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## 4,5-Diaza-9-fluorenone Isonicotinoylhydrazone Monohydrate

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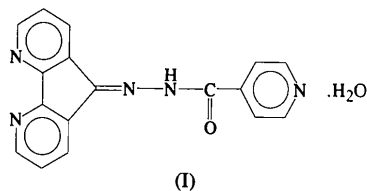
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### Abstract

The title compound, C<sub>17</sub>H<sub>11</sub>N<sub>5</sub>O.H<sub>2</sub>O, forms two-dimensional layers parallel to the (101) plane. The dihedral angle between the planes of the diazafluorene moiety and the pyridine ring is 27.74(4)°. The crystal structure is stabilized by O—H···N, N—H···O, C—H···O and C—H···N hydrogen bonds.

### Comment

Since the discovery of the usefulness of 2,2'-bipyridine (bpy) as a probe for ions, hundreds of its derivatives and their metal complexes have been synthesized due to their wide range of applications in the fields of photochemistry and photophysics (Zissel & Lehn, 1990; Beer, Kocian, Mortimer & Spencer, 1992). The coordination chemistry of aroylhydrazines has also received considerable attention over the past two decades (Lu, Wu, Liang, Song & Ma, 1994; Dutta & Hossain, 1985). The combination of the bpy and aroylhydrazone subunits yielding ligands capable of forming polymetallic complexes would therefore be of interest for their potential multi-redox, catalytic, electronic and energy-transfer properties. As part of studies on the synthesis and characterization of new aroylhydrazone derivatives, we report the crystal structure of 4,5-diaza-9-fluorenone isonicotinoylhydrazone monohydrate, (I).



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A displacement ellipsoid plot of (I) with the atom-numbering scheme is shown in Fig. 1. The bond lengths and angles observed in this structure are normal and comparable to those found in the structures of other nicotinoylhydrazine and 4,5-diazafluorene derivatives (Lu *et al.*, 1995, 1996; Fun *et al.*, 1996*a,b*). The dihedral angle between the diazafluorene moiety and the pyridine ring is 27.74(4)°. The molecules, connected by hydrogen bonds, form two-dimensional layers (sheets) parallel to the (10 $\bar{1}$ ) plane; the two O—H···N hydrogen bonds involving the water molecule link the title molecules into chains and a C8—H8···O1 contact cross-links these chains into sheets (Table 3). The two other major hydrogen bonds, N4—H4N···O1W and C15—H15···O1, form the interlayer connections.

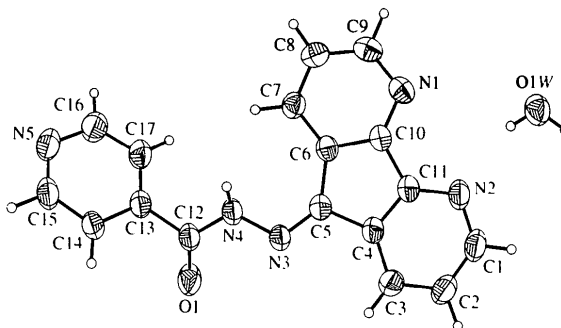


Fig. 1. A 50% displacement ellipsoid plot of the title molecule with the atom-numbering scheme.

We have observed previously that due to the possibility of different charge concentrations between the two pyridinyl N atoms of the diazafluorene moiety, the one with the greater charge is involved in the stronger intermolecular hydrogen bonds, whereas the other may be involved in only a weak interaction (Fun, Sivakumar, Zhu & You, 1995; Lu *et al.*, 1995). In the title structure, the same pattern is observed; the N2 atom is involved in a strong O—H···N (O1W···N2) contact, while the N1 atom has a very weak interaction with the C17 atom in the form of a C—H···N contact. We note also that the aroylhydrazone derivatives crystallize in hydrated forms only.

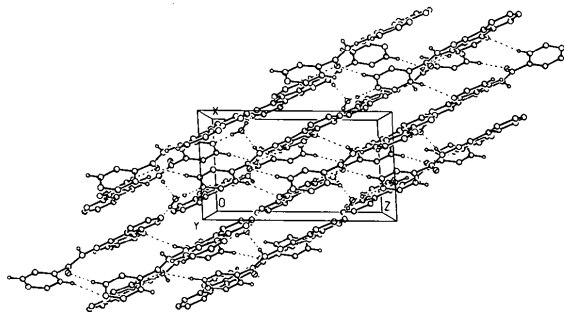


Fig. 2. Packing viewed down the *b* axis.

