Acta Cryst. (1992). C**48**, 1874–1876

Structure of a Bicyclic Guanidinium Nitrite Salt

By A. Meetsma

Crystal Structure Center, Nijenborgh 4, 9747 *AG Groningen, The Netherlands*

and E. van Aken and Hans Wynberg*

Department of Organic Chemistry, Nijenborgh 4, 9747 *AG Groningen, The Netherlands*

(*Received* 16 *December* 1991; *accepted* 18 *February* 1992)

Abstract. 3,4,6,7,8,9-Hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidinium nitrite, $C_7H_{14}N_3^+.NO_2^-$, $M_r = 186.22$, monoclinic, $P2_1/c$, $a = 6.657$ (1), $b = 8.742$ (1), $c = 15.894$ (1) Å, $\beta = 101.232$ (6)°, $V = 907.24$ (18) Å^3, $Z = 4$, $D_x = 1.363$ g cm^{-3}, λ(Mo $K\overline{\alpha}$) = 0.71073 Å, $\mu = 1.0$ cm^{-1}, $F(000) = 400$, $T = 130$ K, $R(F) = 0.043$ for 1268 unique observed reflections with $I \geq 2.5\sigma(I)$ and 174 refined parameters. The basic structure consists of a guanidinium moiety coupled by hydrogen bonds to a nitrite moiety. Essential is the complementarity of the structures of both the nitrite anion and the guanidinium cation.

Experimental. A large transparent multi-layer plate-shaped crystal was grown from toluene/pentane at room temperature. It was formed by mixing 3-methyl-1-nitrobutane and 1,5,7-triazabicyclo-[4.4.0]dec-5-ene (tbd) 1:1 in toluene/pentane. According to ^{1}H NMR the nitroalkane was deprotonated by tbd, but no crystals were formed. Only after several weeks was nitric acid eventually eliminated from the nitroalkane and the tbd/nitric acid salt crystallized from the solution. The fragment used for characterization and data collection was cleaved under hexane. The single crystal was glued on top of a glass fibre and transferred to the goniostat and cooled to 130 K using an on-line liquid-nitrogen cooling system, mounted on an Enraf–Nonius CAD-4F diffractometer interfaced to a VAX-11/730 computer. Unit-cell parameters were determined from a least-squares treatment of the setting angles of 22 reflections with $10.18 < \theta < 19.18°$ in four alternate settings (de Boer & Duisenberg, 1984). The space group was derived from the observed systematic extinctions. The unit cell was identified as monoclinic, space group $P2_1/c$. Reduced-cell calculations did not indicate any higher metrical lattice symmetry (Spek, 1988). Examination of the final atomic coordinates of the structure did not yield extra symmetry elements (Le Page, 1988).

Crystal and/or instrumental instability was monitored by measurement of the intensities of three reference reflections that were collected after every 3 h of X-ray exposure time; these exhibited no significant decay during data collection. A 360° ψ scan for the close to axial reflection ($\overline{1}0\overline{2}$) showed an intensity variation up to 6% about the mean value. The net intensities of the data were corrected for the scale variation, Lorentz and polarization, but not for absorption effects. Standard deviations $\sigma(I)$ in the intensities were increased according to an analysis of the excess variance of the reference reflection: variance was calculated based on counting statistics and the term $(PI)^2$, where P (= 0.0159) is the instability constant (McCandlish, Stout & Andrews, 1975). Equivalent reflections were averaged, resulting in 1268 reflections satisfying the $I \geq 2.5\sigma(I)$ criterion of observability.

Table 1. *Experimental details*

Crystal data, data collection and structure determination	
Approx. crystal dimensions (mm)	0.13 × 0.18 × 0.38
Radiation, λ (Å)	Mo $K\overline{\alpha}$, 0.71073
Monochromator	Graphite
θ range minimum, maximum (°)	1.31, 27.0
$\omega/2\theta$ scan width (°)	$\Delta\omega = 0.85 + 0.34\tan\theta$
Data set	h $-8\rightarrow8$, k $-1\rightarrow11$, l $0\rightarrow20$
Crystal to receiver distance (mm)	173
Horizontal, vertical aperture (mm)	$3.2 + \tan\theta$, 4.0
Reference reflection, r.m.s. deviation (%)	$02\overline{4}$, 1.0; $\overline{1}2\overline{1}$, 0.9; $\overline{1}\overline{2}1$, 0.6; $\overline{4}\overline{4}\overline{4}$, 2.0
Instability constant, P	0.0159
Drift correction	1.00–1.02
X-ray exposure time (h)	53.3
Total data	2451
Unique data	1966
Observed data [$I \geq 2.5\sigma(I)$]	1268
$R_1[=\sum(I-\bar{I})/\sum I]$	0.021
$R_2[=\sum\sigma/\sum I]$	0.035
Number of equivalent reflections	490
Refinement	
Number of reflections	1268
Number of refined parameters	174
$R(F)$	0.043
wR [$w = 1/\sigma^2(F)$]	0.035
S	1.816
Residual electron density in final difference Fourier map (e Å^{-3})	−0.24,0.21
Maximum shift/σ in final cycle	0.0406
Average shift/σ in final cycle	0.0040

