Synthesis, Characterization, Crystal and Molecular Structure of 1,5-Dihydro-2*H*-cyclopenta[1,2-*b*:5,4-*b*′]dipyridin-2-imine

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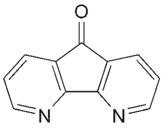
The reaction of 1,5-dihydro-2*H*-cyclopenta[1,2-*b*:5,4-*b*′]dipyridin-2-one (**3**) with an alkylamine (butylamine, hexylamine or ethylenediamine) yields, quite unexpectedly and in the absence of catalyst, the novel compound 1,5-dihydro-2*H*-cyclopenta[1,2-*b*:5,4-*b*′]dipyridin-2-imine (**4**) as the sole, analytically pure, solid product, which was fully characterized. The structure of **4** was unequivocally solved by single-crystal X-ray-diffraction analysis. The compound crystallizes in a monoclinic cell (space group $P\,2_1/c$), with two molecules in the asymmetric unit, held together by intermolecular H-bonds. Compound **4** could be interesting as a bi- or even tridentate ligand, and exhibits a strong fluorescence upon excitation at 310 nm. A mechanism, based on the observed C–N bond cleavage, is proposed.

Introduction. – 4,5-Diaza-9*H*-fluoren-9-one (daf; **1**)[2] has several distinct properties compared to 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen). For example, there are clear distinctions between daf and bipy in terms of bonding and coordination to transition metals [1]. The N(1)–C(2)–C(2′) angle in bipy has been reported to be 116° [2]. In the case of daf, this angle is enlarged to 126° due to the additional methylene bridge [3]. This distortion causes an increase in the 'bite angle' of daf (**1**) compared to bipy. The increased bite angle, in turn, leads to a reduction in the overlap between metal and ligand orbitals. As a result, daf (**1**) appears to be a weaker ligand than bipy (in spectrochemical series), which translates into a significant energy change in the ligand-field (LF) states [4]. Consequently, daf complexes are expected to exhibit spectroscopic properties different from those with bipy and phen ligands.



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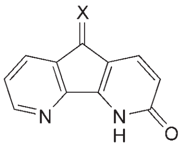
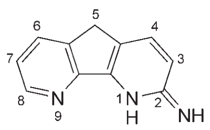


2 X = O
3 X = H_2



4
Arbitrary atom numbering

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[1] Authors responsible for X-ray crystal-structure analysis.
[2] Systematic name: 5*H*-cyclopenta[1,2-*b*:5,4-*b*′]dipyridin-5-one.

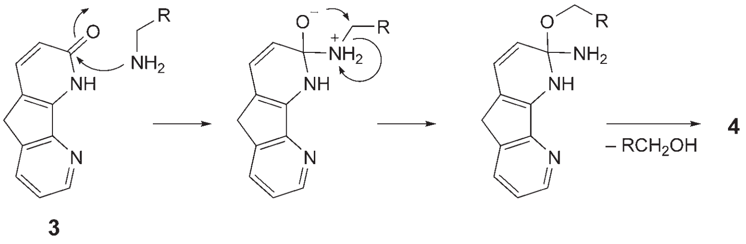
The chemistry of diazafluorenes has been rarely reported [3][4c] [5]. These compounds can be prepared from 1,10-phenanthroline. For example, permanganate oxidation of 1,10-phenanthroline yields two compounds [6], daf proper (**1**) and 1*H*-cyclopenta[1,2-*b*:5,4-*b*′]dipyridine-2,5-dione (**2**), besides 2,2′-bipyridine-3,3′-dicarboxylic acid, whereby **1** can be converted to **2** by oxidation. Compound **2** has two C=O groups that differ from each other. The C=O group in position 2 can be isomerized to its enolic form, with the involvement of the NH group, and in basic solution. The C=O group in position 5 cannot undergo any tautomerism because of the lack of a vicinal H-atom. This distinction provides an opportunity to reduce only one of the two C=O groups (the one in position 5) in basic solution. Indeed, in the presence of hydrazine as basic reducing agent, we were able to reduce compound **2** to the analogue **3**, which, in turn, was converted to the title compound **4**. Herein, we report the synthesis, purification, and characterization of the two new 4,5-diazafluorene derivatives **3** and **4**.

