Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-(2,4-Dibromophenylamino)-7-nitrobenzisoselenazol-3-one

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.033
wR factor = 0.085
Data-to-parameter ratio = 14.4

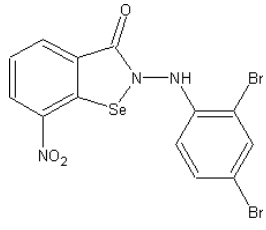
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 6 June 2002
Accepted 2 July 2002
Online 12 July 2002

The crystal structure determination of the title compound, $C_{13}H_7Br_2N_3O_3Se$, was undertaken in the course of a study on 1,2-benzoselenazin-4-one heterocycle homologues of ebselen, a well known anti-oxidizing agent. It allowed unambiguous identification of the molecular formula of the compound. The Br atom in the 4 position is split into two sites with occupation factors of 55 and 45%. The dihedral angle between the phenyl and benzisoselenazole mean planes is 85.0 (5)°. Analysis of the crystal packing shows infinite chains of molecules along the *b* axis, linked together by an N—H···O intermolecular hydrogen bond.

Comment

Although it has attractive anti-inflammatory activity and low toxicity, ebselen (Natterman/RP, 1981; Dupont *et al.*, 1990) exhibits some physicochemical failings. Its low solubility in organic solvents and its high melting point (453–455 K) induce a feeble metabolism. Moreover, a photochemical reaction is observed with the time and enjoins particular form of conditioning; the drug capsules must have an opaque envelope to protect the drug from light. In the course of synthesizing new molecules of benzo[*e*]-1,2-selenazin-4-one family which could be potential anti-oxidizing agents, the title compound, (I), was obtained and the unexpected structure determined by X-ray diffraction.



(I)

In the final cycles of refinement, the position of atom Br2 was split into two sites, Br2*A* and Br2*B*, with occupation factors of 0.45 and 0.55, respectively. The introduction of this disordered distribution greatly improved the residual densities in the final difference map and also the conventional *R* and *wR*2 values. The distances and angles are similar to those found in 7-nitro-2-phenyl-1,2-benzisoselenazol-3(2*H*)-one, (II) (Dupont *et al.*, 1988). In (II) the dihedral angle between the phenyl and heterocycle mean planes is 13.2 (1)°, whereas in (I) the corresponding planes are nearly orthogonal [85.0 (5)°]. The cohesion of the crystal is the result of an N—H···O hydrogen bond, which links molecules indefinitely along the *b* axis (Fig. 2), and of van der Waals interactions. There is also a short intramolecular N3···Br1 contact

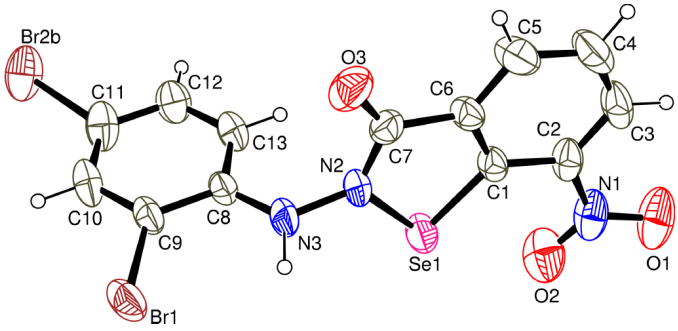


Figure 1
The molecular structure of (I), with the atom-labelling scheme. Displacement ellipsoids are shown at 50% probability levels. Atom Br2*A* (occupation factor = 45%) has been omitted.

[3.074 (3) Å], but, as the N—H···Br angle is rather narrow [103 (3)°], it could hardly be considered as a hydrogen bond. The packing shows five other short intermolecular contacts: Br1···Br2A^{i} 3.629 (6), Br1···Br2B^{i} 3.524 (5), Br1···O2^{ii} 3.376 (4), Br2A···O1^{iii} 3.261 (7) and Br2B···O1^{iii} 3.368 (6) Å [symmetry codes: (i) $1-x$, $-1/2+y$, $1/2-z$; (ii) $1/2-x$, $1/2+y$, z; (iii) $-x$, $1/2+y$, $3/2-z$].

Experimental

The title compound was prepared by treatment of 2-methylseleno-3-nitro-3′-*N*-phenylbenzoylhydrazide with 3 equivalents of bromine in a solution of dichloroethane (Messali, 2001). An orange single crystal was obtained by slow evaporation of a toluene solution.

