2),  $\Delta C(11)$ : 0.494 (2) Å].

It can be concluded that in contrast with the silatranes (Hencsei & Párkányi, 1985) where Si←N bond lengths can be correlated with the character of the *R* substituents, in silatranones the effect of the C=O group on their bonding weakens the direct influence of the *R* substituents. This is substantiated by the structure determination of the title compound with *R* = CH<sub>3</sub>, the Si←N distance of which falls in the middle of the range observed for the known silatranone structures.

The authors thank Mr Cs. Kertész for his technical assistance.

This work was supported by the Institute for Science Management and Informatics, Ministry of Education, Budapest, Hungary.

*Acta Cryst.* (1988). **C44**, 723–725

## Structure of *tert*-Butylhydrazine Hydrochloride

BY T. HÖKELEK

*Hacettepe University, Department of Physics, Beytepe, Ankara, Turkey*

AND R. YAĞBASAN

*İnönü University, Department of Physics, Malatya, Turkey*

(Received 6 October 1987; accepted 18 December 1987)

**Abstract.** C<sub>4</sub>H<sub>12</sub>N<sub>2</sub>·HCl, *M<sub>r</sub>* = 124.613, orthorhombic, *Pbca*, *a* = 9.878 (4), *b* = 10.638 (1), *c* = 13.751 (2) Å, *V* = 1444.98 (6) Å<sup>3</sup>, *Z* = 8, *D<sub>m</sub>* = 1.125 (9), *D<sub>x</sub>* = 1.145 g cm<sup>-3</sup>, λ(Cu Kα) = 1.54180 Å, μ(Cu) = 39.342 cm<sup>-1</sup>, *F*(000) = 544, *T* = 293 K, *R* = 0.048 for 956 observed reflections. The structure consists of symmetry-related [(CH<sub>3</sub>)<sub>3</sub>C(NH)(NH<sub>2</sub>)] and HCl moieties arranged in a chain structure on the *yz* plane. (CH<sub>3</sub>)<sub>3</sub>C and (NH)(NH<sub>2</sub>) are coordinated by a C—N bond. The coordination around the C bonding to C atoms of (CH<sub>3</sub>)<sub>3</sub> is a slightly distorted tetrahedron. Hydrogen bonds contribute significant stabilizing force in holding the molecule in a stable crystalline state.

**Introduction.** The title compound is of chemical importance as it is used to determine some organic compounds (e.g. aldehydes) in certain organic reactions. Its crystal and molecular structures are therefore described here.

**Experimental.** Prismatic colourless crystals were obtained by slow evaporation of an aqueous solution of [(CH<sub>3</sub>)<sub>3</sub>C(NH)(NH<sub>2</sub>)]·HCl at room temperature for a week. Experimental data and structure refinement procedures are listed in Table 1. The H atoms were located on difference Fourier maps and a riding model was used in the refinement of H positions.

## References

- DAI, J., ZHANG, J. & WU, Y. (1983). *Jiegou Huaxue*, **2**, 107–113.  
 DAI, J., ZHANG, J., WU, Y. & WU, G. (1983). *Jiegou Huaxue*, **2**, 207–211.  
 FRENZ, B. A. (1983). *Enraf-Nonius SDP-Plus Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.  
 HENCSEI, P. & PÁRKÁNYI, L. (1985). *Review on Silicon, Germanium, Tin and Lead Compounds*, Vol. 8, edited by M. GIELEN, pp. 191–218. Tel-Aviv: Freund Publishing House.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)  
 KEMZ, A., BLEIDELIS, J., LAPSINA, A., FLEISHER, M., ZELČANS, G. & LUKEVICS, E. (1985). *Latv. PSR Zināt. Akad. Vēstis Kim. Ser.* pp. 242–245.  
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN82. A System of Computer Programs for the Automatic Solution of Crystal Structures for X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.  
 MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.  
 PÁRKÁNYI, L., BIHÁTSI, L. & HENCSEI, P. (1978). *Cryst. Struct. Commun.* **7**, 435–440.  
 PÁRKÁNYI, L., HENCSEI, P., CSONKA, G. & KOVÁCS, I. (1987). *J. Organomet. Chem.* **329**, 305–311.  
 PÁRKÁNYI, L., HENCSEI, P. & POPOWSKI, E. (1980). *J. Organomet. Chem.* **197**, 275–283.  
 POPOWSKI, E., MICHALIK, M. & KELLING, H. (1975). *J. Organomet. Chem.* **88**, 157–164.  
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.  
 WIBERG, K. B. (1968). *Tetrahedron*, **24**, 1083–1096.

