Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Low-temperature redetermination of benzofurazan 1-oxide

Seik Weng Ng

Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia
Correspondence e-mail: seikweng@um.edu.my

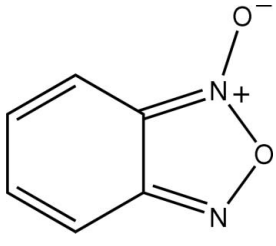
Received 3 May 2009; accepted 6 May 2009

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.035; wR factor = 0.110; data-to-parameter ratio = 11.8.

In the six-membered ring of the low-temperature crystal structure of benzofurazan 1-oxide, $C_6H_4N_2O_2$, the two C atoms adjacent to the N atoms are linked by a delocalized aromatic bond [1.402 (2) Å]; each is connected to its neighbour by a longer, more localized, bond [1.420 (2), 1.430 (2) Å]. However, the next two bonds in the ring approximate double bonds [1.357 (2), 1.366 (2) Å]. As such, the six-membered ring is better described as a cyclohexadiene system, in contrast to the description in the room-temperature structure reported by Britton & Olson (1979) [*Acta Cryst.* B**35**, 3076–3078].

Related literature

For the room-temperature structure in the $P\overline{1}$ setting [6.772 (3), 7.515 (4), 7.759 (4) Å, 99.08 (3), 114.94 (3), 112.67 (3) °], see: Britton & Olson (1979). For the geometry-optimized structure, see: Friedrichsen, 1995; Ponder *et al.* (1994); Rauhut (1996). For details of the synthesis, see: Terrian *et al.* (1992); Wolthius (1979). For work mentioning the original structure, see: Ammon & Bhattacharjee (1982); Bird (1993); Cerecetto & González (2007); Ojala *et al.* (1999); Ramm *et al.* (1991).



Experimental

Crystal data

$C_6H_4N_2O_2$ M_r = 136.11
Triclinic, $P\overline{1}$
a = 6.6751 (2) Å
b = 7.3256 (2) Å
c = 7.6842 (2) Å
α = 100.710 (2)°
β = 114.265 (2)°
γ = 111.747 (2)°
V = 291.71 (1) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 100 K
0.30 × 0.25 × 0.10 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: none
1952 measured reflections
1276 independent reflections
1110 reflections with $I > 2\sigma(I)$
R_{int} = 0.012

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.110
S = 1.03
1276 reflections
108 parameters
4 restraints
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Selected bond lengths (Å).

O1—N1	1.230 (1)	C1—C2	1.430 (2)
O2—N2	1.381 (1)	C2—C3	1.357 (2)
O2—N1	1.443 (2)	C3—C4	1.436 (2)
N1—C6	1.336 (2)	C4—C5	1.366 (2)
N2—C1	1.327 (2)	C5—C6	1.420 (2)
C1—C6	1.409 (2)		

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2009).

I thank the University of Malaya for supporting this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2443).

References

Ammon, H. L. & Bhattacharjee, S. K. (1982). *Acta Cryst.* B**38**, 2498–2502.
Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Bird, C. W. (1993). *Tetrahedron*, **49**, 8441–8448.
Britton, D. & Olson, J. M. (1979). *Acta Cryst.* B**35**, 3076–3078.
Bruker (2008). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cerecetto, H. & González, M. (2007). *Topics Heterocycl. Chem.* **10**, 265–308.
Friedrichsen, W. (1995). *J. Mol. Struct. (Theochem)*, **342**, 23–31.
Ojala, C. R., Ojala, W. H., Britton, D. & Gougoutas, J. Z. (1999). *Acta Cryst.* B**55**, 530–542.
Ponder, M., Fowler, J. E. & Schaeffer, H. F. (1994). *J. Org. Chem.* **59**, 6431–6436.
Ramm, M., Schultz, B., Rudert, R., Göhrmann, B. & Niclas, H.-J. (1991). *Acta Cryst.* C**47**, 1700–1702.
Rauhut, G. (1996). *J. Comput. Chem.* **17**, 1848–1856.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Terrian, D. L., Houghtaling, M. A. & Ames, J. R. (1992). *J Chem. Educ.* **69**, 589–590.
Westrip, S. P. (2009). *publCIF*. In preparation.
Wolthius, E. (1979). *J. Chem. Educ.* **56**, 343–344.

