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Structure of 5,7-Dinitro-2,1,3-benzoxadiazol-4-yl Phenyl Diketone

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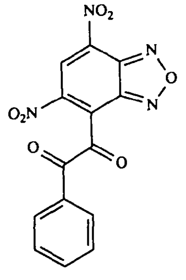
Abstract

In comparison to previous results, the bond lengths C(1)—C(2) and C(1)—C(6) (IUPAC numbering: C4—C3a, C4—C5) in the title compound are significantly shortened. The endocyclic angle C(3)—C(4)—C(5) (IUPAC numbering: C7a—C7—C6) is, in contrast to those in nitro-substituted benzene rings, smaller than 120°. A polymethinic structure of the dinitrobenzofurazan fragment is assumed. Stacking between the phenyl and furazan rings indicates weak π-electron interactions.

Comment

4,6-Dinitrobenzofurazan derivatives are of special significance because of their extraordinary electrophilic character. During the course of our studies of this type of compound, we have been interested in relationships between molecular structure and chemical reactivity; for example, 4-anilino-5,7-dinitrobenzofurazan was found to have a partial polymethinic structure and unusual chemical behaviour (Niclas, Göhrmann, Ramm & Schulz, 1990). In the present paper we report the crystal structure of 5,7-dinitrobenzofurazan-4-yl phenyl diketone (1) (5,7-dinitro-2,1,3-benzoxadiazol-4-yl phenyl diketone) which was prepared by nitric acid oxidation of 7-[aroyl(dimethylsulfonio)methyl]-4,6-dinitrobenzofurazanide (Niclas & Kind, 1993).



(1)

A drawing of the molecule with the atomic numbering scheme is shown in Fig. 1. The six-membered ring of the benzofurazan fragment contains two bonds which are significantly shorter [C(1)—C(6) 1.352 (2), C(4)—C(5) 1.340 (2) Å] than the others [1.423 (3)–1.429 (2) Å]. However, these bond lengths show small deviations in comparison to previous results (Mathew & Palenik, 1971; Niclas, Göhrmann, Ramm & Schulz, 1990). The C(1)—C(2) and C(1)—C(6) bonds are shortened significantly. The bond lengths correspond to the canonical form of the molecule with double bonds C(1)=C(6) and C(4)=C(5) and single bonds between the other C atoms. The C—NO_2 bond lengths [1.459 (3), 1.467 (2) Å] lie between those of *p*-dinitrobenzene [1.478 (2) Å; Di Rienzo, Domenicano & Riva di Sanseverino, 1980] and *p*-nitroaniline [1.434 Å; Colapietro, Domenicano, Manciante & Portalone, 1982], but closer to that of *p*-dinitrobenzene. The bond lengths of the furazan ring are in good agreement with previous findings (Mathew & Palenik, 1971; Niclas, Göhrmann, Ramm & Schulz, 1990).

Surprisingly, the angle C(3)—C(4)—C(5) is 119.5 (2)°. Comparable angles were measured in other benzofurazans and benzofuroxans (*cf.* Mathew & Palenik, 1971; Niclas, Göhrmann, Ramm & Schulz, 1990; Lowe-Ma, 1986). This is in contrast to nitro-substituted benzenes such as trinitrobenzene (Herbstein, Kapon & Reiner, 1986) and *m*-dinitrobenzene (Trotter & Williston, 1966). In these cases, the corresponding angles lie between 122.7 and 123.6°.

The average deviations of the atoms from the least-squares planes of the five and six-membered rings of the benzofurazan fragment are 0.001 (2) and 0.021 (2) Å, respectively. The five- and six-membered rings of the benzofurazan fragment are twisted by 4.3 (8)°. The two six-membered rings of the molecule enclose a dihedral angle of 67.7 (5)°. The nitro groups at C(4) and C(6) are inclined at 14.5 (5) and 15.4 (3)°, respectively, to the six-membered ring.

The geometry and CNDO/2 calculations for comparable systems (Niclas, Göhrmann, Ramm & Schulz, 1990; Ramm, Niclas & Göhrmann, 1992) let us conclude that the aromatic character of the six-membered ring C(1)–C(6) has disappeared and a polymethinic state, characterized by strong π-electron density alternation (Dähne & Kulpe, 1977), is present in the dinitrobenzofurazan fragment.

The bond lengths of the carbonyl groups and in the phenyl fragment are in the normal range. As expected, the bond C(1)—C(7) [1.516 (3) Å] has single-bond character.

The packing of the molecules in the unit cell is shown in Fig. 2. The molecular arrangement is determined by van der Waals interactions and stacking between the phenyl ring (x, y, z) and furazan ring ($1-x$, $\frac{1}{2}+y$, $1-z$). The mean distance of 3.506 (2) Å between these two rings indicates weak π-electron interactions.

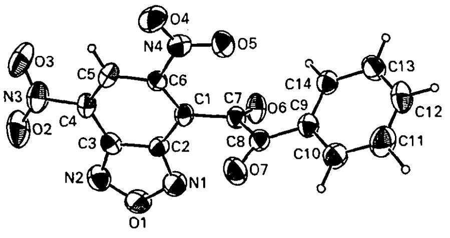


Fig. 1. *ORTEP* (Johnson, 1971) drawing of the molecular structure showing crystallographic numbering scheme (50% probability thermal ellipsoids).

