

C2—C3	1.393 (2)	C9—C10	1.382 (2)
C3—C4	1.390 (2)	C10—C11	1.391 (2)
C4—N5	1.345 (1)	C11—C12	1.380 (2)
N5—C6	1.324 (1)	C12—C13	1.496 (1)
C6—C7	1.485 (1)	C13—O14	1.213 (1)
C2—C1—C6	119.67 (9)	C12—C7—C6	108.48 (8)
C2—C1—C13	131.72 (9)	C7—N8—C9	114.09 (9)
C6—C1—C13	108.61 (8)	N8—C9—C10	124.98 (10)
C1—C2—C3	116.21 (10)	C9—C10—C11	119.82 (10)
C4—C3—C2	119.88 (10)	C12—C11—C10	116.30 (10)
N5—C4—C3	124.30 (10)	C11—C12—C7	119.53 (9)
C6—N5—C4	114.95 (9)	C11—C12—C13	131.70 (9)
N5—C6—C1	124.99 (9)	C7—C12—C13	108.77 (8)
N5—C6—C7	126.27 (8)	O14—C13—C1	127.81 (10)
C1—C6—C7	108.73 (8)	O14—C13—C12	126.79 (10)
N8—C7—C12	125.25 (9)	C1—C13—C12	105.40 (7)
N8—C7—C6	126.27 (8)		

All the H atoms were located from difference Fourier maps and refined isotropically.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976), SHELXTL/PC (Sheldrick, 1990). Software used to prepare material for publication: SHELXL93. Geometric calculations: PARST (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1169). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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p-Dimethylaminobenzaldehyde 4,5-Diaza-9-fluorenylidenehydrazone Monohydrate

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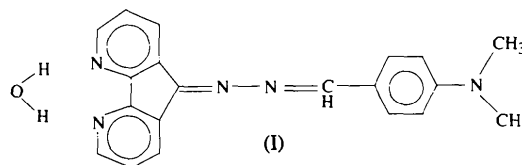
(Received 2 February 1995; accepted 27 March 1995)

Abstract

The X-ray analysis reveals that the title compound, C₂₀H₁₇N₅.H₂O, is an electron-delocalized planar molecule. The molecules are stacked as non-bonding dimeric pairs about the crystallographic inversion centre in the crystal lattice. The lone water molecule present in the unit cell is hydrogen bonded to both N atoms in the diazafluorene moiety.

Comment

Recently, nonlinear optical organic materials have aroused considerable interest as a result of their wide application in science and technology (Chemla & Zyss, 1987). Schiff base compounds having extensively conjugated π -electron systems have been reported to display second harmonic generations (Houlton *et al.*, 1992; Velavan, Sivakumar & Anbu, 1995). The title compound, (C₁₀H₆N₂)C=N—N=CH(C₆H₄)N(CH₃)₂.H₂O, (I), is a Schiff base derivative; this crystal structure determination forms part of our search for and study of new materials for nonlinear optical applications.



An ORTEPII (Johnson, 1976) plot of the molecule with atom-numbering scheme is shown in Fig. 1. The bond lengths and angles observed in this structure show

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that the molecule has a highly conjugated π system. This is also supported by the almost complete planarity of the molecule. The dihedral angle between the planes of the phenyl and diazafluorene fragments is $3.73(5)^\circ$; the two fragments make angles of $2.1(1)$ and $5.4(1)^\circ$ with the plane of the central hydrazone linkage. In the diazafluorene moiety, C2 deviates by a maximum of $0.042(3)$ Å from the mean plane and the dimethylamino group is tilted by $7.0(2)^\circ$ from the plane of the phenyl ring. The short C20—N23 bond length, $1.368(3)$ Å, reflects the partial double-bond nature of this bond, which is in consistent with the electron delocalization in the whole molecule.

