Table 2. *Geometric parameters* (Å, °)

O1—C7	1.438 (5)	N2—C13	1.338 (4)
O1—C8	1.354 (4)	N2—C14	1.465 (5)
O2—C8	1.222 (4)	C9—C10	1.534 (6)
O3—C13	1.241 (4)	C10—C11	1.501 (6)
O4—C16	1.202 (5)	C11—C12	1.548 (5)
O5—C16	1.318 (5)	C12—C13	1.526 (5)
N1—C8	1.332 (4)	C14—C15	1.537 (6)
N1—C9	1.484 (5)	C14—C16	1.534 (5)
N1—C12	1.472 (4)	C14—C17	1.551 (6)
C7—O1—C8	117.0 (3)	O3—C13—C12	119.7 (3)
C9—N1—C12	113.5 (3)	O3—C13—N2	121.8 (3)
C8—N1—C12	124.9 (3)	N2—C14—C17	113.3 (3)
C8—N1—C9	121.3 (3)	N2—C14—C16	105.9 (3)
C13—N2—C14	123.0 (3)	N2—C14—C15	111.3 (3)
O1—C7—C6	109.9 (3)	C16—C14—C17	108.6 (3)
O2—C8—N1	125.7 (3)	C15—C14—C17	109.7 (3)
O1—C8—N1	110.9 (3)	C15—C14—C16	107.8 (3)
O1—C8—O2	123.4 (3)	O5—C16—C14	112.5 (3)
N1—C9—C10	102.8 (3)	O4—C16—C14	123.5 (4)
N1—C12—C13	109.9 (3)	O4—C16—O5	124.0 (3)
N2—C13—C12	118.6 (3)	C14—C17—C18	114.7 (3)

Program used to solve structure: *SHELXS*86 (Sheldrick, 1986). The structure was refined by blocked full-matrix least squares with anisotropic thermal parameters for all non-H atoms. H atoms were either located on a ΔF map or calculated. The H atoms attached to C1, C2, C3, C4, C5 and C15 were not refined; all other H atoms were refined isotropically. Program used to refine structure: *SHELX*76 (Sheldrick, 1976).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71302 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1011]

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Structure of Bis(2-amino-5-benzoylphenyl) Diselenide

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Abstract

The title compound, 3,3′-diselenobis(4-aminobenzophenone), is one of a series of antioxidant drugs, which has glutathione peroxidase activity. This diselenide can be generated *in vivo* by administration of the corresponding benzoselenazolinone as a pro-drug. It is important to correlate the structure with the pharmacological parameters. In an initial approach the structure of this compound was determined by X-ray analysis; this, in turn, dictates the structure of the corresponding benzoyl benzoselenazolinone.

Comment

Recently, simple seleno-organic compounds were shown to mimic *in vitro* the enzymic activity of glutathione peroxidase, an important system of cell defence against oxidative stress (Parnham & Graf, 1987; Günzler, Steffens & Grossman, 1982). Such molecules are able to convert hydroperoxides into alcohols with their selenium-containing active centre. The catalytic process involves a selenolate anion, as the active form, reducing hydroperoxides (Günzler, Steffens & Grossman, 1982). An isoselenazolin-3-one ring or a diselenide entity are then generated as reaction products (Reich & Jasperse, 1987; Parnham & Kindt, 1984; Chan, Cotelle, Cotelle, Bernier & Hénichart, 1991). Finally the active form is restored by a glutathione nucleophilic attack.

The development of synthetic compounds with glutathione peroxidase activity found its basis in the aforementioned catalytic redox cycle. The more promising molecules were 2-phenyl-1,2-benzoselenazol-3(2*H*)-one or ebselen (1), a heterocyclic compound related to the isoselenazole intermediate (Wendel, Fausel, Safayhi, Tiegs & Otter, 1984; Renson & Dereu, 1990), and various aromatic diselenides (Wilson, Zucker, Huang & Spectror, 1989). Such molecules are potentially useful as antioxidant and anti-inflammatory drugs.

