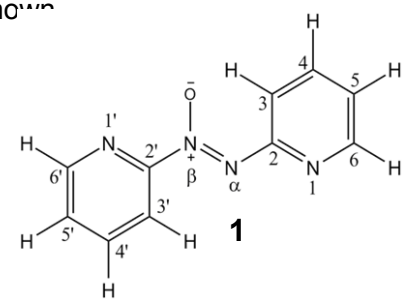
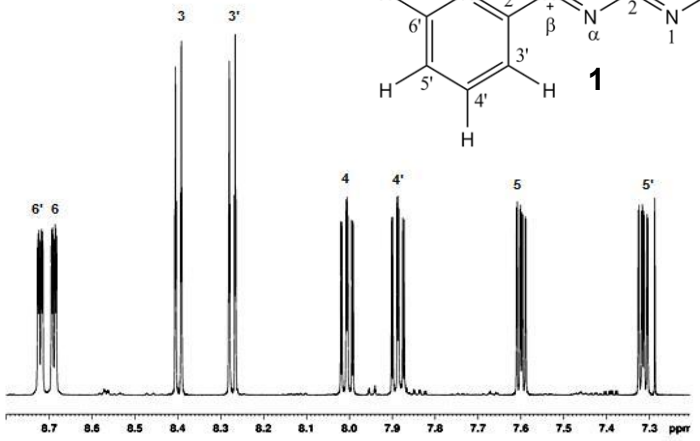
A reaction has produces two compounds, **1** and **2**, the structure of compound **2** is unknown

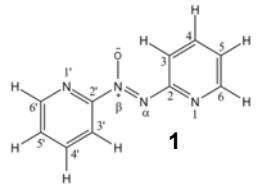
^{1}H NMR spectrum and structure of **1**





The assignment of primed and non-primed rings can be interchanged.

NMR data of **1**



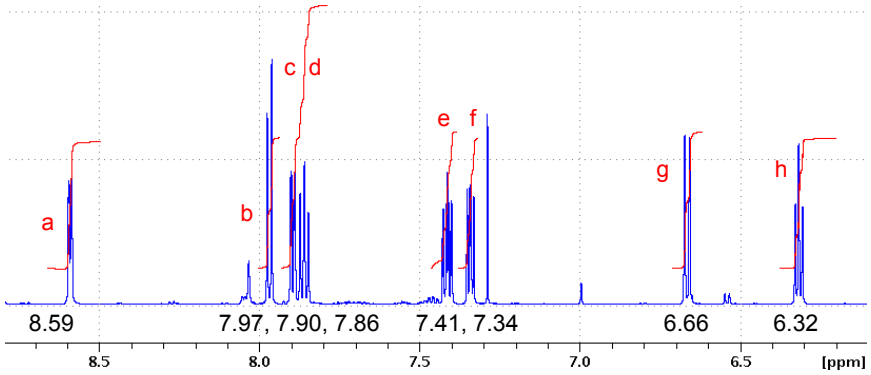
1

The assignment of primed and non-primed rings can be interchanged.

Number	^{1}H chemical shift (ppm)	Multiplicity/Coupling Constant (Hz)	^{13}C chemical shift (ppm)[a]	^{15}N chemical shift (ppm)
1				292
2			157.12, s	
3	8.40	dt: 8.2, 0.9, 0.9	117.67, d	
4	8.01	ddd: 8.2, 7.4, 1.9	139.21, d	
5	7.60	ddd: 7.4, 4.7, 1.0	127.24, d	
6	8.69	ddd: 4.7, 1.8, 0.9	148.68, d	
1’				304
2’			156.27, s	
3’	8.27	dt: 8.2, 1.0, 1.0	118.55, d	
4’	7.89	ddd: 8.2, 7.5, 1.9	137.86, d	
5’	7.32	ddd: 7.5, 4.7, 1.0	123.78, d	
6’	8.72	ddd: 4.7, 1.9, 0.9	149.61, d	
α				330
β				331

