Crystal Structure of the [Protonated 2-(phenylazo)pyridine and Protonated 2-(4-hydroxyphenylazo)pyridine (3:1)]tetrafluoroborate

Kaliyamoorthy PANNEERSELVAM,* Kanidtha HANSONGNERN,** Nattaporn RATTANAWIT,**
Fen-Ling LIAO,*** and Tian-Huey LU*†

*Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300, R.O.C.

**Department of Chemistry, Faculty of Science, Prince of Songkla University,
Hat-Yai, Songkla 90112, Thailand

***Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300, R.O.C.

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In general, geometrical isomerism of azo-compounds is known to exist in two forms, *cis* and *trans*. However, 2-(phenylazo)pyridine (or azpy) was synthesized to be in *trans* form only by Campbell and coworkers.¹ The azpy molecule contains one nitrogen on pyridine and one on the azo moiety. They are acting as the donor atoms to metal ions.² In acidic solution, both nitrogens can react with protons. However, this gives rise to a question, which nitrogen is more basic towards protons. In this work, we confirm that the azo nitrogen is more basic than the other by X-ray analysis (Fig. 1).

The 2-(phenylazo)pyridine (or azpy) was synthesized using literature procedures.¹ Concentrated HCl 2.5 mL was added to the aqueous solution containing CoCl₂·H₂O 0.5 mmol. Azpy 1.5 mmol in ethanolic solution was added to the cobalt solution. The mixture was stirred at room temperature for 10 min. Then H₂O₂ 30% 3.5 mL and NH₄PF₆ 2.5 mmol were added to the solution mixture. Single crystals of the protonated azpy were

grown at 298 K by slow diffusion of hexane into the reaction mixture.

The molecular structure of the title compound is shown in Fig. 2. When azpy ligand reacts with the metal, N(1) and N(3) are bonded to metal ion. This means that N(1) is more basic than N(2) and should be protonated. The difference-Fourier map showed a big electron density near N(1). The results from X-ray data indicate that the protonation occurs at the azo nitrogen (N1) and it is more strongly basic than the pyridine nitrogen (N3). In addition, N(1)–N(2) distance, which is similar to that of the azobenzene, is 1.248(4) Å.³ The benzene ring and

Fig. 1 Structural chemical diagram.

Fig. 2 The molecular structure showing with the labeling atoms. Thermal ellipsoids are drawn at the 30% probability level. The dashed lines indicate the intramolecular N–H...N hydrogen bond.

Table 1 Crystal and experimental data

Formula: (C ₁₁ H ₁₀ N ₃ O _{0.25}) (BF ₄)	
Formula weight = 275.03	
Crystal system: monoclinic	Z = 8
Space group: C2/c	
a = 29.875(4) Å	
b = 5.930(1) Å	
c = 13.743(2) Å	
β = 91.16(1)°	
V = 2434.2(6) Å ³	
D _x = 1.501 g/cm ³	
μ(Mo Kα) = 0.135 mm ⁻¹	
T = 293(2) K	
Color: brown	
F(0 0 0) = 1120	
0.32 × 0.25 × 0.20 mm	
Radiation: Mo Kα (λ = 0.71073 Å)	
2θ _{max} = 56.0°	
No. of reflections measured: 6553	
R = 0.074 (on F)	
Rw = 0.219 (on I)	
No. of reflection used = 1472 (I > 2σ(I))	
No. of parameters = 181	
Goodness-of-fit = 1.04	
(Δ/σ) _{max} final cycle: 0.001	
(Δρ) _{max} = 0.36 e Å ⁻³	
(Δρ) _{min} = -0.28 e Å ⁻³	
Measurements: Siemens SMART CCD	
Program system: NRCVAX	
Structure determination: heavy atom methods (SHELXS-97)	
Refinement: full matrix least-squares (SHELXL-97)	

† To whom correspondence should be addressed.

Table 2 Final coordinates and equivalent temperature factors ($\text{\AA}^2$) for non-H atoms

