References

CHANDRAKANTHA, T. N., NIRMALA, K. A., PUTTARAJA & NETHAJI, M. (1990). Acta Cryst. C46, 1051–1053.

CHANDRASEKHAR, K. & PATTABHI, V. (1980). Acta Cryst. B36, 1165–1169.

EVERETT, J. H., REYNOLDS, C. D., SPARKS, C. A., PANGBORN, W., STRONG, P., BAILEY, P. D., DAUTER, Z., HELLIWELL, M. & HOLLINSHEAD, S. P. (1989). Acta Cryst. C45, 1805–1808.

FALKENBERG, G. & CARLSTRÖM, D. (1971). Acta Cryst. B27, 411–418.

GADAGINAMATH, G. S. & SIDDAPPA, S. (1975). Indian J. Chem. 13, 1247–1250.

HENDI, S. B. & BASANGOUDAR, L. D. (1981). Indian J. Chem. 208, 285–287.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). PLUTO. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

NARDELLI, M. (1983). Comput. Chem. 7, 95–98.

ROYCHOWDHURY, P. & BASAK, B. S. (1975). Acta Cryst. B31, 1559–1563.

SHELDRICK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1986). SHELXS86. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

VIJAYALAKSHMI, B. K. & SRINIVASAN, R. (1975). Acta Cryst. B31, 999–1003.

WARING, P., EICHNER, R. D., PALNI, U. T. & MULLBACHER, A. (1986). Tetrahedron Lett. 27, 735–738.

Structure of 2-(4-Nitrophenyl)-2-trichloromethyloxirane

BY D. F. MULLICA* AND E. L. SAPPENFIELD

Department of Chemistry, Baylor University, Waco, Texas 76798, USA

AND W. P. REEVES* AND G. M. SCHEIDE

Department of Chemistry, Texas Lutheran College, Seguin, Texas 78155, USA

Abstract. $C_9H_6Cl_3NO_3$, $M_r = 282.51$, monoclinic, $P2_1/n$, $a = 6.104$ (2), $b = 19.538$ (2), $c = 9.286$ (2) Å, $\beta = 93.28$ (2)°, $V = 1105.6$ (7) Å^3, $Z = 4$, $D_x = 1.697$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.820$ mm^{-1}, $F(000) = 568$, $T = 292$ K, final $R = 0.068$ for 885 reflections. The title compound is a halogenated p-nitroacetophenone synthesized under phase-transfer catalytic (PTC) conditions. The molecules in the crystal lattice are held together by van der Waals forces (m.p. 387 K). Bond lengths and angles are internally consistent and the van der Waals interactions are normal. The nitrophenyl, trichloromethyl and oxirane groups are oriented in a slightly distorted trigonal planar arrangement. The averaged bond angles within the epoxy group and about the trichloro-$C(sp^3)$ atom are 60.0 (7) and 109.5 (17)°, respectively. Selected mean geometric details are: C—O = 1.428 (4), N—O = 1.208 (3), C—Cl = 1.766 (3) and C—C (ring) = 1.383 (9) Å.

Experimental. Clear colorless irregular shaped crystals of the title compound (I) were prepared

according to a published procedure (Reeves, Creswell, Glass & Scheide, 1985). Crystals suitable for X-ray analysis were obtained after recrystallization from ethanol.

(I)
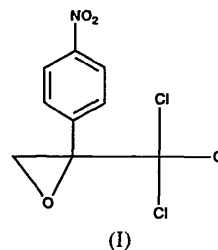
After verifying homogeneity and the biaxial nature of the system by a conoscopic examination, a single crystal of dimensions 0.15 × 0.26 × 0.59 mm was selected for data collection. Data were collected on an Enraf–Nonius CAD-4F diffractometer equipped with a graphite monochromator utilizing Mo $K\alpha$ radiation, take-off angle 5.8°. 25 diffractometer-measured reflections with $4.57 \leq 2\theta \leq 15.59°$ were used to obtain the orientation matrix and initial cell parameters. Final unit-cell parameters were