Results and Discussion. – Using hydrazine as reducing agent [6], compound **2** was selectively reduced to 1,5-dihydro-2*H*-cyclopenta[1,2-*b*:5,4-*b*′]dipyridin-2-one (**3**). As expected, only the C=O group in position 5 was reduced by hydrazine. The fact that the C=O group in position 2 remained untouched is attributed to its conversion to an enolic OH group in basic solution (tautomerism). Compound **3** was isolated as an analytically pure, colorless solid, and characterized by IR, ^{1}H-, and ^{13}C-NMR spectroscopy, as well as elemental analysis (see *Exper. Part*).

The reaction of **3** with an alkylamine is expected to afford the corresponding imine. However, when we tried to react **3** with ethylenediamine (=ethane-1,2-diamine) in EtOH to obtain the corresponding ethylene-bridged diimine, a different product was formed, *i.e.*, **4**. This compound crystallized in the reaction solution, forming red crystals suitable for structure determination by X-ray diffraction (see below).

The conversion of **3** to **4** was found to occur only in protic solvents such as EtOH. No reaction was observed in anhydrous THF or Et_2O. We also tested other amines such as ethylenediamine, butylamine, and hexylamine, but in all cases, compound **4** was isolated in yields of 70–80%, along with the formation of the corresponding alcohol (derived from the amine), as determined by gas chromatography (GC). A mechanism proposed for the unexpected conversion of **3** to **4** is proposed in the *Scheme.* Although various resonance structures are possible for compound **3**, for clarity, only one of them is explicitly drawn.

Scheme. *Proposed Mechanism for the Conversion of* **3** *to* **4**



The molecular structure of **4** was unequivocally determined by single-crystal X-ray diffraction (*Fig. 1*; see also *Table 3* in the *Exper. Part*). The monoclinic unit cell of **4** contains two molecules of the formula $C_{11}H_9N_3$ in the asymmetric unit. Each molecule is planar, excluding the H-atoms of the CH_2 group. Two molecules are almost parallel to each other in the asymmetric unit. The dihedral angle between the planes of the two moieties is 7.64(5)°. The smallest distance between these two molecules is 4.304(4) Å (N(2)–H···H–C(6))[3]. Selected bond lengths and angles are given in *Table 1*. It is worth to note that the imine bond distance (N(3)–C(10) 1.205(5) Å, N(3′)–C(10′) 1.199(5) Å)[4] is considerably shorter than the distances of the other C–N bonds in the molecule.

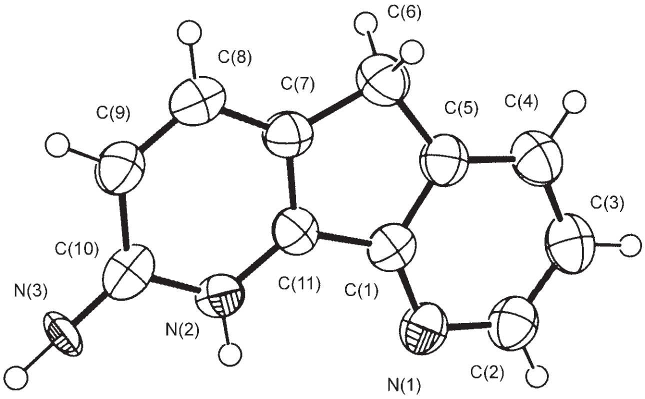


Fig. 1. *Solid-state structure of* **4**. Displacement ellipsoids are shown at 50% probability. Arbitrary atom numbering.

As shown in *Fig. 2,a*, the molecules in the crystal are held together by intermolecular H-bonds between N-atoms, with six intermolecular H-bonds in the asymmetric unit cell (*Table 2*). The molecular packing in the crystal is square pyramidal, as shown in *Fig. 2,b*, as viewed along the diagonal of the *a*/*b* axes.