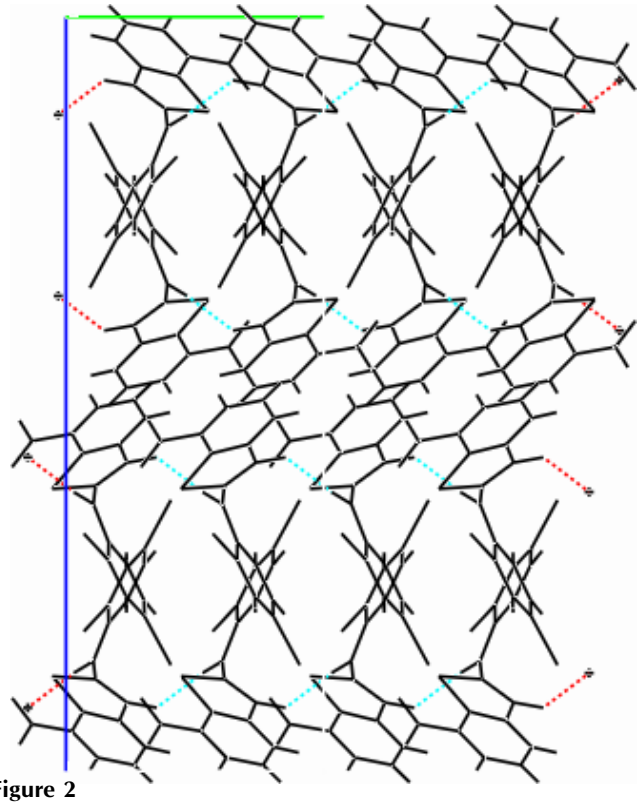


Figure 2
Projection of the structure along *a*, with the scheme of hydrogen bonds. The packing range is expanded horizontally along *b*, to show two unit cells.

Crystal data

$C_{13}H_7Br_2N_3O_3Se$
M_r = 492.00
Orthorhombic, *Pbca*
a = 13.8685 (10) Å
b = 8.6075 (10) Å
c = 25.233 (2) Å
V = 3012.1 (5) Å^3
Z = 8
D_x = 2.170 Mg m^{-3}
Cu *Kα* radiation
Cell parameters from 25 reflections
θ = 30–42°
μ = 9.75 mm^{-1}
T = 293 (2) K
Prism, orange
0.30 × 0.25 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
θ/2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.12, T_{max} = 0.39
3587 measured reflections
3075 independent reflections
2634 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 74.2°
h = −17 → 10
k = 0 → 10
l = 0 → 31
3 standard reflections
every 200 reflections
intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.085
S = 1.10
3075 reflections
213 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0307P)^2 + 4.0625P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br1—C9	1.890 (4)	N1—C2	1.446 (5)
Se1—C1	1.855 (3)	N2—C7	1.355 (5)
Se1—N2	1.899 (3)	N2—N3	1.386 (4)
O1—N1	1.228 (4)	N3—C8	1.385 (5)
O2—N1	1.230 (5)	C11—Br2*A*	1.847 (6)
O3—C7	1.220 (4)	C11—Br2*B*	1.939 (6)
C1—Se1—N2	83.82 (14)	C7—N2—Se1	117.5 (2)
O1—N1—O2	123.9 (4)	N3—N2—Se1	121.6 (3)
C7—N2—N3	120.6 (3)	C8—N3—N2	119.3 (3)
C1—Se1—N2—C7	1.2 (3)	Se1—N2—N3—C8	−93.8 (4)
C1—Se1—N2—N3	−173.1 (3)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H30···O3^{i}	0.93 (4)	1.98 (4)	2.826 (4)	151 (4)

Symmetry code: (i) $\frac{1}{2}-x, y-\frac{1}{2}, z$.

Least-squares restraints were applied to refine the disordered positions of Br2*A* and Br2*B*. All H atoms, with the exception of the nitrogen-bound atom (H30), were included in the refinement in the riding-model approximation, with isotropic displacement parameters fixed at $1.2U_{eq}$ of the parent atom. H30 was refined isotropically, its displacement parameters being fixed at $1.2U_{eq}$ of the attached N atom.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*,

1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *MERCURY* 1.1 (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL*97.

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