## Experimental

The synthesis of the title compound was carried out by refluxing a mixture of 4,5-diaza-9-fluorenone and isonicotinoyl-hydrazine in ethanol solution for 3 h. Single crystals suitable for X-ray analysis were obtained by recrystallization from ethanol.

### Crystal data

C<sub>17</sub>H<sub>11</sub>N<sub>5</sub>O.H<sub>2</sub>O

*M<sub>r</sub>* = 319.32

Monoclinic

*P*2<sub>1</sub>/*c*

*a* = 7.2382 (5) Å

*b* = 15.9407 (14) Å

*c* = 13.1520 (11) Å

β = 93.473 (7)°

*V* = 1514.7 (3) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.400 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25

reflections

θ = 8–25°

μ = 0.097 mm<sup>-1</sup>

*T* = 293 (2) K

Block cut from long needle

0.58 × 0.40 × 0.38 mm

Colourless

### Data collection

Siemens *P4* diffractometer

θ/2θ scans

Absorption correction:

none

4571 measured reflections

3462 independent reflections

2416 observed reflections

[*I* > 2σ(*I*)]

*R<sub>int</sub>* = 0.020

θ<sub>max</sub> = 27.50°

*h* = -1 → 9

*k* = -1 → 20

*l* = -17 → 17

3 standard reflections

monitored every 97

reflections

intensity decay: 3%

### Refinement

Refinement on *F*<sup>2</sup>

*R*(*F*) = 0.0404

w*R*(*F*<sup>2</sup>) = 0.1149

*S* = 0.966

3462 reflections

270 parameters

All H-atom parameters

refined

w = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0684*P*)<sup>2</sup>]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/*σ*)<sub>max</sub> < 0.001

Δρ<sub>max</sub> = 0.223 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.201 e Å<sup>-3</sup>

Extinction correction:

*SHELXL93*

Extinction coefficient:

0.0072 (15)

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 (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
O1	0.4651 (2)	0.76507 (8)	0.24277 (9)	0.0724 (4)
N1	0.8133 (2)	0.44434 (8)	0.60807 (9)	0.0469 (3)
N2	0.9388 (2)	0.60471 (9)	0.71471 (9)	0.0514 (3)
N3	0.6907 (2)	0.68362 (7)	0.38467 (8)	0.0414 (3)
N4	0.6148 (2)	0.64590 (8)	0.29730 (9)	0.0423 (3)
N5	0.2850 (2)	0.55473 (10)	-0.02903 (10)	0.0597 (4)
C1	0.9871 (3)	0.68282 (12)	0.74358 (13)	0.0586 (4)
C2	0.9685 (2)	0.75255 (12)	0.68236 (13)	0.0563 (4)
C3	0.8916 (2)	0.74507 (10)	0.58358 (13)	0.0490 (4)
C4	0.8374 (2)	0.66536 (9)	0.55213 (10)	0.0405 (3)
C5	0.7517 (2)	0.63290 (9)	0.45500 (10)	0.0380 (3)
C6	0.7396 (2)	0.54027 (8)	0.46728 (10)	0.0371 (3)
C7	0.6735 (2)	0.47501 (9)	0.40621 (11)	0.0427 (3)

C8	0.6806 (2)	0.39461 (10)	0.44689 (12)	0.0479 (4)
C9	0.7501 (2)	0.38254 (10)	0.54598 (13)	0.0502 (4)
C10	0.8065 (2)	0.52065 (9)	0.56733 (10)	0.0379 (3)
C11	0.8658 (2)	0.59865 (9)	0.61950 (11)	0.0408 (3)
C12	0.5078 (2)	0.69247 (10)	0.23023 (10)	0.0453 (4)
C13	0.4353 (2)	0.64268 (9)	0.13904 (10)	0.0417 (3)
C14	0.4526 (2)	0.67247 (10)	0.04091 (11)	0.0472 (4)
C15	0.3781 (3)	0.62613 (12)	-0.03966 (12)	0.0554 (4)
C16	0.2673 (3)	0.52744 (12)	0.06608 (14)	0.0612 (5)
C17	0.3421 (3)	0.56832 (11)	0.15097 (12)	0.0534 (4)
O1W	1.1556 (2)	0.46051 (8)	0.80295 (10)	0.0562 (3)