The spectroscopic data of **4** are in accord with the molecular structure determined by X-ray crystallography. Noteworthy is the observation of ^1H-NMR signals at δ(H) 11.12 and 1.68 due to the imine H-atom (C=N–H) and H–N(1), respectively. The presence of the imino group is also evident from the IR absorption band at 1663 cm^{-1} (C=N stretching) and the ^{13}C-NMR chemical shift for C(2) at δ(C) 163.83.

In *Fig. 3*, the UV/VIS and emission spectra of **4** in deoxygenated CH_2Cl_2 solution are shown. Since the absorptions occur in the blue region, the compound appears red, with a strong fluorescence upon excitation at 310 nm.

Conclusions. – The new diazafluorene-based imine **4** was prepared and characterized spectroscopically, by mass spectrometry, and by X-ray diffraction. The

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[3] Arbitrary atom numbering (see *Fig. 1*).

[4] Primed numbers refer to the second molecule in the unit cell.

Table 1. *Selected Bond Lengths* (in Å)*, and Bond Angles and Torsion Angles* (in °). Arbitrary atom numbering (see *Fig. 1*).

N(1)−C(1)	1.332(5)	N(1′)−C(1′)	1.340(5)
N(1)−C(2)	1.345(5)	N(1′)−C(2′)	1.348(5)
N(2)−C(10)	1.390(5)	N(2′)−C(10′)	1.403(5)
N(2)−C(11)	1.358(5)	N(2′)−C(11′)	1.356(5)
N(2)−H	0.85(4)	N(2′)−H′)	0.78(4)
N(3)−C(10)	1.205(5)	N(3′)−C(10′)	1.199(5)
C(1)−C(5)	1.395(5)	C(1′)−C(5′)	1.400(5)
C(1)−C(11)	1.456(5)	C(1′)−C(11′)	1.465(5)
C(5)−C(6)	1.497(6)	C(5′)−C(6′)	1.503(6)
C(6)−C(7)	1.503(6)	C(6′)−C(7′)	1.503(6)
C(6)−$\mathrm{H_A}$	0.97(4)	C(6′)−$\mathrm{H_A}'$	1.03(4)
C(6)−$\mathrm{H_B}$	1.05(5)	C(6′)−$\mathrm{H_B}'$	0.97(4)
N(1)−C(1)−C(11)	126.8(4)	N(1′)−C(1′)−C(11′)	127.6(4)
N(1)−C(2)−C(3)	124.2(4)	N(1′)−C(2′)−C(3′)	124.1(4)
N(1)−C(1)−C(5)	125.7(4)	N(1′)−C(1′)−C(5′)	125.1(4)
N(2)−C(11)−C(1)	128.9(4)	N(2′)−C(11′)−C(1′)	128.0(4)
N(2)−C(11)−C(7)	121.5(4)	N(2′)−C(11′)−C(7′)	121.7(4)
N(2)−C(10)−C(9)	114.0(4)	N(2′)−C(10′)−C(9′)	112.6(4)
N(3)−C(10)−N(2)	121.4(4)	N(3′)−C(10′)−N(2′)	121.1(4)
N(3)−C(10)−C(9)	124.6(4)	N(3′)−C(10′)−C(9′)	126.3(4)
C(1)−N(1)−C(2)	114.5(4)	C(1′)−N(1′)−C(2′)	114.4(4)
C(1)−C(5)−C(6)	110.3(4)	C(1′)−C(5′)−C(6′)	109.9(4)
C(11)−N(2)−C(10)	123.1(4)	C(11′)−N(2′)−C(10′)	123.4(4)
C(11)−C(7)−C(6)	110.2(4)	C(11′)−C(7′)−C(6′)	109.4(4)
C(11)−C(7)−C(8)	119.0(4)	C(11′)−C(7′)−C(8′)	118.7(4)
C(4)−C(5)−C(6)	131.1(4)	C(4′)−C(5′)−C(6′)	131.3(4)
C(5)−C(6)−C(7)	102.3(3)	C(7′)−C(6′)−C(5′)	103.2(4)
C(5)−C(1)−C(11)	107.5(3)	C(5′)−C(1′)−C(11′)	107.3(4)
C(8)−C(7)−C(6)	130.7(4)	C(8′)−C(7′)−C(6′)	131.9(4)
$\mathrm{H_A}$−C(6)−$\mathrm{H_B}$	111(3)	$\mathrm{H_A}'$−C(6′)−$\mathrm{H_B}'$	106(3)
N(2)−C(11)−C(1)−N(1)	1.1(6)	N(2′)−C(11′)−C(1′)−N(1′)	1.8(7)
C(1)−C(5)−C(6)−C(7)	1.8(5)	C(1′)−C(5′)−C(6′)−C(7′)	1.0(5)
C(11)−C(7)−C(6)−C(5)	− 1.4(5)	C(11′)−C(7′)−C(6′)−C(5′)	− 1.0(5)