The structure was solved by direct methods with *SHELXS*86 (Sheldrick, 1986) and the positional and the anisotropic displacement parameters for the non-H atoms were refined with block-diagonal least-

---

* Author to whom correspondence should be addressed.

0108-2701/92/101874-03$06.00

Table 2. *Final fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for non-*H *atoms of the asymmetric unit*

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

	x	y	z	$U_{\rm eq}$
Residue 1				
O(1)	0.7786 (2)	0.2070 (2)	0.61685 (10)	0.0324 (6)
O(2)	0.8786 (2)	0.4177 (2)	0.57309 (10)	0.0283 (6)
N(4)	0.9150 (3)	0.3060 (2)	0.62228 (12)	0.0237 (6)
Residue 2				
N(1)	0.6004 (3)	0.4099 (2)	0.40708 (13)	0.0225 (6)
N(2)	0.2906 (2)	0.3051 (2)	0.33888 (11)	0.0181 (6)
N(3)	0.4359 (3)	0.2364 (2)	0.47828 (13)	0.0233 (6)
C(1)	0.6088 (4)	0.5173 (3)	0.33831 (17)	0.0244 (8)
C(2)	0.5008 (4)	0.4477 (3)	0.25452 (16)	0.0257 (8)
C(3)	0.2858 (4)	0.4007 (3)	0.26242 (15)	0.0220 (8)
C(4)	0.1078 (3)	0.2115 (3)	0.34087 (16)	0.0246 (8)
C(5)	0.0740 (4)	0.1937 (3)	0.43136 (16)	0.0264 (8)
C(6)	0.2672 (4)	0.1378 (3)	0.48884 (17)	0.0266 (8)
C(7)	0.4398 (3)	0.3185 (3)	0.40810 (14)	0.0177 (7)

Table 3. *Selected interatomic distances* (Å), *bond angles* (°), *torsion angles* (°) *and hydrogen-bond geometry* (Å, °)

Residue 1			
O(1)—N(4)	1.245 (2)	O(2)—N(4)	1.245 (2)
O(1)—N(4)—O(2)	116.84 (18)		
Residue 2			
N(1)—C(1)	1.450 (3)	C(3)—C(7)	1.331 (3)
N(1)—C(7)	1.337 (3)	C(1)—C(2)	1.513 (4)
N(2)—C(3)	1.470 (3)	C(2)—C(3)	1.518 (4)
N(2)—C(4)	1.472 (3)	C(4)—C(5)	1.506 (4)
N(2)—C(7)	1.336 (3)	C(5)—C(6)	1.507 (4)
N(3)—C(6)	1.451 (3)		
C(1)—N(1)—C(7)	123.0 (2)	N(2)—C(3)—C(2)	110.7 (2)
C(3)—N(2)—C(4)	116.67 (18)	N(2)—C(4)—C(5)	110.8 (2)
C(3)—N(2)—C(7)	121.59 (18)	C(4)—C(5)—C(6)	110.1 (2)
C(4)—N(2)—C(7)	121.08 (18)	N(3)—C(6)—C(5)	109.0 (2)
C(6)—N(3)—C(7)	124.0 (2)	N(1)—C(7)—N(2)	120.7 (2)
N(1)—C(1)—C(2)	108.8 (2)	N(1)—C(7)—N(3)	118.6 (2)
C(1)—C(2)—C(3)	109.3 (2)	N(2)—C(7)—N(3)	120.7 (2)
C(2)—C(1)—N(1)—C(7)	−35.2 (3)	C(5)—C(6)—N(3)—C(7)	−24.8 (3)
N(1)—C(1)—C(2)—C(3)	54.5 (3)	N(2)—C(7)—N(1)—C(1)	10.3 (3)
C(1)—C(2)—C(3)—N(2)	−51.8 (3)	N(3)—C(7)—N(1)—C(1)	−172.5 (2)
C(2)—C(3)—N(2)—C(4)	−161.06 (19)	N(1)—C(7)—N(2)—C(3)	−6.2 (3)
C(2)—C(3)—N(2)—C(7)	28.2 (3)	N(1)—C(7)—N(2)—C(4)	−176.6 (2)
C(5)—C(4)—N(2)—C(3)	−147.6 (2)	N(3)—C(7)—N(2)—C(3)	176.6 (2)
C(5)—C(4)—N(2)—C(7)	23.2 (3)	N(3)—C(7)—N(2)—C(4)	6.2 (3)
N(2)—C(4)—C(5)—C(6)	−52.0 (3)	N(1)—C(7)—N(3)—C(6)	177.4 (2)
C(4)—C(5)—C(6)—N(3)	52.0 (3)	N(2)—C(7)—N(3)—C(6)	−5.3 (3)

