X-ray Structure of *N*-(4-Nitrophenacyl)-4,5-diazafluoren-9-onium Bromide

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The X-ray structure of the salt *N*-(4-nitrophenacyl)-4,5-diazafluoren-9-onium bromide **1**, in the form of an acetic acid solvate, is reported. The compound crystallizes in the space group $P\bar{1}$ with $a = 6.2483(1)\text{\AA}$, $b = 11.8182(2)\text{\AA}$, $c = 14.8931(3)\text{\AA}$, $\alpha = 67.543(1)^\circ$, $\beta = 86.754(1)^\circ$, $\gamma = 79.304(1)^\circ$ and $Z = 2$. The quaternization of a nitrogen atom of the 4,5-diazafluoren-9-one molecule, manifested in the title cation, introduces significant asymmetry, reflected in differences in the geometries of the two pyridyl moieties. In contrast to related, previously reported tetracyclic systems that display a high degree of helical distortion, steric congestion in the title cation is minimal, rendering the 4,5-diazafluoren-9-onium moiety virtually planar. This is consistent with predictions based on NMR spectroscopy.

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Helicity may be induced *via* intramolecular strain. This type of distortion has usually been associated with systems containing five or more *ortho*-condensed aromatic rings.¹ Recently, helical distortion was detected by NMR spectroscopy and X-ray analysis in novel tetracyclic moieties synthesized from 1,10-phenanthroline and 4,5-diazafluoren-9-one salts.² Also, in the NMR spectra of *N*-phenacyl 1,10-phenanthroline bromides, the methylenic protons appear as a broad singlet, suggesting a strained stereostructure due to an intramolecular hydrogen bond near the coalescence temperature, which was eventually proved by X-ray analysis.³ However, in the case of 4,5-diazafluoren-9-one salts, the methylenic signal appears as a sharp singlet, indicating no intramolecular strain, or less strain than in the case of *N*-(4-chlorophenacyl)phenanthroline bromides.³ Furthermore, preliminary molecular modeling with various methods, such as MM2, MM3, PM5 and MNDO, resulted in a planar structure for the 4,5-diazafluoren-9-onium moiety. In order to verify these deductions, the representative compound **1** (Fig. 1) was subjected to X-ray analysis. Compound **1** was prepared according to a reported method⁴ from 4,5-diazafluoren-9-one and 2-bromo-4'-nitroacetophenone. Suitable crystals for X-ray crystallography were obtained by recrystallization from acetic acid.

Fig. 1 Chemical structure of the compound **1**.

A single crystal measuring 0.15×0.08×0.15 mm was selected for intensity data collection, mounted on a diffractometer and cooled in a continuous stream of nitrogen vapor at 113±2 K. Structure solution by direct methods revealed that a molecule of acetic acid co-crystallizes with the formula unit **1**, yielding a solvate. All hydrogen atoms were first located in difference Fourier maps and subsequently added at idealized positions with U_{iso} set at 1.2-times those of their parent atoms. A full-matrix

Table 1 Crystal and experimental data

CCDC deposition number	646399
Formula	(C ₁₉ H ₁₂ N ₃ O ₄) ⁺ ·Br ⁻ ·(CH ₃ COOH)
Formula weight	486.28
Crystal system	triclinic
Space group	$P\bar{1}$
Z	2
a	6.2483(1)Å
b	11.8182(2)Å
c	14.8931(3)Å
α	67.543(1)°
β	86.754(1)°
γ	79.304(1)°
V	998.58(3)Å ³
D_x	1.617 g cm ⁻³
No. of reflections used	4749
$2\theta_{max}$	55.6° with Mo K_α
R (3712 data, $I > 2\sigma(I)$)	0.0343
wR_2 (all 4749 data)	0.0653
$(\Delta/\sigma)_{max}$ final cycle	0.001
$(\Delta\rho)_{max}$	0.36 eÅ ⁻³
$(\Delta\rho)_{min}$	-0.32 eÅ ⁻³
Measurement	Nonius Kappa CCD
Absorption correction	SADABS
Program system	DENZO-SMN
Structure Determination	SHELXS-97
Refinement	full-matrix: SHELXL-97

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Fig. 2 ORTEP drawing of the asymmetric unit of **1** at the 50% probability level.

least-squares refinement on F^2 followed. All non-H atoms were treated anisotropically. Table 1 lists the crystal data and refinement details.