We report here the refined crystal structure of a new molecule with glutathione peroxidase activity (Galet, 1991) consisting of a 5-substituted phenyl diselenide stabilized by an *ortho*-amino group, namely bis(2-amino-5-benzoylphenyl) diselenide (2). This product is synthesized from the alkaline opening of 6-benzoylbenzoselenazolinone (3), which is obtained by the reaction of benzoic acid with benzoselenazolinone in the presence of polyphosphoric acid. Knowledge of the crystal structure was essential in order to ascertain that the synthetic route unequivocally leads to 6-substituted compounds, and also to measure interatomic distances and dihedral angles related to the noticeable stability of the molecule. This is crucial in terms of structure–activity and structure–toxicity relationships.

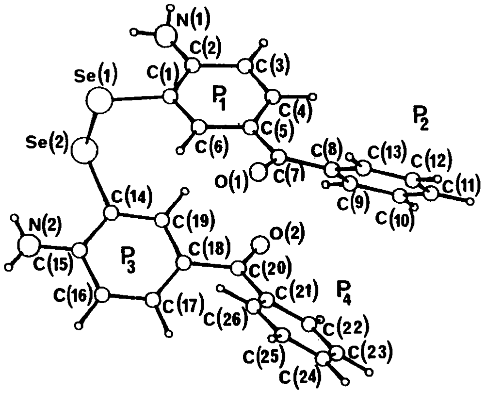

Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) perspective view of the title compound.

The general conformation of the molecule is that of a skewed structure with a dihedral angle of 28° between the mean planes (*P*1,*P*2) and (*P*3,*P*4). The two phenyl rings bound to the Se atoms are roughly parallel and may establish an electron charge transfer, considering their adequate interatomic distance. The phenyl rings of the benzophenone moieties are twisted by 54° around their link. The two C═O bonds point in opposite directions so that the general geometry corresponds to minimum steric and electronic interactions. Furthermore, convincing evidence is established here that the synthetic method used to prepare the aroyl benzoselenazolinones (precursors of the presented aroyl diselenides) specifically leads to 6-substituted compounds. This information is important, from a chemical point of view, for the design of new compounds with similar biological activity.

Experimental

Crystal data

$C_{26}H_{20}N_2O_2Se_2$
$M_r = 550.2$
Monoclinic
$P2_1/a$
$a = 17.030\ (5)$ Å
$b = 15.030\ (4)$ Å
$c = 8.874\ (4)$ Å
$\beta = 92.87°$
$V = 2268.56$ Å^3
$Z = 4$

$D_x = 1.61$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 10$–$20°$
$\mu = 3.18$ mm^{-1}
$T = 293$ K
0.40 × 0.40 × 0.30 mm
Orange

Data collection

Philips PW1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6846 measured reflections
6178 independent reflections
2626 observed reflections [$I > 3\sigma(I)$]

$\theta_{\max} = 30°$
$h = -23 \rightarrow 22$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 12$
5 standard reflections
frequency: 120 min
intensity variation: 5%

Refinement

Refinement on F
Final $R = 0.040$
$wR = 0.040$
$S = 1.93$
2626 reflections
348 parameters
Unit weights applied
$(\Delta/\sigma)_{\max} = 0.12$

$\Delta\rho_{\max} = 0.60$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) and Stewart, Davidson & Simpson (1965)

Computer programs: *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); *SHELX*76 (Sheldrick, 1976).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