supplementary materials

Acta Cryst. (2009). E**65**, o1275 [**doi:10.1107/S1600536809017036**]

Low-temperature redetermination of benzofurazan 1-oxide

S. W. Ng

Comment

Researchers have used the published structure of benzofurazan 1-oxide (Britton & Olson, 1979) in, for example, studies on packing (Ammon & Bhattacharjee, 1982; Ojala *et al.*, 1999; Ramm *et al.*, 1991), influence of *N*-oxide formation on heteroaromaticity (Bird, 1993), and reactivity and biology (Cerecetto & González, 2007). Bond dimensions from geometry-optimization calculations (Friedrichsen, 1995; Ponder *et al.*,1994; Rauhut, 1996) have also been compared with values taken from the solid-state structure.

The present low-temperature structure (Fig. 1 & Table 1) reveals features quite distinct from those disclosed in the original, room-temperature, analysis (Britton & Olson, 1979). In the six-membered ring, the two carbon atoms adjacent to the nitrogen atoms are linked by a delocalized aromatic bond [1.402 (2) Å]; each is connected to its neighbor by a longer, more localized, bond [1.420 (2), 1.430 (2) Å]. However, the next two bonds in the ring approximate double-bonds [1.357 (2), 1.366 (2) Å]. As such, the six-membered ring is better described as a cyclohexadiene system.

Experimental

The compound was synthesized according to a reported procedure (Terrian *et al.*, 1992; Wolthius, 1979). Crystals were grown with THF as solvent.

Refinement

The carbon-bound H-atoms were restrained to C—H 0.95±0.01 Å; their temperature factors were freely refined.

Figures

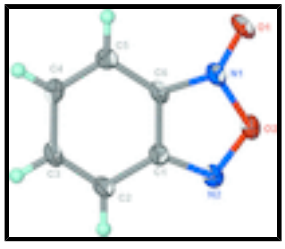


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 70% probability level, and hydrogen atoms are drawn as spheres of arbitrary radius.

(I)

Crystal data

$C_6H_4N_2O_2$	$Z = 2$
$M_r = 136.11$	$F_{000} = 140$

Triclinic, $P\bar{1}$	D_x = 1.550 Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 6.6751 (2) Å	Cell parameters from 1320 reflections
b = 7.3256 (2) Å	θ = 3.2–28.3º
c = 7.6842 (2) Å	μ = 0.12 mm^{-1}
α = 100.710 (2)º	T = 100 K
β = 114.265 (2)º	Irregular block, yellow-orange
γ = 111.747 (2)º	0.30 × 0.25 × 0.10 mm
V = 291.71 (1) Å^3	

Data collection

Bruker SMART APEX diffractometer	1110 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.012
Monochromator: graphite	θ_{max} = 27.5º
T = 100 K	θ_{min} = 3.2º
ω scans	h = −7→8
Absorption correction: None	k = −9→9
1952 measured reflections	l = −9→9
1276 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.035	All H-atom parameters refined
$wR(F^2)$ = 0.110	$w = 1/[\sigma^2(F_o^2) + (0.0685P)^2 + 0.0855P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.03	$(\Delta/\sigma)_{max}$ = 0.001
1276 reflections	$\Delta\rho_{max}$ = 0.33 e Å^{-3}
108 parameters	$\Delta\rho_{min}$ = −0.21 e Å^{-3}
4 restraints	Extinction correction: SHELXL, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.03 (1)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1	0.1183 (2)	0.2141 (2)	−0.0082 (1)	0.0274 (3)
O2	0.5178 (2)	0.2611 (2)	0.1146 (1)	0.0271 (3)
N1	0.3061 (2)	0.2329 (2)	0.1385 (2)	0.0211 (3)
N2	0.7112 (2)	0.2839 (2)	0.2955 (2)	0.0257 (3)
C1	0.6232 (2)	0.2701 (2)	0.4219 (2)	0.0188 (3)