Table 1. *Experimental data and structure refinement parameters*

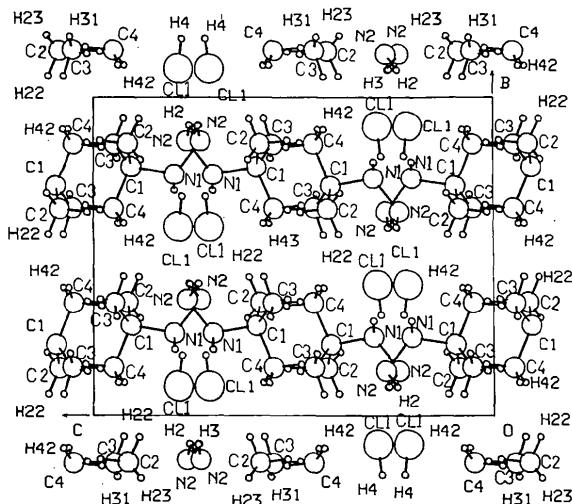
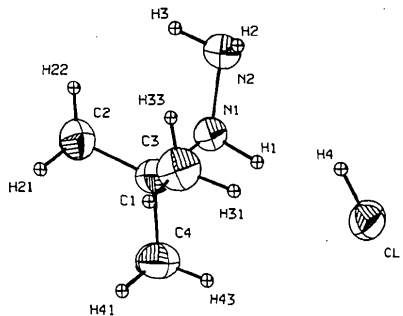
Method of measuring $D_m$	Pycnometer (CCl <sub>4</sub> )
Crystal shape and size (mm)	Prismatic, 0.1 × 0.15 × 0.25
Diffractometer used and data collection technique	$\omega$ -2 $\theta$ scan, four-circle diffractometer (Enraf-Nonius) CAD-4
Number and $\theta$ range of reflections used for measuring lattice parameters	25 reflections with $11^\circ \leq 2\theta \leq 22^\circ$
Absorption correction applied	Semi-empirical (North, Phillips & Mathews, 1968)
Maximum value of $(\sin\theta)/\lambda$ reached in intensity measurements ( $\text{\AA}^{-1}$ )	0.638
Range of $h, k$ and $l$	$-1 \leq h \leq 12, -1 \leq k \leq 13, -1 \leq l \leq 17$
Standard reflections and their intensity variation throughout experiment	$\bar{1}\bar{2}\bar{2}, \bar{1}\bar{2}\bar{2}, \bar{1}\bar{2}\bar{2}$ , variation (%) 6, 5, 3 respectively
Number of reflections measured	2272
Number of unique reflections	1466
Number of unobserved reflections	510
Criterion for recognizing unobserved reflections	$I \leq 3\sigma(I)$
Method used to solve structure	Direct methods
Use of $F$ or $F^2$ magnitudes in least-squares refinement	$F$
Parameters refined	(Coordinates and anisotropic temperature factors of non-hydrogen atoms) 63
Values of $R, wR$	0.048, 0.052, $S$ not calculated
Method used to calculate $w$	$w = 1$
Final residual electron densities ( $e \text{\AA}^{-3}$ ) for max. and min. peaks	+0.47 and -0.30
Max. $(\Delta/\sigma)$	+0.41
Source of atomic scattering factors and $f', f''$ values	<i>International Tables for X-ray Crystallography</i> (1974).
Computer programs used	<i>SHELXS86</i> (Sheldrick, 1986), <i>CRYSTALS</i> (Watkin, Carruthers & Betteridge, 1985), <i>SNOOPI</i> (Davies, 1983).