D—H⋯A	D⋯A	D—H	H⋯A	D—H⋯A
N(1)—H(1)⋯O(2$^{\rm i}$)	2.914 (3)	0.81 (2)	2.11 (2)	174 (2)
N(3)—H(3)⋯O(1$^{\rm i}$)	2.857 (3)	0.84 (2)	2.03 (2)	171 (2)

Symmetry code: (i) x, y, z.

squares procedures (*CRYLSQ;* Olthof-Hazekamp, 1990) minimizing the function $Q = \sum_h[w||F_o| - |F_c||)^2]$. A subsequent difference Fourier synthesis gave all the H atoms. The H atoms attached to N, involved in the two hydrogen bonds, could be identified. The H atoms were included in the final refinement in which the coordinates and the isotropic displacement parameters were refined. Weights were introduced in the final refinement cycles. Full-matrix least-squares refinements (based on F_o), with anisotropic displacement parameters for the non-H atoms and isotropic displacement parameters for the H atoms, converged satisfactorily. This gave the corresponding final discrepancy indices summarized in Table 1. A final difference Fourier map did not show residual peaks outside the range ±0.21 e Å^{-3}. Crystal data and experimental details of the structure determination are compiled in Table 1. The final fractional atomic coordinates and equivalent isotropic displacement parameters for the non-H atoms are presented in Table 2. Molecular geometry data are collected in Table 3.* Scattering factors were taken from Cromer & Mann (1968). Anomalous-dispersion factors taken from Cromer & Liberman

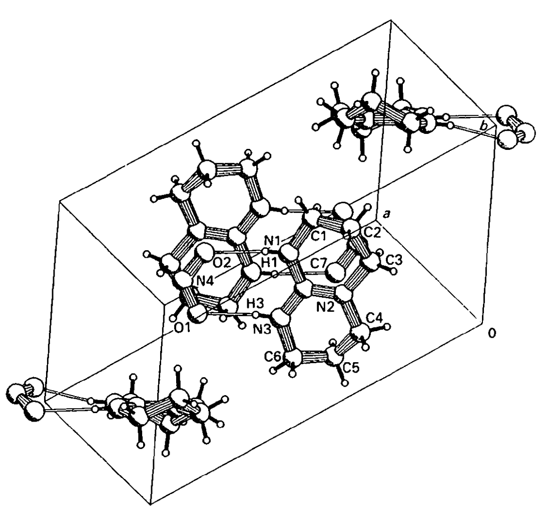

Fig. 1. *PLUTO* drawing of the molecule illustrating the conformation and the adopted numbering scheme.

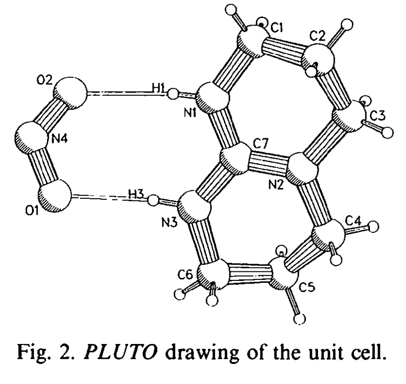

Fig. 2. *PLUTO* drawing of the unit cell.

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances, bond angles and torsion angles, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55202 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(1970) were included in F_c. All calculations were performed on the CDC-Cyber 962-31 computer of the University of Groningen with the program packages *Xtal* (Hall & Stewart, 1990) and *PLATON* (Spek, 1990); Figs. 1 and 2 were produced using a program by Meetsma (1991), a modified version of *PLUTO* (Motherwell & Clegg, 1978).