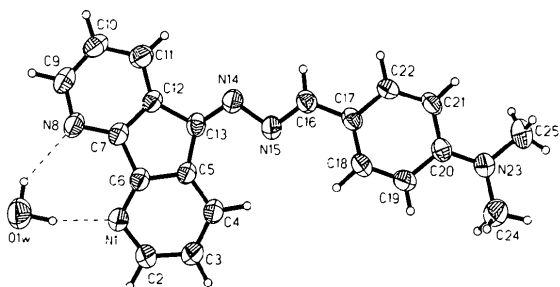


Fig. 1. Structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

The water molecule present in this structure also lies in the same plane of the molecule and deviates by $0.055(2)$ Å from the best plane of the diazafluorene moiety. The position of the water molecule means it can form hydrogen bonds with both N atoms of the pyridine moieties: $O1W \cdots N1$ $2.938(3)$, $O1W \cdots N8$ $3.047(3)$ Å. It should be noted that the N atoms in diazafluorene structures are always involved in $O—H \cdots N$ hydrogen bonds, even though more negative carbonyl O atoms are present in the structure (Baxter, Connor, Wallis, Povey & Powell, 1992). For these two N atoms, the charge concentration is greater on one (N1 in this case) than the other, which is justified by the shorter donor-acceptor distance $O1W \cdots N1$. This is also observed in the structure of 4,5-diazafluorene-9-one, where only one N atom is involved in a $C—H \cdots N$ hydrogen bond (Fun, Sivakumar, Zhu & You, 1995).

In the crystal lattice, the molecules exist as non-bonding dimers about the crystallographic inversion centre. These planar molecules pack in two individual parallel layers; the dihedral angle between these two layers is equal to β^* (66.4°). No second harmonic generation was observed in this compound owing to its centrosymmetric solid-state structure.

Experimental

The synthesis of the compound was carried out by refluxing 4,5-diazafluorene-9-hydrazine and dimethylaminobenzaldehyde in ethanol solution for 3 h. Single crystals were obtained by recrystallization from ethanol.

Crystal data

$C_{20}H_{17}N_5 \cdot H_2O$
 $M_r = 345.40$
 Monoclinic
 C_2/c
 $a = 18.250(4)$ Å
 $b = 16.424(4)$ Å
 $c = 12.639(2)$ Å
 $\beta = 113.56(2)^\circ$
 $V = 3472.6(13)$ Å³
 $Z = 8$
 $D_x = 1.321$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 8–22.5^\circ$
 $\mu = 0.086$ mm⁻¹
 $T = 293(2)$ K
 Prism
 $0.44 \times 0.22 \times 0.18$ mm
 Red

Data collection

Siemens P4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: none
 2750 measured reflections
 2275 independent reflections
 1435 observed reflections
 $[I > 2\sigma(I)]$
 $R_{int} = 0.0437$

$\theta_{max} = 22.5^\circ$
 $h = -1 \rightarrow 19$
 $k = -1 \rightarrow 17$
 $l = -13 \rightarrow 12$
 3 standard reflections monitored every 100 reflections
 intensity decay: $< 3\%$

Refinement

Refinement on F^2
 $R(F) = 0.0399$
 $wR(F^2) = 0.0914$
 $S = 1.066$
 2275 reflections
 312 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0490P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.165$ e Å⁻³
 $\Delta\rho_{min} = -0.158$ e Å⁻³
 Extinction correction: *SHELXL93* (Sheldrick, 1993)
 Extinction coefficient: 0.0021 (3)
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$			
	x	y	z	U_{eq}
N1	0.25495 (12)	0.13231 (13)	0.4032 (2)	0.0501 (6)
C2	0.1862 (2)	0.1660 (2)	0.3988 (3)	0.0545 (8)
C3	0.1108 (2)	0.1390 (2)	0.3289 (2)	0.0523 (8)
C4	0.1017 (2)	0.0714 (2)	0.2590 (2)	0.0457 (7)
C5	0.17091 (13)	0.03367 (14)	0.2633 (2)	0.0387 (6)
C6	0.24517 (13)	0.06764 (14)	0.3355 (2)	0.0412 (6)
C7	0.30884 (14)	0.01804 (14)	0.3234 (2)	0.0422 (7)
N8	0.38840 (12)	0.02996 (13)	0.3776 (2)	0.0514 (6)
C9	0.4326 (2)	-0.0262 (2)	0.3520 (3)	0.0566 (8)
C10	0.4028 (2)	-0.0909 (2)	0.2787 (3)	0.0568 (8)
C11	0.3208 (2)	-0.1017 (2)	0.2240 (3)	0.0536 (8)
C12	0.27360 (13)	-0.04604 (15)	0.2480 (2)	0.0413 (6)
C13	0.18568 (14)	-0.03935 (15)	0.2089 (2)	0.0416 (6)
N14	0.14003 (12)	-0.09514 (13)	0.1427 (2)	0.0503 (6)
N15	0.05854 (12)	-0.08287 (13)	0.1156 (2)	0.0518 (6)
C16	0.0172 (2)	-0.1423 (2)	0.0525 (2)	0.0459 (7)
C17	-0.06909 (14)	-0.14622 (14)	0.0102 (2)	0.0434 (6)
C18	-0.1150 (2)	-0.0877 (2)	0.0345 (2)	0.0502 (7)
C19	-0.1964 (2)	-0.0927 (2)	-0.0092 (2)	0.0495 (7)
C20	-0.23795 (15)	-0.15725 (15)	-0.0830 (2)	0.0428 (7)
C21	-0.1915 (2)	-0.21629 (15)	-0.1075 (2)	0.0462 (7)
C22	-0.1097 (2)	-0.2109 (2)	-0.0616 (2)	0.0476 (7)
N23	-0.31965 (12)	-0.16060 (13)	-0.1301 (2)	0.0529 (6)

