Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1194). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Asgarouladi, B., Full, R., Schaper, K.-J. & Siebert, W. (1974). *Chem. Ber.* **107**, 34–47.

Bartell, L. S. & Carroll, B. L. (1965). *J. Chem. Phys.* **42**, 3076–3078.

Clement, R. (1965). *C. R. Acad. Sci.* **261**, 4436–4438.

Cotton, F. A. & Wilkinson, G. (1980). In *Advanced Inorganic Chemistry*, 3rd ed. New York: John Wiley.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Main, P., Germain, G. & Woolfson, M. M. (1984). *MULTAN84. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Universities of York, England, and Louvain, Belgium.

Sakurai, T. (1967). Editor. *Universal Crystallographic Computation Program System.* The Crystallographic Society of Japan, Tokyo, Japan.

Schacht, W. & Kaufmann, D. (1987). *J. Organomet. Chem.* **331**, 139–152.

Siebert, W., Schaper, K.-J. & Asgarouladi, B. (1974). *Z. Naturforsch. Teil B*, **29**, 642–646.

Zettler, F., Hausen, H. D. & Hess, H. (1974). *J. Organomet. Chem.* **72**, 157–162.

Acta Cryst. (1996). C52, 993–995

cis-1,5-Dimethyl-2,4-dinitro-2,4-diazabicyclo[3.2.0]heptan-3-one and *cis*-1,5-Dimethyl-2,4-dinitro-2,4-diazabicyclo[3.1.0]hexan-3-one

Jeffrey R. Deschamps,[a] Clifford George,[a]* Richard D. Gilardi,[a] Janet L. Gagnon[b] and Walter W. Zajac Jr[b]

[a]*Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC 20375, USA, and* [b]*Department of Chemistry, Villanova University, Villanova, PA 19805, USA. E-mail: george@roentgen.nrl.navy.mil*

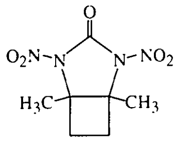
(*Received 24 May 1995; accepted 9 October 1995*)

Abstract

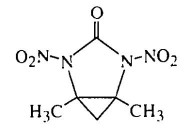
The title compounds, $C_7H_{10}N_4O_5$, (I), and $C_6H_8N_4O_5$, (II), each consist of a five-membered ring fused to a smaller ring. In compound (I), the C—C bridging bond distance [1.571 (4) Å] is longer than the expected distance of 1.54 Å for a C—C bond in a cyclobutane ring. In compound (II), however, the corresponding C—C bridging bond distance [1.507 (5) Å] is consistent with the expected bond length (1.51 Å) in a cyclopropane ring. The increase in the C—C bridge distance in compound (I) is most likely due to steric effects resulting from the additional methyl substituents.

Comment

The ideal bond distances for cyclobutane and cyclopropane rings are 1.54 and 1.51 Å, respectively (Wilson, 1992). A search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) revealed 14 structures with the same bicyclic ring system as that found in compound (I) and 31 structures with the same bicyclic ring system as that found in compound (II).



(I)



(II)

In all but two of the structures similar to compound (I), the zero-bridged bond was longer than the expected value of 1.54 Å [the mean bond length was 1.558 (4) Å and the range of observed values was 1.525–1.583 Å]. There is, however, no correlation of this bond length with the electronegativity of the substituents on the bridged C atoms. In compound (I), the bridge distance (*i.e.* C1—C5) is 1.571 (4) Å (Fig. 1). Here, and in the related compounds, the bond length increase is most likely due to steric effects. In the opposing cyclobutane C—C distance involving unbridged C atoms, where strain due to crowding is less likely, the electronegativity of the substituents is well correlated with the bond distance.

In compound (II), the C1—C5 bond distance is 1.507 (5) Å, which is consistent with the expected value (Fig. 2). In the 31 similar structures found in the Cambridge Structural Database, the mean C—C bridge distance was 1.513 (4) Å and the range 1.464–1.561 Å.

