Refinement

Refinement on F^2
$R(F) = 0.038$
$wR(F^2) = 0.111$
$S = 1.04$
2387 reflections
229 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 0.2606P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O1—C1	1.377 (2)	O3—C8	1.443 (2)
O1—C16^i	1.437 (2)	O3—C9	1.382 (2)
O2—C2	1.360 (2)	O4—C10	1.377 (2)
O2—C7	1.425 (2)	O4—C15	1.442 (2)
C1—O1—C16^i	114.6 (1)	O2—C7—C8	108.1 (1)
C2—O2—C7	117.1 (1)	O3—C8—C7	108.1 (1)
C8—O3—C9	114.1 (1)	O3—C9—C10	122.1 (2)
C10—O4—C15	116.1 (1)	O3—C9—C14	118.5 (1)
O1—C1—C2	120.9 (1)	O4—C10—C9	121.5 (1)
O1—C1—C6	119.3 (2)	O4—C10—C11	118.5 (1)
O2—C2—C1	115.9 (1)	O4—C15—C16	110.1 (1)
O2—C2—C3	124.9 (1)	O1^i—C16—C15	107.5 (1)
O1—C1—C2—O2	−2.8 (2)	O3—C9—C10—O4	2.0 (2)
O2—C7—C8—O3	−67.2 (2)	O4—C15—C16—O1^i	72.1 (2)

Symmetry code: (i) $1 - x, 1 - y, -z$.

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

Cg1 = centroid of the C1—C6 ring; Cg2 = centroid of the C9—C14 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8A···O4	1.01 (2)	2.48 (2)	3.062 (2)	116 (2)
C15—H15A···O3	1.01 (2)	2.54 (2)	3.008 (2)	107.7 (13)
C16—H16A···O2^i	0.96 (2)	2.44 (2)	2.979 (2)	115.4 (11)
C7—H7B···Cg2^{ii}	0.98 (2)	2.81	3.70	152
C12—H12···Cg2^{iii}	1.00 (2)	2.79	3.72	156
C13—H13···Cg1^{iv}	0.99 (2)	2.74	3.65	152
C15—H15B···Cg1^v	0.99 (2)	2.80	3.65	144

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $x, y, 1+z$; (iii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iv) $-x, 1-y, -z$; (v) $1-x, 1-y, 1-z$.

Anisotropic displacement parameters were used for all non-H atoms. All H atoms were located and their positional parameters allowed to refine, and each was given an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of the C atom to which they were attached. C—H bond lengths are in the range 0.96 (2)–1.01 (2) Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Siemens, 1995). Software used to prepare material for publication: *PLATON* (Spek, 1998).

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4-Heptamethyleneimino-7-nitrobenzo-2-oxa-1,3-diazole†

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Abstract

The title compound, $C_{13}H_{16}N_4O_3$, crystallized in the $P\bar{1}$ (No. 2) space group from ethyl acetate. The asymmetric unit contains two molecules with similar geometry. The

† Alternative name: 4-(azocan-1-yl)-7-nitro-2,1,3-benzoxadiazole.

cyclic amino moieties of the two independent molecules are in the boat–chair conformation and the amino-N atom is not in the plane of the aromatic ring. The bond distance between the amino N and the attached C atom of the 7-nitrobenzofurazan system is shorter than a normal C—N single bond. The other C—N bond, which connects the nitro group with the ring, is also shorter than usual.

Comment

The crystal structure of the title compound, (I), was determined in order to find out whether the photo-

(I)
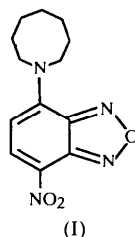
physical properties of the molecule can be correlated with its ground-state structure. This compound is highly fluorescent in non-polar media. However, in a polar environment, the fluorescent yield is considerably lower due presumably to some internal motion in the molecule. Internal rotation around the C—N(amino) bond, ring inversion or inversion of the amino-N atom can be thought of as being responsible for the low fluorescence efficiency of the compound in polar media. Dynamic NMR spectroscopy shows rotation around the C—N(amino) bond to be small. The crystallographic measurements provide information on the bond order of the C—N(amino) bond, which in turn helps in determining whether internal rotation around this bond could be responsible for the rapid non-radiative decay of the excited state of the molecule, as is observed in polar media.

The crystal structure contains two formula units. The *ORTEX* diagram (McArdle, 1995) of the structure is shown in Fig. 1. The C—N(amino) bond length [1.352 (3) Å, average of the two molecules in the asymmetric unit] is shorter than the usual C—N single bond distance. The C—N(nitro) bond distance is also shorter than expected. This indicates that there is a considerable through-bond charge separation between the donor amino group and the acceptor nitro group. The cyclic amino moiety is found to be in a boat–chair (Ōki, 1985) conformation. Furthermore, the amino-N atom is not far from a planar configuration (Table 1). The packing diagram (Fig. 2) shows that the molecules are packed in layers and that there is a pseudo-*a*-glide plane perpendicular to the *b* axis, *i.e.* a non-crystallographic symmetry.
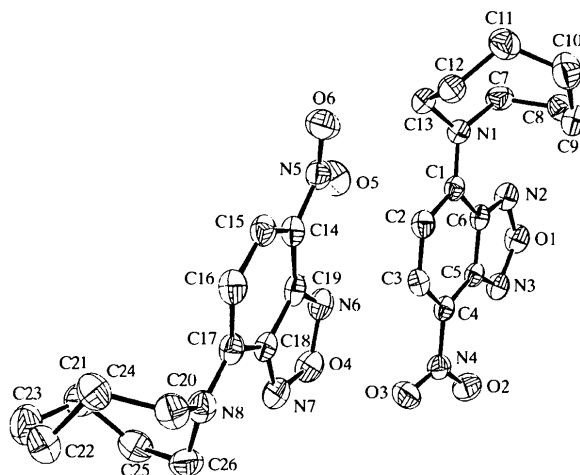