C24	-0.3665 (2)	-0.1059 (2)	-0.0931 (4)	0.0673 (9)
C25	-0.3621 (2)	-0.2250 (2)	-0.2097 (3)	0.0683 (10)
O1W	0.42272 (15)	0.17651 (14)	0.5381 (2)	0.0772 (7)

Table 2. Selected geometric parameters (Å, °)

N1—C6	1.331 (3)	C12—C13	1.482 (3)
N1—C2	1.352 (3)	C13—N14	1.295 (3)
C2—C3	1.377 (4)	N14—N15	1.401 (3)
C3—C4	1.387 (4)	N15—C16	1.295 (3)
C4—C5	1.388 (3)	C16—C17	1.448 (4)
C5—C6	1.411 (3)	C17—C18	1.387 (3)
C5—C13	1.460 (3)	C17—C22	1.401 (3)
C6—C7	1.476 (3)	C18—C19	1.366 (4)
C7—N8	1.349 (3)	C19—C20	1.415 (3)
C7—C12	1.393 (3)	C20—N23	1.368 (3)
N8—C9	1.346 (3)	C20—C21	1.402 (3)
C9—C10	1.372 (4)	C21—C22	1.371 (4)
C10—C11	1.387 (4)	N23—C24	1.442 (4)
C11—C12	1.370 (3)	N23—C25	1.451 (4)
C6—N1—C2	114.6 (2)	C11—C12—C7	119.8 (2)
N1—C2—C3	124.6 (3)	C11—C12—C13	131.9 (2)
C2—C3—C4	120.0 (3)	C7—C12—C13	108.3 (2)
C3—C4—C5	117.2 (2)	N14—C13—C5	133.9 (2)
C4—C5—C6	118.2 (2)	N14—C13—C12	119.6 (2)
C4—C5—C13	133.2 (2)	C5—C13—C12	106.4 (2)
C6—C5—C13	108.6 (2)	C13—N14—N15	113.7 (2)
N1—C6—C5	125.4 (2)	C16—N15—N14	110.0 (2)
N1—C6—C7	126.7 (2)	N15—C16—C17	122.7 (3)
C5—C6—C7	107.9 (2)	C18—C17—C16	123.4 (2)
N8—C7—C12	124.5 (2)	C22—C17—C16	119.3 (2)
N8—C7—C6	126.8 (2)	N23—C20—C21	121.8 (2)
C12—C7—C6	108.7 (2)	N23—C20—C19	121.4 (2)
C9—N8—C7	113.9 (2)	C20—N23—C24	121.2 (2)
N8—C9—C10	125.4 (3)	C20—N23—C25	121.2 (3)
C9—C10—C11	119.6 (3)	C24—N23—C25	117.2 (3)
C12—C11—C10	116.9 (3)		

All the H atoms were located from difference Fourier maps and refined isotropically.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976), SHELXTL/PC (Sheldrick, 1990). Software used to prepare material for publication: SHELXL93. Geometric calculations: PARST (Nardelli, 1983).

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Benzyl 3-(4-Dimethylaminobenzylidene)-dithiocarbazate

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Abstract

The title Schiff base compound, C₁₇H₁₉N₃S₂, crystallizes in the triclinic system with two molecules in the asymmetric unit. The dimethylaminophenyl and carbazate parts of the molecule lie in one plane, perpendicular to the plane of the *S*-benzyl group. One of the two molecules in the asymmetric unit displays lateral disorder of the *S*-benzyl group. The molecular packing is

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