* To whom correspondence should be addressed.

determined at high angles $(28 < 2\theta < 47°)$. 1400 reflections were collected using the ω–2θ-scan method ($h\ 0 \rightarrow 5$, $k\ -10 \rightarrow 18$, $l\ -8 \rightarrow 8$), variable scan speed of 0.49–3.44° min^{-1} in ω, scan range (ω) $(1.30 + 0.344\tan\theta)°$, and $3.0 < 2\theta < 40.0°$. Intensities of two standard reflections ($\overline{1}7\overline{4}$ and 210), measured as a function of time (every 2 h), revealed a slow decay of -0.068% h^{-1} which constituted a maximum correction of 1.03608. Lorentz–polarization corrections were made, as well as a numerical absorption correction with minimum 0.6718 and maximum 0.7802 (Coppens, Leiserowitz & Rabinovich, 1965). Of the 1400 reflections measured, 1027 were independent, and 885 with $F > 4.0\sigma(F)$ were included in the refinement ($R_{int} = 0.021$).

The structure was solved by direct methods using Siemens *SHELXTL-PC* (Sheldrick, 1989) and by successive electron-density calculations. The structure was refined using full-matrix least squares, anisotropically for all non-H atoms and using the riding model (constrained at 0.96 Å on connected C atoms) with fixed isotropic thermal parameters ($U_{iso} = 0.8$ Å^2) for H atoms. 146 parameters were refined and $\Sigma w(|F_o| - |F_c|)^2$ was minimized, where $w = [\sigma^2(|F_o|) + 0.0025(|F_o|)^2]^{-1}$. For the secondary extinction, $\chi = 0.0002\,(8)\,e^{-2}$ where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$ (Sheldrick 1989). $R = 0.0680$, $wR = 0.0662$ and $S = 1.38$. $(\Delta/\sigma)_{max} = 0.014$ in the final refinement cycle and the largest difference hole and peak in the ΔF map were -0.54 and $0.53\ e\ $Å^{-3} in the vicinity of the Cl atoms; elsewhere only random fluctuations were observed. Atomic scattering factors and anomalous-dispersion correction terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 72–151). Final atomic positional parameters and equivalent isotropic thermal parameters of the non-H atoms are listed in Table 1;† derived interatomic lengths and angles are given in Table 2. Fig. 1 is an *ORTEP* (Johnson, 1965) drawing of the molecule. The molecules in the crystal lattice are held together by van der Waals forces (m.p. 387 K).

Related literature. A standard procedure in organic chemistry laboratories is the use of phase-transfer catalysis (Weber & Gokel, 1977; Dehmlow & Dehmlow, 1980). The use of PTC in halogenation of ketones, sulfones and alcohols has been minimal (Jonczyk, Kwast & Makosza, 1979; Lauritzen, Romming & Skattebol, 1981; Jonczyk & Radwan-

Table 1. *Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) with e.s.d.'s in parentheses*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	3859 (6)	8926 (2)	2544 (5)	38 (2)
C(2)	5967 (7)	9186 (3)	2633 (5)	46 (2)
C(3)	7072 (8)	9308 (3)	3960 (6)	48 (2)
C(4)	5986 (7)	9157 (3)	5183 (5)	41 (2)
C(5)	3888 (7)	8912 (3)	5130 (5)	44 (2)
C(6)	2804 (8)	8789 (3)	3799 (5)	44 (2)
N	7095 (9)	9287 (2)	6614 (5)	55 (2)
O(1)	6074 (8)	9210 (3)	7679 (5)	83 (2)
O(2)	8999 (9)	9457 (3)	6633 (4)	87 (2)
C(7)	2711 (7)	8804 (3)	1093 (5)	39 (2)
C(8)	2198 (10)	9376 (3)	150 (6)	65 (2)
O(3)	529 (6)	9061 (2)	947 (4)	67 (2)
C(9)	2936 (8)	8087 (3)	479 (4)	48 (2)
Cl(1)	1822 (3)	7491 (1)	1673 (2)	76 (1)
Cl(2)	5741 (3)	7903 (1)	317 (2)	73 (1)
Cl(3)	1536 (3)	7988 (1)	−1223 (2)	80 (1)