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

	x	y	z	$U_{\rm eq}$
Se(1)	0.0128 (1)	0.0211 (1)	0.2527 (1)	0.052 (1)
Se(2)	0.0294 (1)	−0.1278 (1)	0.1831 (1)	0.044 (1)
N(1)	0.1501 (3)	0.0557 (4)	0.0407 (6)	0.059 (7)
O(1)	0.1971 (3)	0.0902 (4)	0.7439 (5)	0.072 (8)
C(1)	0.1211 (3)	0.0472 (4)	0.2994 (6)	0.038 (7)
C(2)	0.1728 (4)	0.0589 (4)	0.1867 (6)	0.043 (7)
C(3)	0.2532 (3)	0.0730 (5)	0.2289 (7)	0.045 (8)
C(4)	0.2776 (3)	0.0760 (4)	0.3784 (7)	0.047 (8)
C(5)	0.2252 (3)	0.0656 (4)	0.4922 (6)	0.041 (7)
C(6)	0.1467 (3)	0.0502 (4)	0.4495 (6)	0.043 (7)
C(7)	0.2470 (4)	0.0764 (5)	0.6548 (7)	0.048 (8)
C(8)	0.3306 (4)	0.0704 (5)	0.7100 (7)	0.048 (9)
C(9)	0.3823 (4)	0.0101 (6)	0.6570 (9)	0.065 (11)
C(10)	0.4591 (5)	0.0067 (7)	0.7174 (12)	0.095 (15)
C(11)	0.4831 (5)	0.0659 (8)	0.8285 (13)	0.088 (18)
C(12)	0.4317 (6)	0.1259 (8)	0.8819 (11)	0.072 (16)

C(13)	0.3554 (5)	0.1292 (6)	0.8237 (8)	0.060 (11)
C(14)	0.0559 (3)	−0.1769 (4)	0.3761 (7)	0.038 (7)
C(15)	−0.0006 (3)	−0.2195 (5)	0.4606 (7)	0.046 (8)
C(16)	0.0233 (4)	−0.2526 (5)	0.6043 (8)	0.059 (9)
C(17)	0.0989 (4)	−0.2407 (5)	0.6604 (7)	0.058 (8)
C(18)	0.1552 (3)	−0.1997 (4)	0.5758 (7)	0.044 (7)
C(19)	0.1327 (3)	−0.1694 (4)	0.4332 (7)	0.041 (7)
C(20)	0.2388 (3)	−0.1914 (4)	0.6285 (8)	0.049 (8)
C(21)	0.2620 (3)	−0.1860 (4)	0.7918 (7)	0.045 (8)
C(22)	0.3347 (4)	−0.2216 (5)	0.8393 (8)	0.059 (9)
C(23)	0.3583 (4)	−0.2164 (5)	0.9902 (10)	0.070 (11)
C(24)	0.3122 (5)	−0.1765 (6)	1.0907 (9)	0.068 (12)
C(25)	0.2415 (5)	−0.1404 (6)	1.0448 (8)	0.071 (11)
C(26)	0.2161 (4)	−0.1464 (5)	0.8952 (8)	0.058 (9)
O(2)	0.2891 (2)	−0.1870 (3)	0.5362 (5)	0.066 (6)
N(2)	−0.0748 (3)	−0.2307 (4)	0.4047 (7)	0.059 (8)

Table 2. *Geometric parameters* (Å, °)