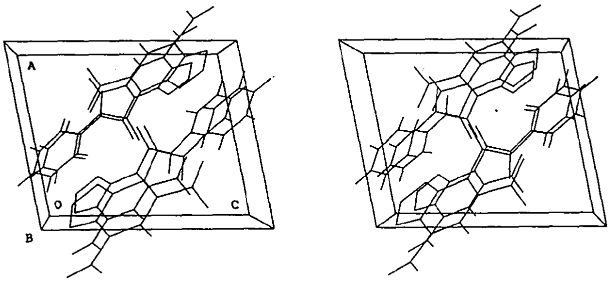


Fig. 2. *PLUTO* drawing (Motherwell & Clegg, 1976) of the molecular packing.

Experimental

Crystal data

$C_{14}H_6N_4O_7$
$M_r = 342.23$
Monoclinic
$P2_1$
$a = 8.9413$ (8) Å
$b = 7.434$ (1) Å
$c = 10.686$ (2) Å
$\beta = 101.27$ (1)°
$V = 696.6$ (3) Å^3
$Z = 2$

$D_x = 1.631$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.1$-17.6°
$\mu = 0.126$ mm^{-1}
$T = 298$ K
0.48 × 0.35 × 0.24 mm
Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans
2307 measured reflections
2061 independent reflections
1993 observed reflections $[F_o > 2\sigma(F_o)]$
$R_{\rm int} = 0.011$

$\theta_{\rm max} = 30°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 10$
$l = -15 \rightarrow 15$
2 standard reflections
frequency: 60 min
intensity variation: 1%

Refinement

Refinement on F
Final $R = 0.032$
$wR = 0.042$
1993 reflections
250 parameters
All H-atom parameters refined

$w = 1/\sigma(F)^2$
$(\Delta/\sigma)_{\rm max} = 0.03$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}
Atomic scattering factors from Enraf-Noniüs *MolEN* (Fair, 1990)

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

$$B_{\rm eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	$B_{\rm eq}$
O(1)	0.8449 (2)	−0.037	0.8323 (1)	4.59 (3)
O(2)	1.1334 (2)	0.4081 (3)	0.8902 (2)	6.10 (4)
O(3)	1.0867 (2)	0.6331 (3)	0.7602 (2)	5.94 (4)
O(4)	0.8251 (2)	0.5085 (2)	0.3367 (1)	4.25 (3)
O(5)	0.6283 (2)	0.3342 (2)	0.3079 (1)	3.68 (3)
O(6)	0.4635 (1)	0.0985 (2)	0.4923 (1)	3.63 (3)
O(7)	0.7367 (1)	−0.1159 (2)	0.3796 (1)	3.87 (3)
N(1)	0.7492 (2)	−0.0355 (3)	0.7159 (1)	3.86 (3)
N(2)	0.9399 (2)	0.1102 (3)	0.8529 (2)	3.90 (3)
N(3)	1.0678 (2)	0.4787 (3)	0.7928 (2)	4.09 (3)
N(4)	0.7439 (2)	0.3967 (2)	0.3729 (1)	2.80 (3)
C(1)	0.7224 (2)	0.1777 (2)	0.5371 (1)	2.32 (3)
C(2)	0.7840 (2)	0.1135 (2)	0.6626 (2)	2.56 (3)
C(3)	0.9026 (2)	0.2044 (3)	0.7474 (2)	2.75 (3)
C(4)	0.9565 (2)	0.3704 (3)	0.7065 (2)	2.90 (3)
C(5)	0.9036 (2)	0.4285 (3)	0.5874 (2)	2.86 (3)
C(6)	0.7900 (2)	0.3280 (3)	0.5034 (1)	2.35 (3)
C(7)	0.5835 (2)	0.0858 (3)	0.4590 (1)	2.47 (3)
C(8)	0.6137 (2)	−0.0417 (3)	0.3553 (2)	2.53 (3)
C(9)	0.4971 (2)	−0.0714 (3)	0.2394 (2)	2.64 (3)
C(10)	0.5115 (2)	−0.2195 (3)	0.1627 (2)	3.55 (4)
C(11)	0.4059 (3)	−0.2455 (4)	0.0509 (2)	4.42 (5)
C(12)	0.2905 (2)	−0.1235 (4)	0.0134 (2)	4.12 (4)
C(13)	0.2756 (2)	0.0246 (3)	0.0882 (2)	3.49 (4)
C(14)	0.3778 (2)	0.0500 (3)	0.2028 (2)	2.99 (3)

Table 2. *Bond lengths* (Å) *and valence angles* (°)