Related literature. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (tbd) as a strong base is a good catalyst for nitroalkanes in C—C bond forming reactions. In its protonated form the structure of the guanidinium cation is complementary to that of a nitronate and nitrite anion. tbd is therefore used as a model catalyst for its chiral analogue as synthesized by Echavarren, Galan, Mendoza, Salmeron & Lehn (1988) and Kurzmeier & Schmidtchen (1990).

Acknowledgement is made to the Dutch foundation for Chemical Research (SON) and the Dutch Organization for Scientific Research (NWO) for funding this research.

References

BOER, J. L. DE & DUISENBERG, A. J. M. (1984). *Acta Cryst.* **A40**, C-410.
CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
ECHAVARREN, A., GALAN, A., MENDOZA, J., SALMERON, A. & LEHN, J.-M. (1988). *Helv. Chim. Acta*, **71**, 685–693.
HALL, S. R. & STEWART, J. M. (1990). Editors. *Xtal*3.0 *User's Manual.* Univs. of Western Australia, Australia, and Maryland, USA.
KURZMEIER, H. & SCHMIDTCHEN, F. P. (1990). *J. Org. Chem.* **55**, 3749–3755.
LE PAGE, Y. (1988). *J. Appl. Cryst.* **21**, 983–984.
MCCANDLISH, L. E., STOUT, G. H. & ANDREWS, L. C. (1975). *Acta Cryst.* **A31**, 245–249.
MEETSMA, A. (1991). Extended version of *PLUTO*. Univ. of Groningen, The Netherlands.
MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
OLTHOF-HAZEKAMP, R. (1990). *CRYLSQ*. In *Xtal*3.0 *Reference Manual*, edited by S. R. HALL & J. M. STEWART. Univs. of Western Australia, Australia, and Maryland, USA.
SHELDRICK, G. M. (1986). *SHELXS*86. Program for the solution of crystal structures. Univ. of Göttingen, Germany.
SPEK, A. L. (1988). *J. Appl. Cryst.* **21**, 578–579.
SPEK, A. L. (1990). *Acta Cryst.* **A46**, C-34.

Acta Cryst. (1992). C**48**, 1876–1878

Structure of 1,1-Dibromo-2-phenylseleno-3-*p*-tolylcyclopropane

BY J. ZUKERMAN-SCHPECTOR AND E. E. CASTELLANO

Instituto de Física e Química de São Carlos, Universidade de São Paulo, Caixa Postal 369,
13560 *São Carlos – SP, Brazil*

AND J. V. COMASSETO AND H. A. STEFANI

Instituto de Química, Universidade de São Paulo, Caixa Postal 20780, 01498 *São Paulo – SP, Brazil*

(*Received* 2 *September* 1991; *accepted* 21 *February* 1992)

Abstract. $C_{16}H_{14}Br_2Se$, $M_r = 445.07$, monoclinic, $P2_1/n$, $a = 12.755\,(1)$, $b = 11.221\,(2)$, $c = 21.770\,(2)$ Å, $\beta = 94.16\,(2)°$, $V = 3107\,(1)$ Å^3, $Z = 8$, $D_x = 1.903$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 74.72$ cm^{-1}, $F(000) = 1712$, $T = 296$ K, final $R = 0.053$ for 1768 independent observed reflections. The two independent molecules in the asymmetric unit are essentially identical. Bond lengths and angles involving selenium are: Se—C(Ph) = 1.92 (1), 1.91 (2) Å, Se—C(sp^3) = 1.94 (1), 1.94 (2) Å and C—Se—C = 95.0 (7), 97.6 (7)°.

Experimental. The synthesis of the title compound is described by Comasseto, Stefani & Silveira (1990); crystals were obtained from chloroform at 277 K. The data collection and refinement parameters are summarized in Table 1.

The structure was solved using standard direct methods and difference Fourier techniques. In the final cycles of the blocked-matrix least-squares refinement, all non-H atoms were treated anisotropically. H atoms included, as fixed contributors, at positions found from a difference Fourier synthesis, all with a common isotropic temperature factor that refined to $U = 0.086\,(4)$ Å^2. The data were corrected for Lp and absorption with maximum and minimum transmission factors of 1.01 and 0.94 (Walker & Stuart, 1983). Scattering factors for non-H atoms were taken from Cromer & Mann (1968) with corrections for anomalous dispersion from Cromer &

0108-2701/92/101876-03$06.00