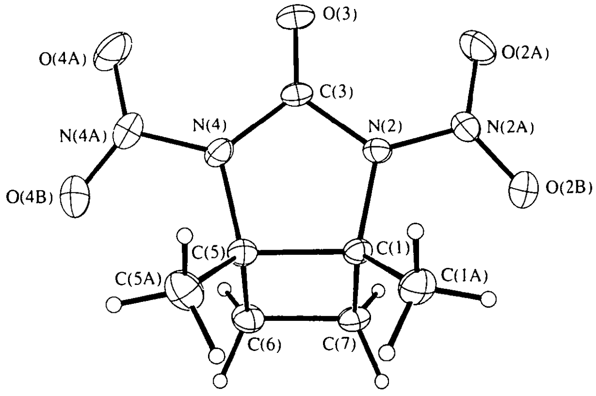


Fig. 1. View of compound (I) showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 20% probability levels and H atoms are drawn as small circles of arbitrary radii.

Acta Crystallographica Section C
ISSN 0108-2701 ©1996

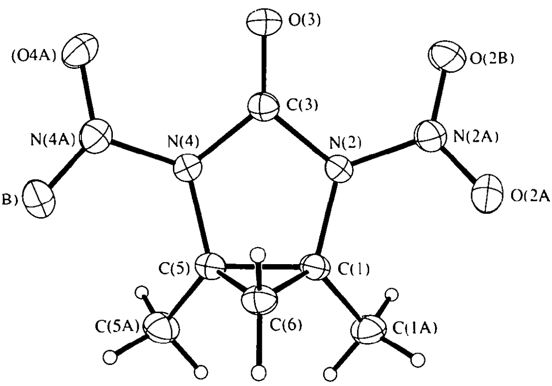


Fig. 2. View of compound (II) showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 20% probability levels and H atoms are drawn as small circles of arbitrary radii.

The angle between the least-squares planes of the two nearly planar rings [r.m.s. deviations of fitted atoms from the least-squares planes are 0.007 and 0.024 Å for compound (I) and 0.00 and 0.047 Å for compound (II)] is 113.9 (1)° in compound (I) and 108.2 (2)° in compound (II). These values are consistent with the values observed in the 14 structures similar to (I) and the 31 structures similar to (II), where the mean value for the angle between the the fused cyclobutane and cyclopentane rings was found to be 116 (3)° and that for the angle between the cyclopropane and cyclopentane rings was 111 (3)°.

Experimental

Compounds (I) and (II) were prepared according to the method of Gagnon & Zajac (1996).

Compound (I)

Crystal data

$C_7H_{10}N_4O_5$
$M_r = 230.19$
Orthorhombic
$P2_12_12_1$
$a = 5.934\ (2)$ Å
$b = 9.237\ (2)$ Å
$c = 17.512\ (5)$ Å
$V = 959.9\ (5)$ Å^3
$Z = 4$
$D_x = 1.593$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13.29–17.96°$
$\mu = 0.137$ mm^{-1}
$T = 293\ (2)$ K
Clear prism
0.62 × 0.25 × 0.15 mm
Colorless

Data collection

Siemens $R3m/V$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1050 measured reflections
1014 independent reflections
866 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0098$
$\theta_{\rm max} = 25.04°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 20$
3 standard reflections monitored every 97 reflections random variation of 1.5%

Refinement

Refinement on F^2
$R(F) = 0.0333$
$wR(F^2) = 0.0904$
$S = 1.071$
1014 reflections
145 parameters
H atoms riding; C—H 0.96 for CH_3 and 0.97 Å for CH_2

$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 0.0948P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.135$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.191$ e Å^{-3}
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) for (I)*