Fig. 1. A view of the molecular structure of (I) showing the atom labels. Displacement ellipsoids are shown at the 50% probability level.
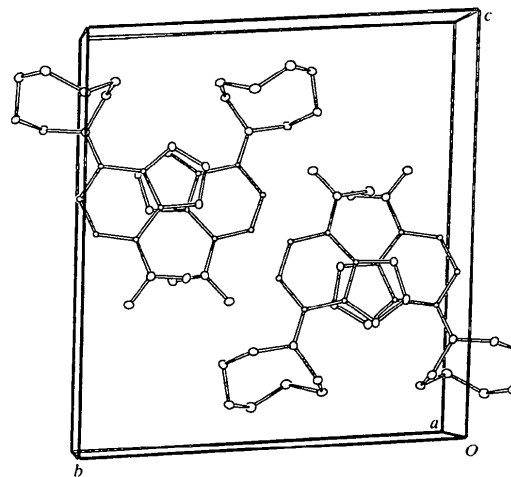

Fig. 2. A packing diagram of the title molecule, viewed down the *a* axis. A pseudo-*a*-glide plane perpendicular to the *b* axis can be noticed between the molecules. H atoms have been omitted for clarity.

Experimental

The title compound was prepared by treating a solution of 7-nitrobenzofurazan chloride in ethyl acetate (1 mol) with hepta-methyleneimine (1.2 mol, dropwise addition) at 273 K. The reaction mixture was stirred for 2 h at room temperature. The solid mass was filtered off and purified by column chromatography using an ethyl acetate/hexane mixture (20:80) as eluent. The product was recrystallized from absolute ethanol.

Crystal data

$C_{13}H_{16}N_4O_3$	Mo $K\alpha$ radiation
$M_r = 276.30$	$\lambda = 0.71073$ Å

Triclinic
$P\bar{1}$
$a = 6.685\,(2)$ Å
$b = 13.2357\,(11)$ Å
$c = 14.8763\,(19)$ Å
$\alpha = 93.677\,(9)°$
$\beta = 98.114\,(16)°$
$\gamma = 90.359\,(14)°$
$V = 1300.3\,(5)$ Å^3
$Z = 4$
$D_x = 1.412$ Mg m^{-3}
D_m not measured

Cell parameters from 25
reflections
$\theta = 1.54–24.97°$
$\mu = 0.103$ mm^{-1}
$T = 293\,(2)$ K
Plate
$0.64 \times 0.44 \times 0.16$ mm
Red

Data collection

Enraf–Nonius CAD-4
diffractometer
ω scans
Absorption correction: none
4562 measured reflections
4562 independent reflections
2806 reflections with
$I > 2\sigma(I)$

$\theta_{max} = 24.97°$
$h = 0 \rightarrow 7$
$k = -15 \rightarrow 15$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.148$
$S = 0.998$
2806 reflections
302 parameters
H-atom parameters
constrained
$w = 1/[\sigma^2(F_o^2) + (0.061P)^2 + 0.9105P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.468$ e Å^{-3}
$\Delta\rho_{min} = -0.253$ e Å^{-3}
Extinction correction:
SHELXL97
Extinction coefficient:
0.0070 (16)
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C1—N1	1.350 (3)	C14—N5	1.426 (3)
C4—N4	1.425 (3)	C17—N8	1.354 (3)
C1—N1—C7	123.2 (2)	C17—N8—C26	123.4 (2)
C1—N1—C13	120.0 (2)	C17—N8—C20	119.5 (2)
C7—N1—C13	116.5 (2)	C26—N8—C20	116.5 (2)

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *Xtal3.5* (Hall *et al.*, 1995). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEX* (McArdle, 1995). Software used to prepare material for publication: *SHELXL97*.

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A 1-alkylated pteridine, $C_{15}H_{19}ClN_6O_3$

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Abstract

The crystal structure of 6-chloro-2-(N,N-dimethyl-aminomethyleneamino)-1-(pivaloyloxymethyl)pteridin-4-one confirms that the reaction of pterin 8-oxide with acetyl chloride in trifluoroacetic acid produces the 6-chloride, and that the minor product from alkylation of 6-chloro-2-(N,N-dimethylaminomethylene-amino)pteridin-4-one with chloromethyl pivaloate in dimethylformamide with potassium carbonate, is N-1-alkylated and not N-8- or C-4-O-alkylated.

Comment

The regioselective N-8-oxidation (Yamamoto *et al.*, 1973) of pterin (2-aminopteridin-4-one), (1*a*), and the conversion (Taylor & Kobylecki, 1978) of this *N*-oxide into 6-chloropterin, (1*b*), with a combination of acetyl chloride and trifluoroacetic acid, is a useful route to a pteridine functionalized on the pyrazine ring, albeit that the regiochemistry of this last transformation is not at all what would have been expected by analogy with other azine *N*-oxide chemistry. No X-ray crystallographic evidence has been advanced for the regiochemical outcome of this transformation.