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4-Hydroxy-3-methoxybenzaldehyde 4,5-diazafluoren-9-ylidenehydrazone

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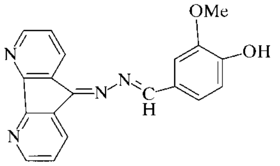
The whole molecule of the title compound, $C_{19}H_{14}N_4O_2$, is essentially planar, with a highly conjugated π system. In the crystal, the molecules are packed as chains along the [011] direction connected by O—H···N intermolecular hydrogen bonds.

Comment

Schiff base compounds having extensively conjugated π-electron systems have been reported to display second harmonic generation (Messier *et al.*, 1991; Zyss, 1994). As part of our work in the research and study of new materials for non-linear optical applications, we report here the crystal structure of the title compound, (I).



(I)

Bond lengths and angles observed in (I) agree well with related structures (Lu *et al.*, 1995, 1997). The diazafluorene substituent does not show relevant distortion from planarity or from C_2 symmetry. The whole molecule is essentially planar. The C—N bond lengths in the hydrazone moiety are short compared with those observed in a related compound, *p*-(dimethylamino)benzaldehyde 4,5-diaza-9-fluorenylidene hydrazone monohydrate (Lu *et al.*, 1995). This indicates that the π-conjugation along the central hydrazone chain is higher in (I). The phenyl group is in an antiperiplanar orientation with respect to the N4—C12 bond.

While substitution at the phenyl C13 atom is angularly symmetric, with C12—C13—C18 = 120.5 (2)° and C12—C13—C14 = 120.0 (2)°, substitution at the diazafluorenyl C11 atom shows quite a relevant angular asymmetry, the angle C1—C11—N3 of 133.1 (2)° being larger than C10—C11—N3 of 120.8 (2)°. This asymmetry seems to be caused by the tendency of the central hydrazone system to be coplanar with fluorenyl due to π-conjugation, and steric hindrance involving the C2—H group with N4 [C2···N4 = 3.004 (4) Å and H2···N4 = 2.53 Å] and C9—H with N3 [C9···N3 = 3.054 (3) Å and H9···N3 = 2.90 Å]. The asymmetry of the exocyclic angles at C17 [C16—C17—O2 = 116.2 (2)° and C18—C17—O2 = 124.4 (2)°] is caused by the tendency of the methoxy group to be coplanar with the phenyl ring, as usually found in anisoles. This tendency can be justified by some degree of conjugation between the oxygen and phenyl, which is shown by some shortening of the C_{ar}—O bond, 1.367 (3) Å (Domiano *et al.*, 1979). Some hindrance occurs between one of the methyl H atoms and the hydrogen bound to C18; H19*C*···H18 = 2.15 Å. The same kind of asymmetry is observed for the exocyclic angles at C16 [C17—C16—O1 = 117.2 (2)° and C15—C16—O1 = 123.6 (2)°], which is common with phenols, the C16—O1 bond being 1.358 (3) Å and the H1···H15 contact 2.30 Å.

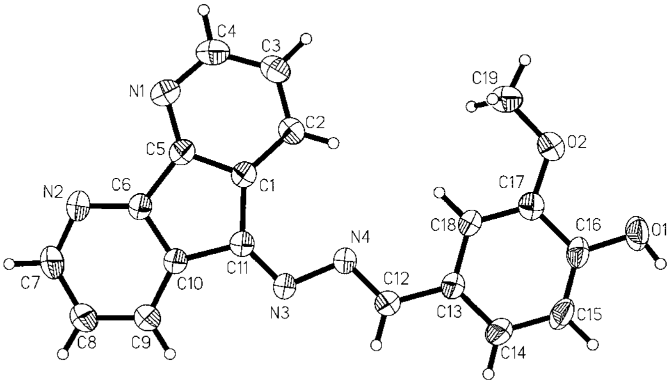


Figure 1
The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

The dihedral angles formed by the planes of the diazafluorene group and the phenyl ring with the central hydrazone (N3, N4, C12) bridge are 4.6 (2) and 3.0 (2)°, and 7.29 (5)° between each other. In the crystal, the molecules are packed as chains along the [011] direction connected by O—H···N intermolecular hydrogen bonds.

Experimental

The synthesis of the title compound was carried out by reaction of 4-hydroxy-3-methoxybenzaldehyde and 4,5-diazafluorene-9-hydrazine in ethanol solution under reflux for 5 h. Single crystals were obtained by recrystallization from ethanol.

Crystal data

$C_{19}H_{14}N_4O_2$
$M_r = 330.34$
Orthorhombic, $Pna2_1$
$a = 7.5130 (2)$ Å
$b = 26.9091 (5)$ Å
$c = 7.9141 (1)$ Å
$V = 1599.98 (6)$ Å^3
$Z = 4$
$D_x = 1.371$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 5698 reflections
$\theta = 1.51$–$28.34°$
$\mu = 0.093$ mm^{-1}
$T = 293 (2)$ K
Slab, yellow
0.38 × 0.30 × 0.12 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
10 894 measured reflections
2115 independent reflections
1577 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.082$
$\theta_{\rm max} = 28.29°$
$h = -9 \rightarrow 10$
$k = -34 \rightarrow 35$
$l = -10 \rightarrow 6$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.093$
$S = 0.931$
2115 reflections
227 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.17$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1997)
Extinction coefficient: 0.0096 (18)

Table 1
Selected geometric parameters (Å, °).

O2—C19	1.424 (3)	N3—N4	1.405 (3)
N3—C11	1.294 (3)	N4—C12	1.283 (3)
C17—O2—C19	116.2 (2)	C12—N4—N3	112.1 (2)
C11—N3—N4	112.5 (2)	N4—C12—C13	120.1 (2)
N4—N3—C11—C10	177.8 (2)	N4—C12—C13—C14	179.0 (2)
N3—N4—C12—C13	178.0 (2)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$A\cdots$N2$^{\rm i}$	0.82	2.11	2.844 (3)	150

Symmetry code: (i) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$.

The collection of intensity data was as described by Shanmuga Sundara Raj *et al.* (1999). The Friedel pairs were not included in the refinement.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL, PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1478). Services for accessing these data are described at the back of the journal.

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