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

	x	y	z	$U_{\rm eq}$
C1	−0.3134 (4)	0.4052 (3)	0.16664 (14)	0.0341 (6)
C1*A*	−0.2248 (6)	0.4260 (3)	0.24757 (14)	0.0527 (8)
N2	−0.1702 (4)	0.3061 (2)	0.12258 (12)	0.0381 (5)
N2*A*	−0.1665 (5)	0.1586 (3)	0.14015 (15)	0.0485 (6)
O2*A*	−0.0449 (5)	0.0807 (3)	0.10335 (15)	0.0754 (8)
O2*B*	−0.2830 (4)	0.1224 (2)	0.19406 (13)	0.0640 (7)
C3	−0.1003 (4)	0.3559 (3)	0.05025 (15)	0.0351 (6)
O3	0.0071 (4)	0.2939 (2)	0.00368 (12)	0.0522 (6)
N4	−0.1801 (4)	0.4984 (2)	0.04900 (12)	0.0408 (6)
N4*A*	−0.1875 (5)	0.5771 (3)	−0.02011 (13)	0.0518 (7)
O4*A*	−0.0622 (5)	0.5412 (3)	−0.07003 (12)	0.0782 (8)
O4*B*	−0.3201 (5)	0.6775 (2)	−0.02069 (13)	0.0656 (7)
C5	−0.3203 (5)	0.5427 (3)	0.11386 (14)	0.0363 (6)
C5*A*	−0.2430 (7)	0.6844 (3)	0.1475 (2)	0.0570 (9)
C6	−0.5750 (5)	0.5180 (3)	0.1025 (2)	0.0476 (7)
C7	−0.5696 (5)	0.3853 (3)	0.1553 (2)	0.0432 (7)

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

C1—N2	1.468 (3)	C3—N4	1.399 (4)
C1—C1*A*	1.524 (3)	N4—N4*A*	1.413 (3)
C1—C7	1.544 (4)	N4—C5	1.466 (3)
C1—C5	1.571 (4)	N4*A*—O4*A*	1.194 (3)
N2—N2*A*	1.396 (3)	N4*A*—O4*B*	1.216 (3)
N2—C3	1.410 (3)	C5—C5*A*	1.507 (4)
N2*A*—O2*A*	1.206 (3)	C5—C6	1.541 (4)
N2*A*—O2*B*	1.217 (3)	C6—C7	1.534 (4)
C3—O3	1.183 (3)		
N2—C1—C1*A*	111.6 (2)	N4—C5—C6	114.5 (2)
N2—C1—C7	115.3 (2)	C5*A*—C5—C6	118.5 (3)
C1*A*—C1—C7	118.3 (2)	N4—C5—C1	102.5 (2)
N2—C1—C5	102.1 (2)	C5*A*—C5—C1	117.6 (2)
C1*A*—C1—C5	117.1 (2)	C6—C5—C1	89.0 (2)
C7—C1—C5	89.7 (2)	C7—C6—C5	91.2 (2)
N4—C5—C5*A*	111.9 (2)	C6—C7—C1	90.2 (2)

Compound (II)

Crystal data

$C_6H_8N_4O_5$
$M_r = 216.16$
Monoclinic
$P2_1/c$
$a = 7.3060\ (10)$ Å
$b = 10.830\ (2)$ Å
$c = 11.525\ (2)$ Å
$\beta = 91.30\ (2)°$
$V = 911.7\ (3)$ Å^3
$Z = 4$
$D_x = 1.575$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.0–17.0°$
$\mu = 0.138$ mm^{-1}
$T = 293\ (2)$ K
Clear rod
0.40 × 0.05 × 0.05 mm
Colorless

Data collection

Siemens $R3m/V$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1810 measured reflections
1621 independent reflections
971 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0096$
$\theta_{\rm max} = 25.08°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 12$
$l = -13 \rightarrow 13$
3 standard reflections monitored every 97 reflections
linear decay of 2.8%

Refinement

Refinement on F^2
$R(F) = 0.0547$
$wR(F^2) = 0.1526$
$S = 1.032$
1621 reflections
136 parameters
H atoms riding; C—H 0.96 for CH_3 and 0.97 Å for CH_2
$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 0.6288P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.265$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.247$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