compound possessed three N-atoms with lone pairs for coordination and, thus, may act as a novel bidentate (or even tridentate) ligand. The complexation properties of **4** towards different transition metals are currently under investigation and will be reported in due course.

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Experimental Part

General. All chemicals and solvents used for synthesis were commercially available, reagent grade, and used without further purification. 1*H*-Cyclopenta[1,2-*b*:5,4-*b*′]dipyridine-2,5-dione (**2**) was prepared according to the literature [6] by either permanganate oxidation of 1,10-phenanthroline or manganate

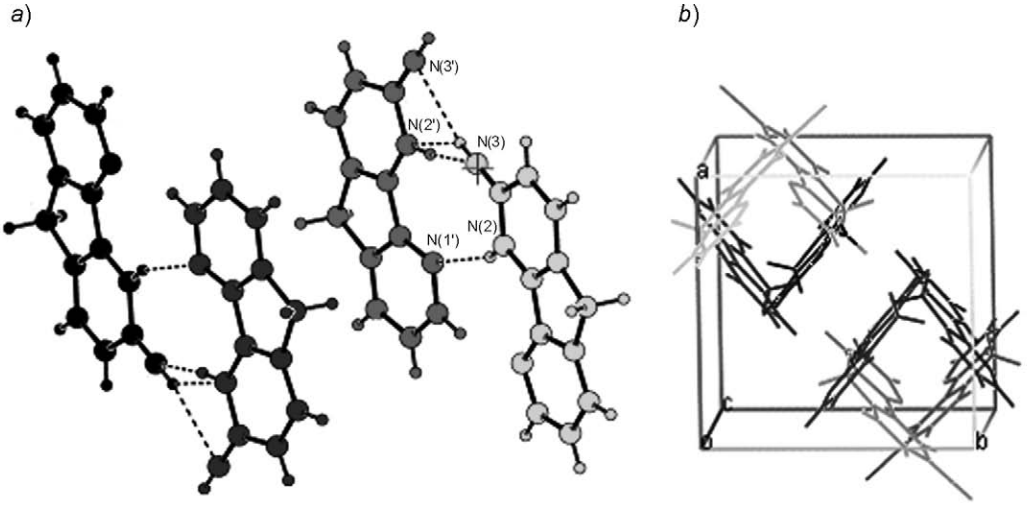

Fig. 2. *Packing diagram of* **4** *showing* a) *H-bonding and* b) *unit-cell geometry*

Table 2. *Selected Hydrogen-Bonding Parameters for* **4**. 'D' and 'A' refer to H-bond donor and acceptor, resp.

D–H···A	D–H [Å]	A···H [Å]	D···A [Å]	D–H···A [°]
N(2)–H···N(1′)[a]	0.85(4)	2.40(4)	3.204(5)	160(3)
N(2′)–H′···N(3)[a]	0.78(4)	2.00(4)	2.743(5)	160(3)
N(3)–H···N(2′)[a]	0.86	2.02	2.743(5)	141
N(3)–H···N(3′)[a]	0.86	2.57	3.388(4)	160
C(4′)–H···N(3′)[b]	0.93	2.61	3.389(5)	142
C(8)–H···N(3)[c]	0.93	2.37	3.282(5)	167