Table 2. Selected bond lengths (Å)

O1—C12	1.212 (2)	C4—C11	1.391 (2)
N1—C10	1.329 (2)	C4—C5	1.479 (2)
N1—C9	1.342 (2)	C5—C6	1.489 (2)
N2—C11	1.333 (2)	C6—C7	1.382 (2)
N2—C1	1.342 (2)	C6—C10	1.409 (2)
N3—C5	1.286 (2)	C7—C8	1.389 (2)
N3—N4	1.381 (2)	C8—C9	1.382 (2)
N4—C12	1.359 (2)	C10—C11	1.471 (2)
N5—C15	1.334 (2)	C12—C13	1.506 (2)
N5—C16	1.338 (2)	C13—C17	1.377 (2)
C1—C2	1.374 (3)	C13—C14	1.388 (2)
C2—C3	1.387 (2)	C14—C15	1.375 (2)
C3—C4	1.386 (2)	C16—C17	1.375 (2)

Table 3. Hydrogen-bonding geometry (Å, °)

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
O1W—H1W···N2	0.80 (3)	2.22 (3)	2.979 (2)	158 (2)
O1W—H2W···N5 <sup>i</sup>	0.89 (3)	1.90 (2)	2.787 (2)	178 (2)
N4—H4N···O1W <sup>ii</sup>	0.90 (2)	1.90 (2)	2.765 (2)	160 (2)
C8—H8···O1 <sup>iii</sup>	0.95 (2)	2.45 (2)	3.359 (2)	160 (1)
C15—H15···O1 <sup>iv</sup>	0.99 (2)	2.48 (2)	3.437 (2)	162 (2)
C7—H7···O1W <sup>v</sup>	0.99 (2)	2.64 (2)	3.250 (2)	120 (1)
C17—H17···N1 <sup>i</sup>	0.94 (2)	2.58 (2)	3.432 (2)	152 (2)

Symmetry codes: (i) 1 + *x*, *y*, 1 + *z*; (ii) 2 - *x*, 1 - *y*, 1 - *z*; (iii) 1 - *x*, *y* - ½, ½ - *z*; (iv) *x*, ¾ - *y*, *z* - ½; (v) 1 - *x*, 1 - *y*, 1 - *z*.

The title structure was solved by direct methods and refined by full-matrix least-squares techniques. The H atoms were located from difference maps and refined isotropically.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTLIPC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTLIPC*. Software used to prepare material for publication: *SHELXL93*. Molecular geometry: *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: CF1063). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Beer, P. D., Kocian, O., Mortimer, R. J. & Spencer, P. (1992). *J. Chem. Soc. Chem. Commun.* pp. 602–605.  
 Dutta, R. L. & Hossain, Md. M. (1985). *J. Sci. Ind. Res.* **44**, 635–674.

- Fun, H.-K., Sivakumar, K., Lu, Z.-L., Duan, C.-Y., Tian, Y.-P. & You, X.-Z. (1996a). *Acta Cryst.* **C52**, 986–988.
- Fun, H.-K., Sivakumar, K., Lu, Z.-L., Duan, C.-Y., Tian, Y.-P. & You, X.-Z. (1996b). *Acta Cryst.* **C52**, 1505–1507.
- Fun, H.-K., Sivakumar, K., Zhu, D.-R. & You, X.-Z. (1995). *Acta Cryst.* **C51**, 2076–2078.
- Lu, Z.-L., Duan, C.-Y., Tian, Y.-P., You, X.-Z., Fun, H.-K. & Sivakumar, K. (1995). *Acta Cryst.* **C51**, 2078–2080.
- Lu, Z.-L., Duan, C.-Y., Tian, Y.-P., You, X.-Z., Fun, H.-K. & Sivakumar, K. (1996). *Acta Cryst.* **C52**, 1507–1509.
- Lu, Z.-L., Wu, X.-L., Liang, Y.-M., Song, Q.-B. & Ma, Y.-X. (1994). *Bull. Soc. Chim. Belg.* **103**, 47–57.
- Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
- Sheldrick, G. M. (1990). *SHELXTL/PC Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1994). *XSCANS. X-ray Single Crystal Analysis System*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Zissel, R. & Lehn, J. M. (1990). *Helv. Chim. Acta.* **73**, 1149–1162.