**Discussion.** The final coordinates and equivalent isotropic thermal parameters are given in Table 2.\* The structure as viewed down the  $x$  axis is shown in Fig. 1. It consists of C-N coordinated  $[(\text{CH}_3)_3\text{C}(\text{NH})(\text{NH}_2)]$  and HCl moieties. The nearest neighbours of C(1) involve three methyl C atoms. The average distance from C(1) to these neighbours is 1.51 Å. A fourth nearest neighbour, N belonging to (NH) at 1.53 Å, completes a slightly distorted tetrahedron (Fig. 2). The symmetry-related molecules are so arranged that one sees them as a chain structure while looking down the  $x$  axis (Fig. 1). As can be seen from Table 3 the bond lengths and angles which were calculated from the final coordinates generally agree with those observed in related compounds. Because of some differences in the bond lengths and angles within the  $(\text{CH}_3)_3$  group from their ideal values, the ligand appears slightly distorted. Most of the H atoms form intramolecular hydrogen bonds with neighbouring atoms. These hydrogen bonds

Table 2. *Atomic coordinates and isotropic or equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_r a_s$$

	$x$	$y$	$z$	$U/U_{eq} (\text{\AA}^2)$
Cl(1)	0.2498 (1)	0.40886 (9)	0.21176 (8)	0.0499
C(1)	-0.0441 (4)	0.2202 (4)	0.0940 (3)	0.0403
C(2)	-0.1745 (5)	0.1474 (4)	0.0855 (3)	0.0511
C(3)	0.0744 (5)	0.1500 (5)	0.0529 (3)	0.0556
C(4)	-0.0557 (5)	0.3510 (4)	0.0502 (3)	0.0546
N(1)	-0.0177 (3)	0.2442 (3)	0.2020 (2)	0.0385
N(2)	0.0007 (4)	0.1384 (3)	0.2667 (3)	0.0474
H(1)	0.0644	0.2949	0.2023	0.0800
H(2)	0.4191	0.5879	0.2383	0.0800
H(3)	0.0772	0.5901	0.2405	0.0800
H(4)	0.2265	0.31337	0.22101	0.0800
H(21)	0.3053	0.1375	0.4837	0.0800
H(22)	0.3300	0.0671	0.3869	0.0800
H(23)	0.2538	0.1965	0.3837	0.0800
H(31)	0.1745	0.1922	0.0588	0.0800
H(32)	0.0670	0.1453	-0.0157	0.0800
H(33)	0.0742	0.0662	0.0752	0.0800
H(41)	-0.0733	0.3418	-0.0192	0.0800
H(42)	-0.1293	0.3977	0.0758	0.0800
H(43)	0.0220	0.3977	0.0624	0.0800

Fig. 1. Crystal structure as viewed down the  $a$  axis.Fig. 2. A *SNOOPI* (Davies, 1983) drawing of the title molecule with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

\* Lists of structure factors, anisotropic thermal parameters and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44627 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond lengths (Å) and bond angles (°) of non-hydrogen atoms with *e.s.d.*'s in parentheses

C(1)–C(2)	1.508 (6)	C(1)–N(1)	1.530 (5)
C(1)–C(3)	1.498 (6)	N(1)–N(2)	1.446 (4)
C(1)–C(4)	1.521 (6)		
C(3)–C(1)–C(2)	112.5 (4)	N(1)–C(1)–C(3)	108.5 (4)
C(4)–C(1)–C(2)	112.0 (4)	N(1)–C(1)–C(4)	104.2 (3)
C(4)–C(1)–C(3)	111.4 (4)	N(2)–N(1)–C(1)	119.2 (3)
N(1)–C(1)–C(2)	107.8 (3)		

contribute significant stabilizing force in holding the molecule in a stable crystalline state.