C2	0.7496 (3)	0.2863 (2)	0.6308 (2)	0.0202 (3)
C3	0.6182 (3)	0.2669 (2)	0.7284 (2)	0.0207 (3)
C4	0.3643 (3)	0.2321 (2)	0.6312 (2)	0.0209 (3)
C5	0.2382 (3)	0.2174 (2)	0.4325 (2)	0.0199 (3)
C6	0.3750 (2)	0.2377 (2)	0.3296 (2)	0.0181 (3)
H2	0.919 (2)	0.310 (3)	0.693 (3)	0.030 (4)*
H3	0.701 (3)	0.278 (3)	0.867 (2)	0.037 (5)*
H4	0.281 (3)	0.221 (3)	0.706 (2)	0.027 (4)*
H5	0.072 (2)	0.197 (3)	0.369 (2)	0.031 (4)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0242 (5)	0.0333 (6)	0.0172 (5)	0.0139 (4)	0.0039 (4)	0.0130 (4)
O2	0.0270 (6)	0.0398 (6)	0.0190 (5)	0.0172 (5)	0.0137 (4)	0.0157 (4)
N1	0.0213 (6)	0.0237 (6)	0.0158 (5)	0.0105 (5)	0.0077 (5)	0.0098 (4)
N2	0.0237 (6)	0.0361 (7)	0.0202 (6)	0.0155 (5)	0.0120 (5)	0.0144 (5)
C1	0.0198 (6)	0.0199 (6)	0.0171 (6)	0.0096 (5)	0.0095 (5)	0.0090 (5)
C2	0.0187 (6)	0.0231 (6)	0.0175 (6)	0.0109 (5)	0.0072 (5)	0.0103 (5)
C3	0.0240 (7)	0.0215 (6)	0.0147 (6)	0.0109 (5)	0.0083 (5)	0.0093 (5)
C4	0.0246 (7)	0.0228 (6)	0.0192 (6)	0.0120 (5)	0.0137 (6)	0.0102 (5)
C5	0.0188 (6)	0.0213 (6)	0.0200 (6)	0.0104 (5)	0.0096 (5)	0.0096 (5)
C6	0.0200 (6)	0.0175 (6)	0.0136 (5)	0.0086 (5)	0.0066 (5)	0.0073 (4)

Geometric parameters (Å, °)

O1—N1	1.230 (1)	C3—C4	1.436 (2)
O2—N2	1.381 (1)	C4—C5	1.366 (2)
O2—N1	1.443 (2)	C5—C6	1.420 (2)
N1—C6	1.336 (2)	C2—H2	0.956 (9)
N2—C1	1.327 (2)	C3—H3	0.948 (9)
C1—C6	1.409 (2)	C4—H4	0.946 (9)
C1—C2	1.430 (2)	C5—H5	0.947 (9)
C2—C3	1.357 (2)		
N2—O2—N1	109.4 (1)	N1—C6—C1	106.9 (1)
O1—N1—C6	136.0 (1)	N1—C6—C5	129.7 (1)
O1—N1—O2	117.7 (1)	C1—C6—C5	123.5 (1)
C6—N1—O2	106.3 (1)	C3—C2—H2	124 (1)
C1—N2—O2	105.0 (1)	C1—C2—H2	119 (1)
N2—C1—C6	112.5 (1)	C2—C3—H3	117 (1)
N2—C1—C2	128.0 (1)	C4—C3—H3	120 (1)
C6—C1—C2	119.5 (1)	C5—C4—H4	118 (1)
C3—C2—C1	116.8 (1)	C3—C4—H4	120 (1)
C2—C3—C4	122.9 (1)	C4—C5—H5	122 (1)
C5—C4—C3	121.9 (1)	C6—C5—H5	122 (1)
C4—C5—C6	115.4 (1)		
N2—O2—N1—O1	178.7 (1)	O1—N1—C6—C1	−178.3 (1)
N2—O2—N1—C6	−0.4 (1)	O2—N1—C6—C1	0.6 (1)

N1—O2—N2—C1	0.1 (1)	O1—N1—C6—C5	1.2 (2)
O2—N2—C1—C6	0.3 (2)	O2—N1—C6—C5	−179.9 (1)
O2—N2—C1—C2	−179.1 (1)	N2—C1—C6—N1	−0.5 (2)
N2—C1—C2—C3	179.9 (1)	C2—C1—C6—N1	178.9 (1)
C6—C1—C2—C3	0.6 (2)	N2—C1—C6—C5	179.9 (1)
C1—C2—C3—C4	−0.1 (2)	C2—C1—C6—C5	−0.7 (2)
C2—C3—C4—C5	−0.4 (2)	C4—C5—C6—N1	−179.2 (1)
C3—C4—C5—C6	0.3 (2)	C4—C5—C6—C1	0.2 (2)

Fig. 1