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### 3-*tert*-Butyl-4-methyl-2-phenyl-3-(trimethylsilyloxy)oxetane and 2-(2-Benzyl-oxyphenyl)-3-*tert*-butyl-3-(trimethylsilyloxy)oxetane

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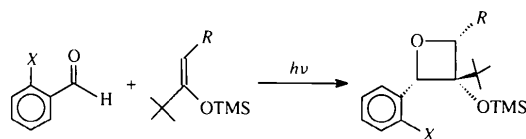
#### Abstract

In the structures of both of the title compounds, C<sub>17</sub>H<sub>28</sub>O<sub>2</sub>Si, (I), and C<sub>23</sub>H<sub>32</sub>O<sub>3</sub>Si, (II), the bulkiest substituents are *trans* with respect to one another, *i.e.* the phenyl group (or substituted phenyl) is *trans* with respect to the *tert*-butyl group. In compound (I), the methyl group at ring-position 4 is in a *trans* configuration relative to the *tert*-butyl group. The oxetane rings in both structures, especially (II), are non-planar. Both structures contain long C—O single bonds in the four-membered ring (1.44–1.46 Å), which is typical of oxetane structures.

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#### Comment

The Paternò–Büchi reaction represents the most convenient and straightforward access to functionalized oxetanes. It has been shown recently that the photocycloaddition of silyl enol ethers to various aldehydes proceeds with excellent regio- and diastereoselectivity (Bach, 1995a). The products formed are 3-silyloxy-substituted oxetanes, which represent versatile vehicles for further synthetic transformations (Bach, 1995b; Bach, Jödicke, Kather & Hecht, 1995). The relative configuration of these heterocycles is presumably controlled by a two-step pathway *via* an intermediate triplet 1,4-biradical (Freilich & Peters, 1981). Details of the synthetic work have been published elsewhere (Bach, 1995a). The crystals used in this work were obtained from an ether/pentane (1:1) solution. The photochemical reaction sequence is depicted in general terms below. The isolated yields were 82% for oxetane (I) and 56% for oxetane (II) after chromatographic purification.



- (I) X = H; R = Me (82%)  
 (II) X = OCH<sub>2</sub>Ph; R = H (56%)

The structural studies of compounds (I) and (II) were undertaken in order to establish the relative configurations of the oxetane rings. The X-ray crystal structures [shown in Figs. 1 and 2 for (I) and (II), respectively] confirm the expected *trans* relationship of the bulkiest substituents. This geometry was also strongly suggested by NMR measurements (difference Nuclear Overhauser Effect) performed earlier (Bach, 1995a). The oxetane rings are not planar and the puckering angles (defined as the dihedral angle between planes C—O—C and C—C—C) are 8.3 (3) and 20.7 (2)° for compounds (I) and (II), respectively. The non-planarity can also be seen from the ring torsion angles, which are clearly different from zero [O1—C2—C3—C4 5.8 (2) in (I) and –14.2 (2)° in (II)]. Previous single-crystal X-ray investigations on substituted oxetane derivatives (Seitz *et al.*, 1994; Khan, Morris, Smith & Walsh, 1991; Morris, Smith & Walsh, 1987; George & Gilardi, 1986; Hospital, Leroy, Bats & Moulines, 1978; Holan, Kowala & Wunderlich, 1973) show that the puckering angles can vary from 0 to 22.9 (2)°. Furthermore, the crystal structure of unsubstituted oxetane has been determined at temperatures of 90 and 140 K (Luger & Buschmann, 1984); the ring exhibits a non-planar structure with puckering angles of 10.7 (1)° at 90 K and 8.7 (2)° at 140 K.

The C—O bond distances [1.442 (3)–1.455 (2) Å] are larger than the average value for saturated heterocyclic C—O single bonds [1.426 (5) Å; Sutton, 1965], but this