O(1)—N(1)	1.365 (2)	C(1)—C(7)	1.516 (2)
O(1)—N(2)	1.377 (2)	C(2)—C(3)	1.424 (2)
O(2)—N(3)	1.210 (2)	C(3)—C(4)	1.423 (3)
O(3)—N(3)	1.221 (3)	C(4)—C(5)	1.340 (2)
O(4)—N(4)	1.215 (2)	C(5)—C(6)	1.428 (2)
O(5)—N(4)	1.219 (2)	C(7)—C(8)	1.522 (2)
O(6)—C(7)	1.198 (2)	C(8)—C(9)	1.472 (2)
O(7)—C(8)	1.212 (2)	C(9)—C(10)	1.393 (3)
N(1)—C(2)	1.310 (3)	C(9)—C(14)	1.394 (2)
N(2)—C(3)	1.314 (2)	C(10)—C(11)	1.384 (3)
N(3)—C(4)	1.459 (3)	C(11)—C(12)	1.374 (3)
N(4)—C(6)	1.467 (2)	C(12)—C(13)	1.382 (3)
C(1)—C(2)	1.429 (2)	C(13)—C(14)	1.390 (2)
C(1)—C(6)	1.352 (2)		

N(1)—O(1)—N(2)	113.3 (1)	C(3)—C(4)—C(5)	119.5 (2)
O(1)—N(1)—C(2)	104.1 (1)	C(4)—C(5)—C(6)	120.3 (2)
O(1)—N(2)—C(3)	104.0 (2)	N(4)—C(6)—C(1)	118.9 (1)
O(2)—N(3)—O(3)	125.6 (2)	N(4)—C(6)—C(5)	116.7 (2)
O(2)—N(3)—C(4)	117.4 (2)	C(1)—C(6)—C(5)	124.4 (1)
O(3)—N(3)—C(4)	117.0 (2)	O(6)—C(7)—C(1)	119.1 (2)
O(4)—N(4)—O(5)	124.9 (1)	O(6)—C(7)—C(8)	124.2 (2)
O(4)—N(4)—C(6)	117.8 (1)	C(1)—C(7)—C(8)	116.0 (1)
O(5)—N(4)—C(6)	117.3 (2)	O(7)—C(8)—C(7)	114.2 (1)
C(2)—C(1)—C(6)	114.6 (1)	O(7)—C(8)—C(9)	125.2 (2)
C(2)—C(1)—C(7)	119.3 (1)	C(7)—C(8)—C(9)	120.6 (1)
C(6)—C(1)—C(7)	125.9 (1)	C(8)—C(9)—C(10)	118.8 (2)
N(1)—C(2)—C(1)	127.6 (2)	C(8)—C(9)—C(14)	121.1 (2)
N(1)—C(2)—C(3)	109.6 (1)	C(10)—C(9)—C(14)	120.0 (1)
C(1)—C(2)—C(3)	122.8 (2)	C(9)—C(10)—C(11)	119.5 (2)
N(2)—C(3)—C(2)	109.0 (2)	C(10)—C(11)—C(12)	120.4 (2)
N(2)—C(3)—C(4)	132.9 (2)	C(11)—C(12)—C(13)	120.6 (2)
C(2)—C(3)—C(4)	118.1 (1)	C(12)—C(13)—C(14)	119.8 (2)
N(3)—C(4)—C(3)	121.0 (1)	C(9)—C(14)—C(13)	119.7 (2)
N(3)—C(4)—C(5)	119.5 (2)		

Crystals were obtained by recrystallization from acetonitrile. Data were corrected for Lorentz and polarization factors. The structure was solved using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and by Fourier methods. Full-matrix least-squares refinement minimized $\Sigma w|F_o-F_c|^2$. H atoms were located by difference Fourier synthesis and refined isotropically. The program system used was Enraf-Nonius *MolEN* (Fair, 1990).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71181 (39 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1037]

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Structure of 5,10-Dihydro-3-phenylimino-1,2,4-thiaselenazolo[4,5-*b*][2,4]benzodiazepine

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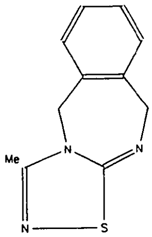
Abstract

The Se—S bond length is 2.199 (2) Å. The C1—Se and C10—S bonds are essentially single bonds of lengths 1.926 (6) and 1.771 (6) Å, respectively. The C1—Se—S and C10—S—Se bond angles are 90.4 (2) and 97.4 (2)°, respectively. The N1=C1 and N3=C10 bonds are localized N=C double bonds. The diazepine ring is folded about the C2–C9 axis into two planar moieties inclined at 119.3 (1)° to one another.

Comment

The determination of the structure of the title compound was carried out to establish whether the product from the reaction of the 1,2,4-thiadiazolo[4,5-*a*][1,3]diazepine (1) with phenyl isoselenocyanate in boiling toluene possesses structure (2) or structure (3), the reaction having taken place with elimination of acetonitrile from (1) and comcomitant addition of one molecule of phenyl isoselenocyanate (Lai, 1990, 1992; Lai & Reid, 1989).



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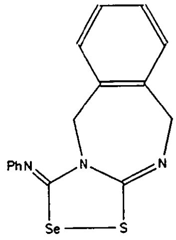

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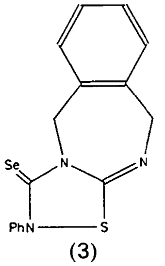

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