The crystal asymmetric unit shown in Fig. 2 comprises one formula unit of the salt **1** and an included molecule of the recrystallization solvent, acetic acid. An examination of the tricyclic system showed that the maximum deviation from the least-squares plane including the C and N atoms is only 0.024(2) Å (for atom C11), with atom O14 deviating by 0.063(2) Å from the former plane. This is analogous to the situation in the planar parent molecule, 4,5-diazafluoren-9-one,⁵ and in sharp contrast to the situation recently found in a compound containing the pyrrolo-diazafluoren-5-one system,² where the more congested tetracyclic ring system is significantly distorted due to an abnormally short intramolecular N...C contact of 2.797(2) Å. In the case of **1**, the absence of a fourth (pyrrolo) ring relieves the steric strain and the closest intramolecular contact in **1**, C15...N9, is significantly longer, namely 2.936(3) Å. This is also significantly longer than the intramolecular contact of 2.743(5) Å in the corresponding 1,10-phenanthroline analogue.³ The X-ray analysis thus confirms the prediction from the NMR data that the tricyclic system in **1** displays negligible helicity. The C15...N9 contact distance suggests the formation of an intramolecular hydrogen bond, C15-H15B...N9, for which H...N = 2.36 Å (whereas in the case of the 1,10-phenanthroline analogue the corresponding distance is 2.12 Å). However, the geometry of this interaction, with the angle C-H...N of 116°, is rather unfavorable as a result of the extended chain N1-C15-C16-C18 being almost orthogonal to the tricyclic system. The torsion angles listed in Table 2 define the overall conformation of the cation, indicating that the entire 4-nitrophenacyl residue lies roughly orthogonal to the plane of the tricyclic system. The second H atom of the methylene group at C15 engages in a similar, attractive interaction with atom O30 of the included acetic acid molecule (C15-H15A...O30, with H...O 2.35 Å, C...O 3.010(3) Å and $\angle$ C-H...O 124°). The methylene hydrogen atoms are thus rendered practically equivalent in the solid state by the interactions described above.

Quaternization of the atom N1 introduces asymmetry in the tricyclic system. Thus, the endocyclic angle at N1 is close to the trigonal value of 120°, while that at N9 (Table 2) is equal to the average of those found at the pyridine N centres in the symmetrical parent 4,5-diazafluoren-9-one (114.95(9) and

Table 2 Selected bond distances (Å), angles (°) and torsion angles (°)

N1 - C2	1.362(3)	N9 - C8	1.345(3)
N1 - C12	1.336(3)	N9 - C10	1.332(3)
N1 - C15	1.474(3)	C10 - C12	1.484(3)
C5 - C11	1.494(3)	C5 - C13	1.505(3)
N24 - O25	1.224(2)	N24 - O26	1.227(2)
C2 - N1 - C12	119.5(2)	C11 - C10 - C12	107.8(2)
C2 - N1 - C15	119.5(2)	C5 - C11 - C10	109.3(2)
C12 - N1 - C15	121.0(2)	C5 - C13 - C12	107.7(2)
N1 - C12 - C10	128.9(2)	C13 - C5 - C11	105.2(2)
C8 - N9 - C10	114.5(2)	C21 - N24 - O25	118.7(2)
N9 - C10 - C12	126.3(2)	C21 - N24 - O26	117.9(2)
C10 - C12 - C13	110.0(2)	O25 - N24 - O26	123.5(2)
N9 - C10 - C12 - N1	2.7(3)	N1 - C15 - C16 - C18	174.9(2)
C2 - N1 - C15 - C16	95.4(2)	C15 - C16 - C18 - C19	162.1(2)
N1 - C15 - C16 - O17	-5.2(3)	C20 - C21 - N24 - O25	-17.5(3)

114.09(9)°).⁵ The distances N1-C2 and C8-N9 likewise differ significantly in **1** (Table 2), the latter being identical to those reported for the parent compound (1.345(1), 1.348(2) Å).⁵

The strongest interaction in the crystal is a nearly linear hydrogen bond formed between the molecule of acetic acid and the bromide ion (O31-H...Br27, with H...Br 2.43 Å, O...Br 3.263(2) Å and $\angle$ O-H...Br 174°). Additional hydrogen bonds stabilizing the crystal structure are of the type C-H...O(nitro), involving each of the atoms C6, C7 and C8 with a different symmetry-related cation and with C...O distances in the range 3.133(3) - 3.399(3) Å. A search for π - π stacking interactions in the crystal revealed that the shortest of these has a ring centroid...centroid separation of ~3.9 Å, indicating that this type of interaction does not contribute significantly towards stabilising the crystal packing.

In conclusion, this is the first report detailing the consequences of unsymmetrical quaternization of the parent molecule 4,5-diazafluoren-9-one effected by a substituent other than a proton. Though significant asymmetry in the resulting 4,5-diazafluoren-9-one occurs, the low steric congestion results in negligible helicity, in keeping with the predictions based on solution NMR data.

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