Atom	x	y	z	U_{eq}
N(1)	0.1778(1)	0.2606(5)	0.3810(2)	0.056(1)
N(2)	0.1650(1)	0.0652(5)	0.3615(2)	0.056(1)
N(3)	0.0927(1)	0.1926(5)	0.4104(2)	0.060(1)
C(1)	0.2244(1)	0.2942(5)	0.3758(2)	0.050(1)
C(2)	0.2404(1)	0.5083(6)	0.4039(2)	0.064(1)
C(3)	0.2850(1)	0.5504(6)	0.4028(2)	0.069(1)
C(4)	0.3150(1)	0.3897(6)	0.3735(2)	0.064(1)
O(1)#	0.3541(3)	0.4792(17)	0.3846(6)	0.066(2)
C(5)	0.2990(1)	0.1816(6)	0.3440(2)	0.059(1)
C(6)	0.2542(1)	0.1332(5)	0.3444(2)	0.051(1)
C(7)	0.1182(1)	0.0368(5)	0.3672(2)	0.053(1)
C(8)	0.0480(1)	0.1680(7)	0.4147(3)	0.074(1)
C(9)	0.0273(1)	-0.0178(8)	0.3736(3)	0.076(1)
C(10)	0.0531(1)	-0.1786(7)	0.3305(3)	0.073(1)
C(11)	0.0989(1)	-0.1538(6)	0.3278(2)	0.064(1)
B(1)	0.4189(1)	0.8661(8)	0.3904(3)	0.066(1)
F(1)	0.3981(1)	0.8956(5)	0.3029(2)	0.113(1)
F(2)	0.3907(1)	0.9484(5)	0.4628(2)	0.114(1)
F(3)	0.4246(1)	0.6398(5)	0.4066(2)	0.113(1)
F(4)	0.4585(1)	0.9723(6)	0.3957(3)	0.142(1)

Occupancy = 0.25. $U_{eq} = (1/3) \sum \sum U_{ij} a_i^* a_j^* (a_i a_j)$.

pyridine rings are almost planar and their interplanar angle is $9.3(1)^\circ$. The azo bond is not in the same plane as the benzene ring with the torsion angle N2-N1-C1-C6 being $5.0(4)^\circ$; meanwhile, that of N1-N2-C7-N3 is $-13.8(4)^\circ$. This implies that the pyridine ring is slightly distorted. This could be due to the repulsion between N1 and N3 besides the hydrogen bond interaction between N3 and H1(N1). The crystal structure is stabilized by intramolecular N-H...N hydrogen bonds and van der Waals forces. In addition, some oxidation products of the azpy compounds were observed as 25% of the total products. This is similar to the oxidation of aromatic compound, using air as the oxidant and Co(III) salts as catalyst.⁴ However, the mechanism to produce such products is too complicated and was not investigated further. All the H-atoms (except the hydroxy group) were fixed geometrically and refined using constraints with isotropic temperature factor.

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Table 3 Bond distances ($\text{\AA}$) and angles ($^\circ$)

N(1)-N(2)	1.248(4)	N(1)-C(1)	1.412(4)
N(2)-C(7)	1.411(4)	N(3)-C(7)	1.344(4)
N(3)-C(8)	1.346(4)	C(1)-C(6)	1.379(4)
C(1)-C(2)	1.408(5)	C(2)-C(3)	1.355(5)
C(3)-C(4)	1.374(5)	C(4)-O(1)	1.290(9)
C(4)-C(5)	1.382(5)	C(5)-C(6)	1.370(4)
C(7)-C(11)	1.375(5)	C(8)-C(9)	1.378(6)
C(9)-C(10)	1.369(5)	C(10)-C(11)	1.377(5)
B(1)-F(4)	1.339(5)	B(1)-F(1)	1.354(5)
B(1)-F(3)	1.370(5)	B(1)-F(2)	1.404(5)

N(2)-N(1)-C(1)	114.8(2)	N(1)-N(2)-C(7)	113.5(3)
C(7)-N(3)-C(8)	121.1(3)	C(6)-C(1)-C(2)	119.5(3)
C(6)-C(1)-N(1)	124.2(3)	C(2)-C(1)-N(1)	116.3(3)
C(3)-C(2)-C(1)	119.4(3)	C(2)-C(3)-C(4)	121.5(3)
O(1)-C(4)-C(3)	106.0(5)	O(1)-C(4)-C(5)	135.2(6)
C(3)-C(4)-C(5)	118.8(3)	C(6)-C(5)-C(4)	121.2(3)
C(5)-C(6)-C(1)	119.5(3)	N(3)-C(7)-C(11)	120.1(3)
N(3)-C(7)-N(2)	120.9(3)	C(11)-C(7)-N(2)	119.0(3)
N(3)-C(8)-C(9)	120.4(3)	C(10)-C(9)-C(8)	118.8(3)
C(9)-C(10)-C(11)	120.4(4)	C(7)-C(11)-C(10)	119.1(3)
F(4)-B(1)-F(1)	112.1(4)	F(4)-B(1)-F(3)	110.3(3)
F(1)-B(1)-F(3)	108.9(3)	F(4)-B(1)-F(2)	109.8(3)
F(1)-B(1)-F(2)	108.2(3)	F(3)-B(1)-F(2)	107.4(4)

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