^{1}H NMR spectrum of **2**

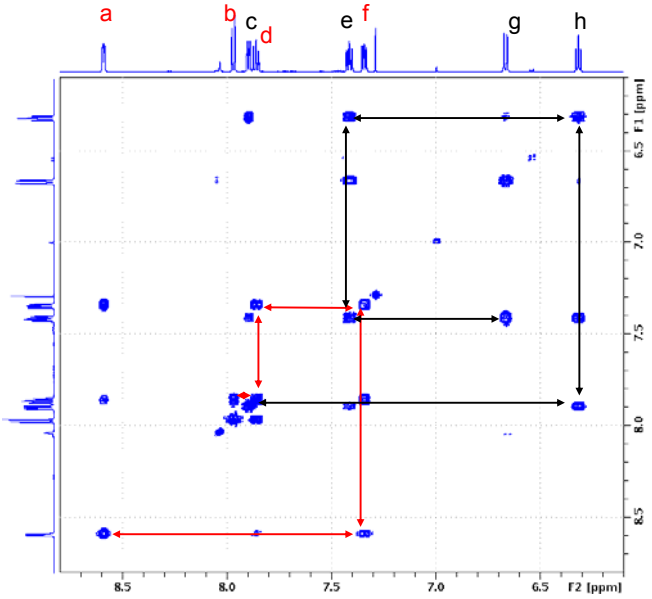
$C_{10}H_8N_2O$ (M_W = 172.18 g/mol)



Tasks.

1. Label the ^{1}H signals a-h starting from the most deshielded proton.

2D COSY spectrum of **2**

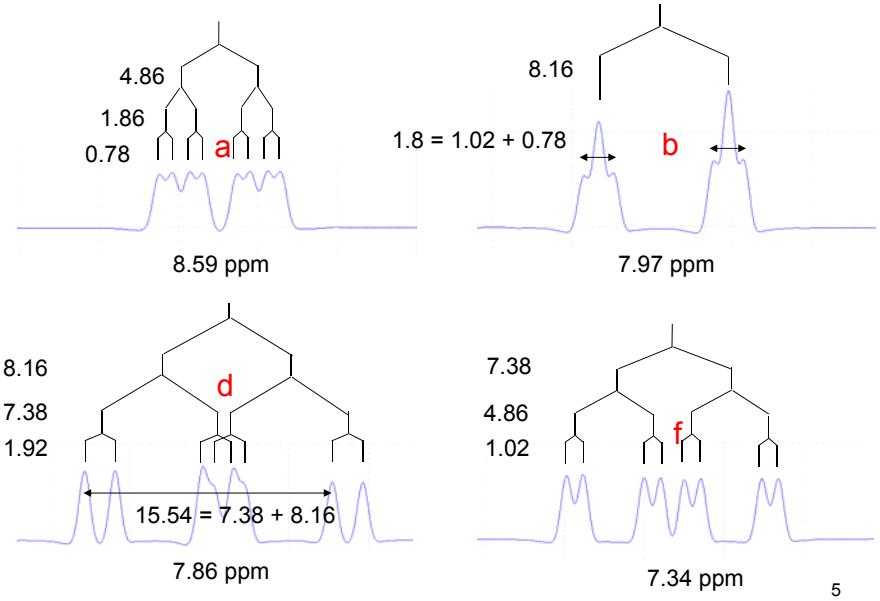


Two spin systems were identified based on the intense cross peaks (large coupling constants):