The authors are grateful to Dr C. K. Prout and Dr D. Watkin of Chemical Crystallography Laboratory,

University of Oxford (UK) for provision of laboratory facilities.

#### References

- DAVIES, K. (1983). *SNOOPI*. Program for drawing crystal and molecular diagrams. Univ. of Oxford, England.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst. A* **24**, 351–359.
- SHELDRIK, G. M. (1986). *SHELXS86*. Program for the automatic solution of crystal structures. Univ. of Göttingen, Federal Republic of Germany.
- WATKIN, D. J., CARRUTHERS, J. R. & BETTERIDGE, D. W. (1985). *CRYSTALS*. Program for crystal structure solution. Univ. of Oxford, England.

*Acta Cryst.* (1988). **C44**, 725–727

## Structure of Thiamine Picrate

BY MOON-JIP KIM AND IL-HWAN SUH

*Chungnam National University, Department of Physics, Daejeon 300-31, Korea*

AND KATSUYUKI AOKI\* AND HIROSHI YAMAZAKI

*The Institute of Physical and Chemical Research, Wako-shi, Saitama 351-01, Japan*

(Received 28 September 1987; accepted 18 December 1987)

**Abstract.**  $C_{12}H_{17}N_4OS^+ \cdot C_6H_2N_3O_7^-$ ,  $M_r = 493.455$ , triclinic,  $P\bar{1}$ ,  $a = 10.464$  (1),  $b = 12.951$  (1),  $c = 8.6615$  (8) Å,  $\alpha = 107.368$  (8),  $\beta = 104.627$  (8),  $\gamma = 70.544$  (9)°,  $V = 1040.9$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.574$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 2.09$  cm<sup>-1</sup>,  $F(000) = 512$ ,  $T = 293$  K,  $R = 0.047$  for 2595 observed reflections. The thiamine molecule adopts the *S* conformation. There are three kinds of ring-stacking interactions: pyrimidine–phenyl, thiazolium–thiazolium and phenyl–phenyl.

**Introduction.** Thiamine (vitamin B<sub>1</sub>), as its pyrophosphate ester, is a cofactor for a number of metabolic enzymes catalyzing the decarboxylation of  $\alpha$ -keto acids and the transfer of aldehyde or acyl groups (Krampitz, 1969). Structural investigations of molecular interactions between thiamine and an anion molecule containing both a carboxyl (or its analogue) group(s) and a ring moiety(ies) are of interest to examine the ring–ring stacking and/or thiamine–carboxyl interaction modes; a carboxyl group functions as a model for the carboxyl group of a substrate that should be

fixed close by the C(2) catalytic site and a ring moiety is a model for the indole  $\pi$  system of the tryptophan residue of the apoenzyme at the active center (Heinrich, Moack & Wiss, 1971; Kochetov & Usmanov, 1970; Kochetov, Usmanov & Mevkh, 1973). We report here the crystal structure of the thiamine picrate, where the picrate anion bears carboxyl-like nitro groups and a phenyl ring; there is a partial overlap between the phenyl ring of picric acid and the neutral pyrimidine moiety of the thiamine molecule which adopts the *S* conformation but no interaction between the nitro group and the thiazolium moiety.

**Experimental.** The complex was prepared by mixing thiamine nitrate (32.7 mg, 0.1 mmol) dissolved in 10 mL of water and sodium picrate (26.9 mg, 0.1 mmol) in 10 mL water and allowing the solution to stand at room temperature. Yellow rod-like crystals formed after a few months. Crystal 0.51 × 0.42 × 0.40 mm, Rigaku diffractometer, graphite-monochromated Mo  $K\alpha$  radiation; cell parameters by a least-squares fitting of diffractometer setting angles for 19 reflections ( $20 < 2\theta < 30^\circ$ ); reflection data  $2\theta_{\max} = 55^\circ$  ( $h = -12$  to 12,  $k = 0$  to 16,  $l = -10$  to 10),

\* To whom correspondence should be addressed.