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

	x	y	z	$U_{\rm eq}$
C1	0.7650 (4)	0.2613 (3)	0.9270 (3)	0.0447 (9)
C1*A*	0.8368 (5)	0.3875 (4)	0.8975 (4)	0.0623 (12)
N2	0.5676 (4)	0.2505 (3)	0.9352 (3)	0.0454 (8)
N2*A*	0.4702 (5)	0.3219 (3)	1.0147 (3)	0.0563 (9)
O2*A*	0.5631 (4)	0.3823 (3)	1.0819 (3)	0.0736 (9)
O2*B*	0.3043 (4)	0.3205 (3)	1.0058 (3)	0.0845 (11)
C3	0.4966 (5)	0.1355 (3)	0.8996 (3)	0.0448 (9)
O3	0.3492 (3)	0.0934 (3)	0.9163 (2)	0.0589 (8)
N4	0.6466 (4)	0.0810 (3)	0.8447 (3)	0.0424 (7)
N4*A*	0.6488 (5)	−0.0473 (3)	0.8245 (3)	0.0525 (8)
O4*A*	0.5023 (4)	−0.1002 (3)	0.8158 (3)	0.0711 (9)
O4*B*	0.7999 (4)	−0.0925 (3)	0.8167 (3)	0.0736 (9)
C5	0.8185 (5)	0.1468 (3)	0.8617 (3)	0.0435 (9)
C5*A*	0.9476 (5)	0.1506 (4)	0.7617 (4)	0.0644 (12)
C6	0.8759 (5)	0.1623 (3)	0.9871 (3)	0.0481 (9)

Table 4. *Selected geometric parameters (Å, °) for (II)*

C1—N2	1.452 (4)	C3—O3	1.189 (4)
C1—C6	1.504 (5)	C3—N4	1.407 (4)
C1—C1*A*	1.506 (5)	N4—N4*A*	1.409 (4)
C1—C5	1.507 (5)	N4—C5	1.454 (4)
N2—N2*A*	1.405 (4)	N4*A*—O4*B*	1.213 (4)
N2—C3	1.406 (5)	N4*A*—O4*A*	1.216 (4)
N2*A*—O2*A*	1.210 (4)	C5—C5*A*	1.506 (5)
N2*A*—O2*B*	1.214 (4)	C5—C6	1.506 (5)
N2—C1—C6	116.0 (3)	N4—C5—C6	113.9 (3)
N2—C1—C1*A*	116.1 (3)	C5*A*—C5—C6	124.5 (3)
C6—C1—C1*A*	124.3 (3)	N4—C5—C1	103.7 (3)
N2—C1—C5	103.6 (3)	C5*A*—C5—C1	122.3 (3)
C6—C1—C5	60.0 (2)	C6—C5—C1	59.9 (2)
C1*A*—C1—C5	122.6 (3)	C1—C6—C5	60.1 (2)
N4—C5—C5*A*	117.7 (3)		

For both compounds, data collection: *SHELXTL-Plus* (Sheldrick, 1991); cell refinement: *SHELXTL-Plus*; data reduction: *SHELXTL-Plus*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

This research was supported in part by the Office of Naval Research and the Naval Research Laboratory.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1098). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.
Gagnon, J. L. & Zajac, W. W. (1996). *Synth. Commun.* **26**. In the press.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Wilson, A. C. J. (1992). Editor. *International Tables for Crystallography*, Vol. C, *Mathematical, Physical and Chemical Tables*, p. 693. Dordrecht: Kluwer Academic Publishers.

Acta Cryst. (1996). C**52**, 995–998

7-Benzyl-3-thia-7-azabicyclo[3.3.1]nonane 3-Oxide

M. Bilayet Hossain,[a] Dick van der Helm,[a]* Subbiah Sangiah[b] and K. Darrell Berlin[c]

[a]*Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma 73019, USA,* [b]*Department of Physiological Sciences, Oklahoma State University, Stillwater, Oklahoma 74078, USA, and* [c]*Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, USA*

(*Received 8 August 1995; accepted 10 November 1995*)

Abstract

The molecular geometry of a major metabolite, $C_{14}H_{19}NOS$, of a potent anti-arrhythmic drug, 7-benzyl-3-thia-7-azabicyclo[3.3.1]nonane (BRB-I-28), has been determined by X-ray diffraction. The 3,7-dihetero bicyclic system of the sulfoxide molecule adopts a chair–chair conformation like that of the $HClO_4$ salt of the BRB-I-28 molecule. The S···N contact distance of 2.863 (2) Å in the present molecule is significantly shorter than that found in the crystal structure of its precursor [3.038 (4) Å]. The overall molecule possesses pseudo-mirror symmetry.