Se(1)—Se(2)	2.341 (2)	C(11)—C(12)	1.358 (15)
Se(1)—C(1)	1.910 (5)	C(12)—C(13)	1.374 (13)
Se(2)—C(14)	1.898 (6)	C(14)—C(15)	1.404 (8)
O(1)—C(7)	1.207 (8)	C(14)—C(19)	1.384 (7)
C(1)—C(2)	1.376 (8)	C(15)—C(16)	1.410 (10)
C(1)—C(6)	1.382 (8)	C(16)—C(17)	1.369 (10)
C(2)—C(3)	1.418 (9)	C(17)—C(18)	1.390 (9)
C(3)—C(4)	1.371 (9)	C(18)—C(19)	1.381 (9)
C(4)—C(5)	1.389 (8)	C(18)—C(20)	1.482 (7)
C(5)—C(6)	1.392 (7)	C(20)—C(21)	1.485 (9)
C(5)—C(7)	1.480 (8)	C(25)—C(26)	1.378 (10)
C(7)—C(8)	1.485 (10)	C(21)—C(22)	1.395 (9)
C(8)—C(9)	1.363 (11)	C(21)—C(26)	1.370 (9)
C(8)—C(13)	1.390 (11)	C(22)—C(23)	1.381 (11)
C(9)—C(10)	1.390 (11)	C(23)—C(24)	1.356 (12)
C(10)—C(11)	1.375 (16)	C(24)—C(25)	1.364 (12)
Se(2)—Se(1)—C(1)	97.2 (2)	C(8)—C(13)—C(12)	119.8 (8)
Se(1)—Se(2)—C(14)	99.2 (2)	Se(2)—C(14)—C(15)	121.4 (4)
Se(1)—C(1)—C(2)	121.0 (4)	Se(2)—C(14)—C(19)	118.5 (4)
Se(1)—C(1)—C(6)	118.1 (4)	C(15)—C(14)—C(19)	120.2 (5)
C(2)—C(1)—C(6)	120.9 (5)	C(14)—C(15)—C(16)	118.0 (6)
C(1)—C(2)—C(3)	118.2 (5)	C(15)—C(16)—C(17)	120.4 (6)
C(2)—C(3)—C(4)	120.1 (6)	C(16)—C(17)—C(18)	121.5 (6)
C(3)—C(4)—C(5)	121.7 (5)	C(17)—C(18)—C(19)	118.3 (6)
C(4)—C(5)—C(6)	117.6 (5)	C(17)—C(18)—C(20)	123.0 (5)
C(4)—C(5)—C(7)	123.9 (5)	C(19)—C(18)—C(20)	118.6 (5)
C(6)—C(5)—C(7)	118.3 (5)	C(14)—C(19)—C(18)	121.5 (5)
C(1)—C(6)—C(5)	121.4 (5)	C(18)—C(20)—C(21)	121.1 (5)
O(1)—C(7)—C(5)	120.5 (6)	C(18)—C(20)—O(2)	119.4 (5)
O(1)—C(7)—C(8)	119.2 (6)	C(21)—C(20)—O(2)	119.6 (5)
C(5)—C(7)—C(8)	120.3 (6)	C(20)—C(21)—C(22)	117.5 (5)
C(7)—C(8)—C(9)	123.4 (6)	C(20)—C(21)—C(26)	123.1 (6)
C(7)—C(8)—C(13)	117.0 (6)	C(22)—C(21)—C(26)	119.4 (6)
C(9)—C(8)—C(13)	119.6 (7)	C(21)—C(22)—C(23)	118.8 (6)
C(8)—C(9)—C(10)	120.1 (8)	C(22)—C(23)—C(24)	120.8 (7)
C(9)—C(10)—C(11)	119.6 (9)	C(23)—C(24)—C(25)	120.7 (8)
C(10)—C(11)—C(12)	120.4 (10)	C(24)—C(25)—C(26)	119.4 (8)
C(11)—C(12)—C(13)	120.4 (10)	C(21)—C(26)—C(25)	120.8 (7)

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and dihedral angles between planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71235 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1036]

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Structure of the Naphthylurethane of *trans*-β-Ionol, a Severely Nonplanar 1,3-Diene

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Abstract

4-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-3-buten-2-yl 1-naphthalenecarbamate, the 1-naphthylurethane of *trans*-β-ionol, possesses a 1,3-diene π system which is grossly nonplanar as a consequence of sterically enforced torsion about the central single bond, the torsion angle between the formal double bonds being 54°. This result is in excellent agreement with conclusions concerning the 'nonvertical' behaviour of the parent *trans*-β-ionol with respect to triplet-excitation transfer.

Comment

It has been accepted generally that nonclassical or nonvertical triplet-excitation transfer to conjugated and flexible π systems is a consequence of double-bond torsion, either prior to or during the electronic energy transfer event (Saltiel, Marchand, Kirkor-