[a]) $1-x$, $2-y$, $1-z$. [b]) x, $3/2-y$, $-1/2+z$. [c]) $2-x$, $-1/2+y$, $1/2-z$.

oxidation of 4,5-diaza-9*H*-fluoren-9-one (**1**) in basic soln. Melting points are uncorrected. UV/VIS and Fluorescence spectra were recorded in CH_2Cl_2 soln. in 1-cm quartz cells. IR Spectra were recorded on an FT-IR spectrometer using KBr discs; in cm^{-1}. NMR Chemical shifts δ and coupling constants J are given in ppm rel. to Me_4Si, and in Hz, resp.

*1,5-Dihydro-2*H*-cyclopenta[1,2-*b*:5,4-*b′*]dipyridin-2-one* (**3**). A soln. of **2** (1.00 g, 5.05 mmol) in hydrazine hydrate (30 ml) was heated at reflux for 8 h, and then left to cool down to r.t. Dist. H_2O (100 ml) was added, and the mixture was left overnight. The resulting light-yellow precipitate was filtered off, dried, and recrystallized from H_2O to afford pure **3**. Yield: 0.74 g (80%). M.p. 258–260°. IR (KBr): 1642 (C=O). ^1H-NMR (400 MHz, CD_2Cl_2)[5]): 8.56 (*d*, $J=4.9$, H–C(8)); 7.78 (*d*, $J=7.4$, H–C(6)); 7.56 (*d*, $J=9.2$, H–C(4)); 7.21 (*dd*, $J=7.4$, 4.9, H–C(7)); 6.51 (*d*, $J=9.2$, H–C(3)); 3.58 (*s*, CH_2(5)). ^{13}C-NMR (100 MHz, CD_2Cl_2): 163.26; 153.98; 148.60; 144.63; 138.39; 138.04; 132.54; 122.09; 121.62; 120.77; 32.06. Anal. calc. for $C_{11}H_8N_2O$: C 71.74, H 4.35, N 15.22; found: C 71.62, H 4.30, N 15.17.

*1,5-Dihydro-2*H*-cyclopenta[1,2-*b*:5,4-*b′*]dipyridin-2-imine* (**4**). Compound **3** (0.25 g, 1.4 mmol) was added to a soln. of ethylenediamine (41 mg, 0.68 mmol) in EtOH (25 ml) at r.t. The mixture was heated at reflux for 4 h. Upon cooling the soln. down to r.t., **4** was obtained as red crystals. Yield: 0.19 g (76%).

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[5]) Arbitrary atom numbering (see chemical formula).

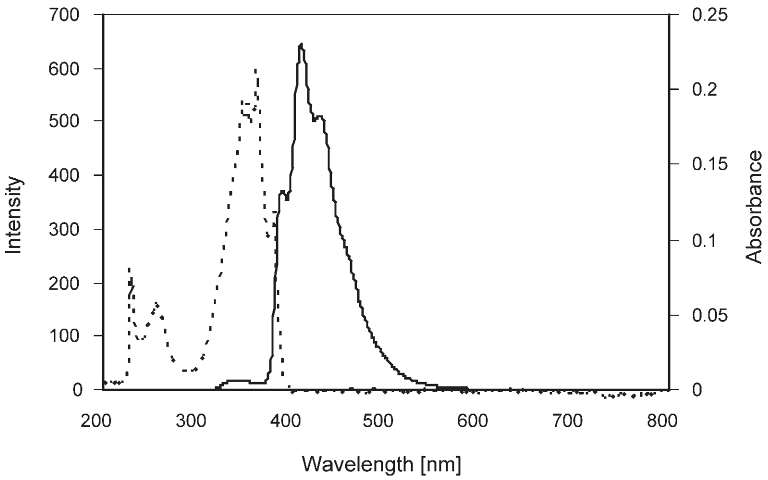

Fig. 3. *UV/VIS* (---) *and Fluorescence* (–) *spectra of* **4** *in deoxygenated* CH_2Cl_2 *soln. at ambient temperature*