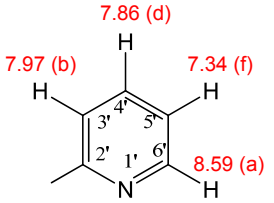
a ↔ f ↔ d ↔ b

c ↔ h ↔ e ↔ g

Selected ^{1}H multiplets of **2**

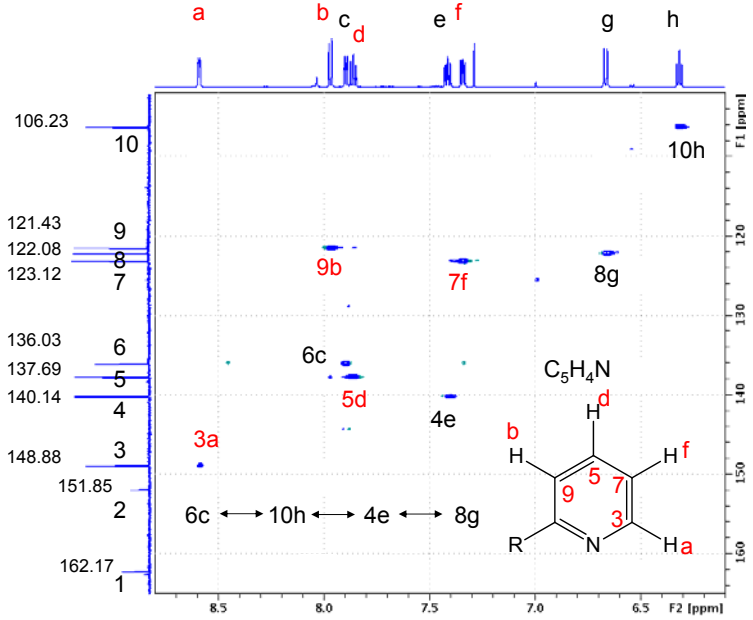


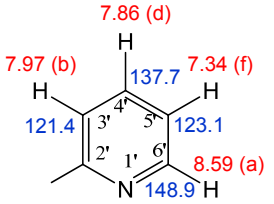
Based on coupling constants and chemical shifts spin system a, f, d, b belongs to a pyridine ring.



Number	^{1}H chemical shift (ppm)	Multiplicity/Coupling Constant (Hz)	^{13}C chemical shift (ppm)[a]	^{15}N chemical shift (ppm)
a	8.59	ddd: 4.9, 1.9, 0.8		
f	7.34	ddd:7.4, 4.9, 1.0		
d	7.86	ddd:8.2, 7.4, 1.9		
b	7.97	ddd: 8.2, 1.0, 0.8		
c	7.90	ddd: 7.1, 2.1, 0.7		
h	6.32	ddd: 6.8, 6.8, 1.3		
e	7.41	ddd: 9.2, 6.5, 2.1		
g	6.66	ddd: 9.2, 1.3, 0.7		

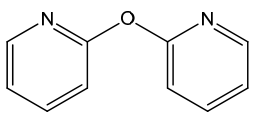
2D ^{1}H, ^{13}C HSQC spectrum of **2**



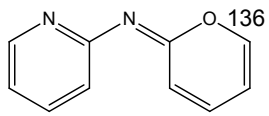


Number	^{1}H chemical shift (ppm)	Multiplicity/Coupling Constant (Hz)	^{13}C chemical shift (ppm)[a]	^{15}N chemical shift (ppm)
a	8.59	ddd: 4.9, 1.9, 0.8	148.9	
f	7.34	ddd:7.4, 4.9, 1.0	123.1	
d	7.86	ddd:8.2, 7.4, 1.9	137.7	
b	7.97	ddd: 8.2, 1.0, 0.8	121.4	
c	7.90	ddd: 7.1, 2.1, 0.7	136.0	
h	6.32	ddd: 6.8, 6.8, 1.3	106.2	
e	7.41	ddd: 9.2, 6.5, 2.1	140.1	
g	6.66	ddd: 9.2, 1.3, 0.7	122.1	

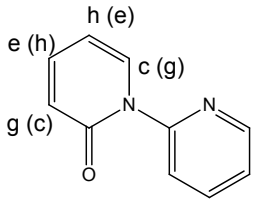
- $C_{10}H_8N_2O$ minus C_5H_4N is C_5H_4NO – the non-pyridine part of the molecule
- $C_aH_bO_cN_d$: Dbe = [(2a+2) – (b-d)]/2
- The double-bond equivalent for $C_{10}H_8ON_2$: $C_aH_bO_cN_d$is Dbe = [(2*10+2) – (8-2)]/2 = 8
- The double-bond equivalent for C_5H_4N and C_5H_4NO is 4.5 each because these are radicals. However, the Dbe of pyridine ring is 4, therefore the other part of the molecule is also 4.
- Candidate structures:



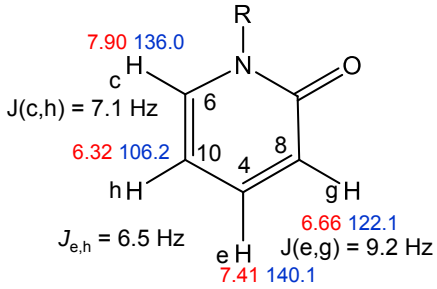
Symmetrical, less signals than observed

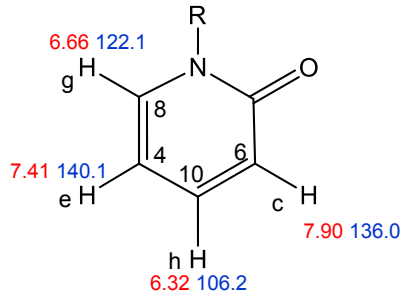


The chemical shift of carbon next to O has too low chemical shift



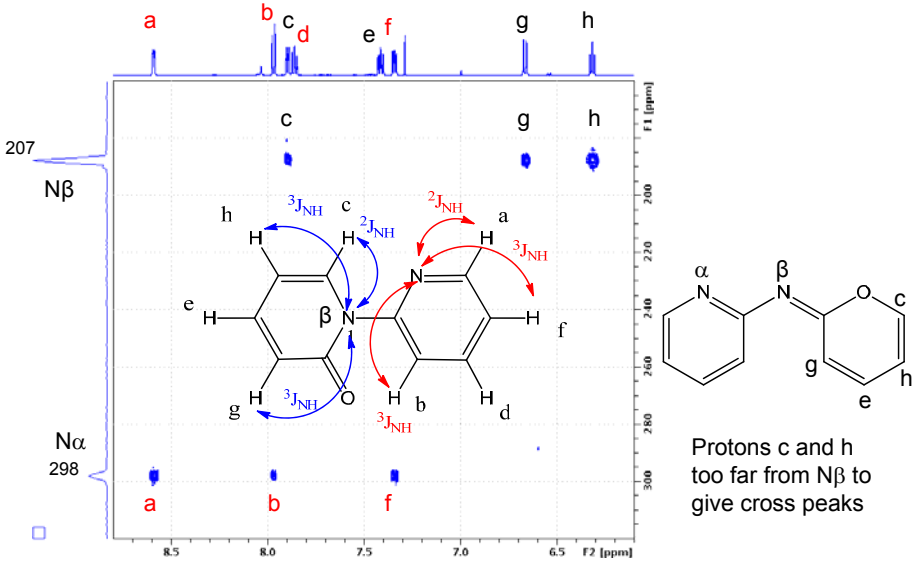
Possible. Two ways of assigning resonances





- Based on the chemical shift of 6c, the assignment on the left is more likely

2D ^{1}H, ^{15}N HMBC spectrum of **2**



Protons c and h too far from Nβ to give cross peaks

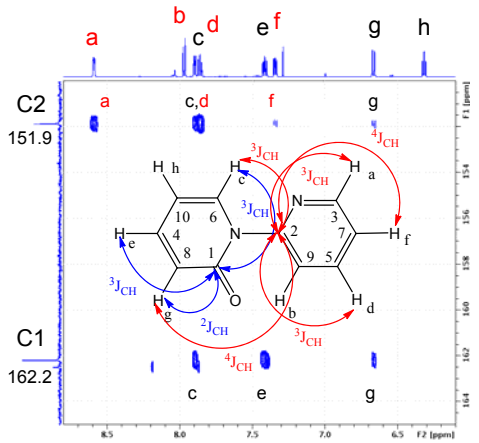
1. The absence of the He, Nβ cross peaks supports the current assignment.
2. The missing (expected) cross peak Hb, Nβ does not invalidate the structure, but it would be nice to have a positive proof for the connection of the two rings.