Table 2. *Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

C(1)—C(2)	1.381 (6)		C(1)—C(6)	1.390 (7)
C(1)—C(7)	1.502 (6)		C(2)—C(3)	1.391 (7)
C(3)—C(4)	1.379 (7)		C(4)—C(5)	1.366 (6)
C(4)—N	1.478 (7)		C(5)—C(6)	1.389 (7)
N—O(1)	1.208 (7)		N—O(2)	1.208 (8)
C(7)—C(8)	1.443 (8)		C(7)—O(3)	1.424 (6)
C(7)—C(9)	1.521 (7)		C(8)—O(3)	1.432 (7)
C(9)—Cl(1)	1.770 (5)			
C(9)—Cl(3)	1.764 (4)			

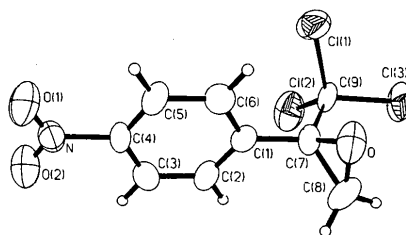|				
C(2)—C(1)—C(6)	119.7 (4)		C(2)—C(1)—C(7)	119.8 (4)
C(6)—C(1)—C(7)	120.4 (4)		C(1)—C(2)—C(3)	121.2 (5)
C(2)—C(3)—C(4)	117.5 (4)		C(3)—C(4)—C(5)	122.6 (4)
C(3)—C(4)—N	119.2 (4)		C(5)—C(4)—N	118.2 (4)
C(4)—C(5)—C(6)	119.4 (4)		C(1)—C(6)—C(5)	119.5 (4)
C(4)—N—O(1)	118.9 (5)		C(4)—N—O(2)	116.8 (5)
O(1)—N—O(2)	124.3 (5)		C(1)—C(7)—C(8)	119.6 (5)
C(1)—C(7)—O(3)	114.5 (4)		C(8)—C(7)—O(3)	59.9 (4)
C(1)—C(7)—C(9)	115.8 (4)		C(8)—C(7)—C(9)	120.5 (4)
O(3)—C(7)—C(9)	113.2 (4)		C(7)—O(3)—C(8)	60.7 (4)
C(7)—C(8)—O(3)	59.4 (3)		C(7)—C(9)—Cl(2)	109.2 (3)
C(7)—C(9)—Cl(1)	109.0 (3)		C(7)—C(9)—Cl(3)	112.7 (3)
Cl(1)—C(9)—Cl(2)	109.2 (3)		Cl(1)—C(9)—Cl(3)	107.8 (3)
Cl(2)—C(9)—Cl(3)	108.9 (2)			

Fig. 1. An *ORTEP* (Johnson, 1965) drawing of the title compound (I) with 50% equiprobability ellipsoids.

Pytlewski, 1983; Reeves *et al.*, 1985). The chlorination and oxidation of *p*-nitroacetophenone using carbon tetrachloride (the source of the trichloromethyl group) and tetrabutylammonium bromide as

the PTC, yielded the title compound. The mechanism of this reaction is not known, as yet. However, it is believed that this X-ray structural investigation will help resolve the problem.

References

COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.

DEHMLOW, E. V. & DEHMLOW, S. S. (1980). *Phase Transfer Catalysis.* Deerfield Beach, Florida: Verlag Chemie.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

JONCZYK, A., KWAST, A. & MAKOSZA, M. (1979). *J. Org. Chem.* **44**, 1192–1194.