Table 3. *Crystal and Refinement Data of* **4**

Formula	$(C_{11}H_8N_3)_2$
M_r [g/mol]	366.43
Crystal system, space group	Monoclinic, $P\ 2_1/c$
Unit cell dimensions [Å, °]:	$a = 10.326(1)$
	$b = 9.716(1)$
	$c = 17.735(3)$
	$\beta = 105.78(1)$
V [Å^3]	1712.2(4)
Z	4
D_x [g cm^{-3}]	1.421
μ [mm^{-1}]	0.089
$F(000)$	768
Temperature [K]	293(2)
Radiation, wavelength [Å]	MoK_α, 0.71073
θ Range [°]	2.39–26.29
Absorption correction	Psi-scan ($T_{\min} = 0.979$, $T_{\max} = 0.982$)
Data set	$-12 \le h \le 0$, $0 \le k \le 12$, $-21 \le l \le 22$
Refinement on F^2	$w = 1/[\sigma^2 F_0^2 + (0.08322PP)^2 + 0.5936P]$
	$P = (F_0^2 + 2F_c^2)/3)$
Nref, Npar refined	3077, 277
$R\ [F^2 > 2\sigma(F^2)]$, $wR(F^2)$	0.0639, 0.1954
$(\Delta/\sigma)_{\max}$	0.000
Goodness of fit	1.023
$\Delta\rho_{\min}$, $\Delta\rho_{\max}$ [e Å^{-3}]	-0.49, 0.33

M.p. 265–266°. IR (KBr): 1663 (C=N). ^{1}H-NMR (400 MHz, CD_2Cl_2)[5]: 11.12 (br. *s*, C(2)=NH); 8.58 (d, $J = 4.8$, H–C(8)); 7.80 (*d*, $J = 7.6$, H–C(6)); 7.58 (*d*, $J = 9.2$, H–C(4)); 7.22 (*dd*, $J = 7.6$, 4.8, H–C(7)); 6.51 (*d*, $J = 9.2$, H–C(3)); 3.60 (*s*, CH_2(5)); 1.68 (br. *s*, H–N(1)). ^{13}C-NMR (100 MHz, CD_2Cl_2)[5]: 163.83;

154.01; 148.62; 144.60; 138.42; 138.16; 132.56; 122.14; 121.59; 120.74; 32.06. Anal. calc. for $C_{11}H_9N_3$: C 72.13, H 4.92, N 22.95; found: C 72.06, H 4.41, N 22.84.

X-Ray Crystal-Structure Analysis[6]). A shapeless, red crystal of **4** (0.3 × 0.2 × 0.2 mm) was used. X-Ray diffraction data were collected on an *Enraf-Nonius CAD4* diffractometer operated in the $\omega/2\theta$ scan mode, using graphite-monochromated MoK_α radiation at r.t. The lattice parameters and their estimated standard deviations were determined from least-squares refinement of 17 centered reflections in the range of $8.69 \leq \theta \leq 18.00°$ by using CAD4 Express [7]. During data collection, three standard reflections were periodically measured every 2 h, which showed no significant intensity variation. A total of 3,243 reflections were collected in the range $2.39 \leq \theta \leq 26.29°$, of which 3,077 independent reflections were used for the structure determination (*Table 3*). Data reduction was carried out with XCAD4 [8]. The structure was solved by direct methods, and refined with the programs SHELXS97 and SHELXL97 [9], resp., in the WinGX software package [10]. A full-matrix least-squares refinement on F^2 converged at $R = 0.053$. Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* [11]. The H-atoms of the CH_2 groups and also on N(2) and N(5) were taken from a difference *Fourier* map and refined, while the other H-atoms were placed with $U_{iso}(H) = 1.2\ U_{eq}(C)$. For all non-H-atoms, anisotropic displacement parameters were refined. *Fig. 1* was drawn with ORTEP [12], and H-bonds and the molecular packing geometry were calculated with PLATON [13].

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[6]) The crystallographic data of **4** have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication number CCDC-623143. Copies of the data can be obtained, free of charge, at http://www.ccdc.cam.ac.uk/data_request/cif.