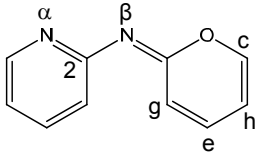
^{15}N chemical shifts are in line with the proposed structure. (pyridine N1 at 292 and 304 ppm in compound **1**.

Number	^{1}H chemical shift (ppm)	Multiplicity/Coupling Constant (Hz)	^{13}C chemical shift (ppm)[a]	^{15}N chemical shift (ppm)
Nα				298
a	8.59	ddd: 4.9, 1.9, 0.8	148.9	
f	7.34	ddd:7.4, 4.9, 1.0	123.1	
d	7.86	ddd:8.2, 7.4, 1.9	137.7	
b	8.16	ddd: 8.2, 1.0, 0.8	121.4	
Nβ				207
c	7.90	ddd: 7.1, 2.1, 0.7	136.0	
h	6.32	ddd: 6.8, 6.8, 1.3	106.2	
e	7.41	ddd: 9.2, 6.5, 2.1	140.1	
g	6.66	ddd: 9.2, 1.3, 0.7	122.1	

Partial 2D ^{1}H, ^{13}C HMBC spectra of **2** (quaternary carbons only) optimised for different couplings

Optimised for $^{n}J_{CH}$ = 10 Hz





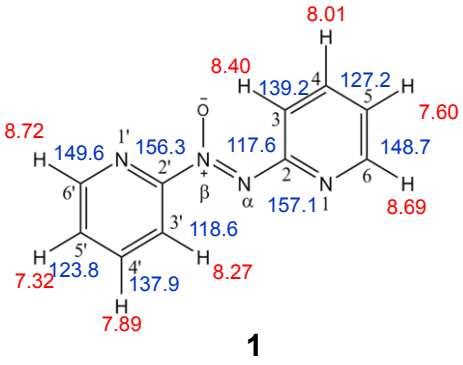
Proton c too far from C2 to give a cross peak

1. The important cross peaks are between C2 and protons c and g.
2. The fact that *J*(C2, Hc) > *J*(C2, Hg) supports the current assignment.

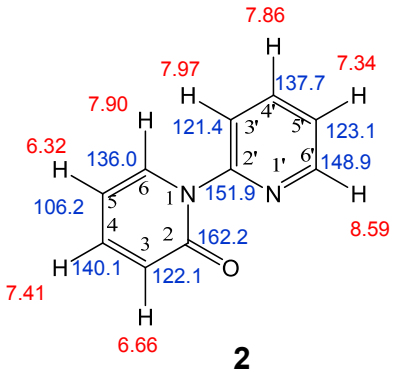
Complete assignment of ^{1}H, ^{13}C and ^{15}N of **2**

Number	^{1}H chemical shift (ppm)	Multiplicity/Coupling Constant (Hz)	^{13}C chemical shift (ppm)[a]	^{15}N chemical shift (ppm)
Nα				298
C2			151.9	
a	8.59	ddd: 4.9, 1.9, 0.8	148.9	
f	7.34	ddd:7.4, 4.9, 1.0	123.1	
d	7.86	ddd:8.2, 7.4, 1.9	137.7	
b	7.97	ddd: 8.2, 1.0, 0.8	121.4	
Nβ				207
C1			162.2	
c	7.90	ddd: 7.1, 2.1, 0.7	136.0	
h	6.32	ddd: 6.8, 6.8, 1.3	106.2	
e	7.41	ddd: 9.2, 6.5, 2.1	140.1	
g	6.66	ddd: 9.2, 1.3, 0.7	122.1	

Comparison of ^{1}H and ^{13}C chemical shifts of **1** and **2**



1



2

Note: The assignment of primed and non-primed rings in compound **1** can be interchanged.