JONCZYK, A. & RADWAN-PYTLEWSKI, T. (1983). *J. Org. Chem.* **48**, 910–912.

LAURITZEN, S. E., ROMMING, C. & SKATTEBOL, L. (1981). *Acta Chem. Scan. Ser. B*, **35**, 263–268.

REEVES, W. P., CRESWELL, M. W., GLASS, D. S. & SCHEIDE, G. M. (1985). *Isr. J. Chem.* **26**, 225–228.

SHELDRICK, G. M. (1989). *SHELXTL-PC.* Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

WEBER, W. P. & GOKEL, G. W. (1977). *Phase Transfer Catalysis in Organic Synthesis.* New York: Springer-Verlag.

Structure of Tetrahydrothiamin Hemihydrate

BY WHANCHUL SHIN* AND JAE HOON SHIM

Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151–742, *Korea*

Abstract. 3-[(4-Amino-2-methyl-5-pyrimidinyl)methyl]-4-methyl-5-thiazolidineethanol hemihydrate, $C_{12}H_{20}N_4OS.\frac{1}{2}H_2O$, $M_r = 277.38$, monoclinic, $P2_1/c$, $a = 9.533\,(2)$, $b = 23.568\,(5)$, $c = 13.666\,(3)$ Å, $\beta = 103.47\,(3)°$, $V = 2986\,(1)$ Å^3, $Z = 8$, $D_x = 1.234$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 18.9$ cm^{-1}, $F(000) = 1192$, $T = 295$ K, $R = 0.048$ for 2071 reflections with $I \geq 2\sigma(I)$. Two independent molecules, both of which are in the *syn* diastereoisomeric form, assume a similar overall conformation. However, only one molecule has an intramolecular hydrogen bond between the thiazolidine N and 4′-amino N atoms. The thiazolidine rings with the sp^3-N atoms assume a half-chair conformation. There are two kinds of hydrogen-bonded molecular dimer which are interconnected by water molecules to form a three-dimensional hydrogen-bonding network.

Experimental. The title compound was prepared by reduction of thiamin with $NaBH_4$ in water (Clark & Sykes, 1967). Colourless tabular crystals were obtained from an ethanol solution by slow evaporation. A crystal *ca* 0.2 × 0.2 × 0.4 mm was used for data collection on a Rigaku AFC diffractometer with graphite-monochromated Cu $K\alpha$ radiation and ω–2θ scans of speed 2° min^{-1} in 2θ, and ω-scan width $(1.7 + 0.1\tan\theta)°$ for $2\theta \leq 110°$. Background was

measured for 10 s on either side of the peak. Cell parameters were determined by least-squares fit to observed 2θ values for 25 centred reflections with $23 \leq 2\theta \leq 48°$. Intensity checks for three standard reflections showed little ($\pm$ 3%) variation. 3627 independent reflections were collected (h 0 to 9, k 0 to 25, l −14 to 14), of which 2071 (57%) were observed with $I \geq 2\sigma(I)$ and used in refinement. Lp corrections, but no absorption or extinction correction were made. The structure was solved by direct methods and refined by full-matrix least squares on F with anisotropic thermal parameters, using *SHELX*76 (Sheldrick, 1976). H atoms were identified in the difference map and refined isotropically.
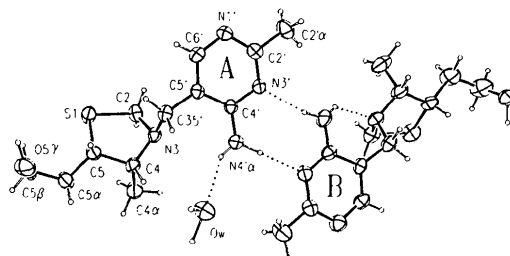

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the asymmetric unit of tetrahydrothiamin hemihydrate with the atomic numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. The dotted line denotes the hydrogen bond. The view is tilted from the pseudo-twofold axis to avoid the overlap of the atoms.