C01 SOLUTION

IR

Signal (cm^{-1})	**Interpretation**
~ 3000	CH_{st}
2250 (sharp)	X≡Y; X=Y=Z
1800-2000 (weak)	Aromatic overtones?
1725 (strong)	C=O

Summary:

hints of triple bond or conjugated double bond, carbonyl and aromatic;

No indication of –OH or -NH

MS

m/z	Δm/z	**Interpretation**
161		$M^{\bullet+}$??; If yes, N contained; no signs of Cl, Br
130	-31	Base peak; loss of CH_3O; CH_3NH_2; N_2H_3?; ^{13}C ~ 9% => ~ 8C
102	-59	loss of C_3H_7O; $C_2H_3O_2$; C_3H_9N?;
39;51;75		Suggestive of aromatic ring

Hint: the fact that the dominant fragments are even-numbered suggests a N-containing compound, thus most likely m/z 161 is the molecular ion.

^{13}C-NMR

δ (ppm)	DEPT	Interpretation
165	C	X-C=O
133	C	Aromatic;olefin;nitrile?
132	CH	
130	CH	
118	C	
116	C	
53	CH_3	X-CH_3

$\Sigma_C \geq 7$; $\Sigma_H \geq 5$

^{1}H-NMR

δ (ppm)	integral	Signal (*J*[Hz])	Interpretation
8.12-8.15	2	d+ higher order (8.4)	Aromatic (para-disubstituted ring; AA'BB')
7.73-7.75	2	d+ higher order (8.4)	
3.9	3	s	X-CH_3

Σ_H=7 (4 aromatic + CH_3)

=> 2 x –CH from ^{13}C-NMR @ 130-132 ppm

=> 9xC + 7xH + O

⇨ Molecular Weight: 131 (+ 30 to reach 161)

MS suggests N, also ^{13}C-NMR suggests a nitrile

=> 9xC + 7xH + O + N

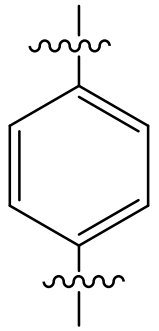
⇨ Molecular Weight: 145 (+ 16 to reach 161), which clearly indicates that the missing heteroatom is oxygen.

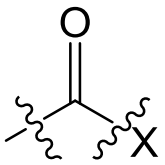
⇨ Chemical Formula: $C_9H_7NO_2$

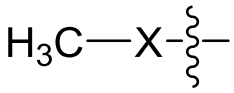
⇨ Molecular Weight: 161

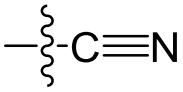
⇨ DBE= 7 (4 from aromatic ring + 3 X≡Y; X=Y=Z)

Fragments

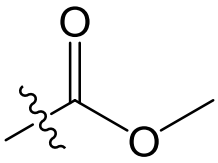


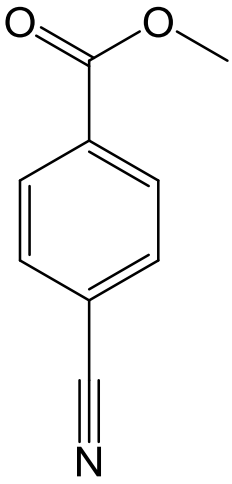






X = O





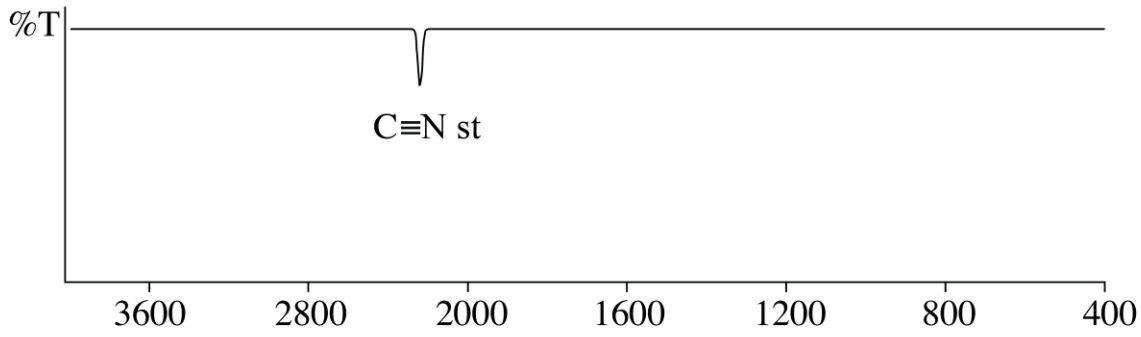
methyl 4-cyanobenzoate

Confirmation

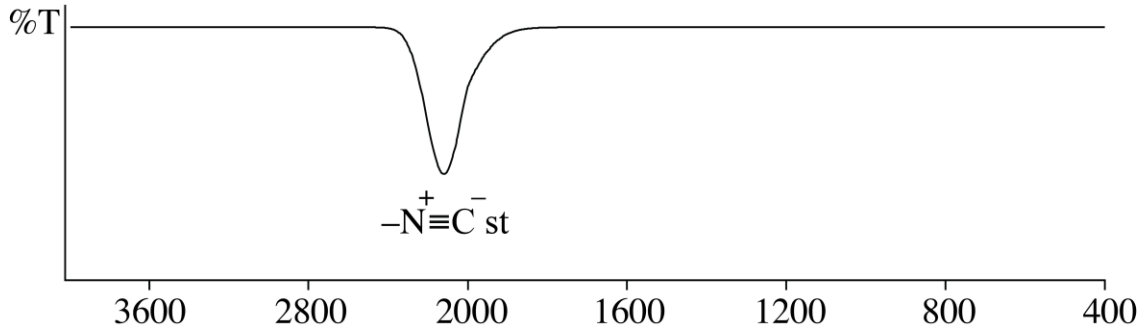
IR

7.9.5 Nitriles and Isonitriles

Nitriles

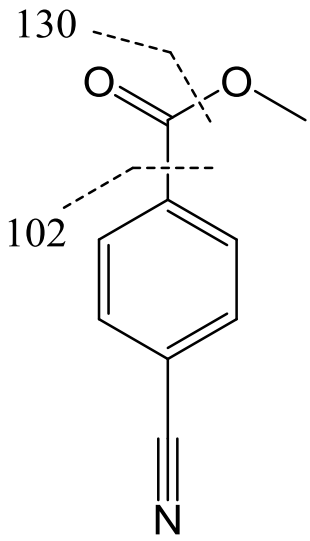


Isonitriles

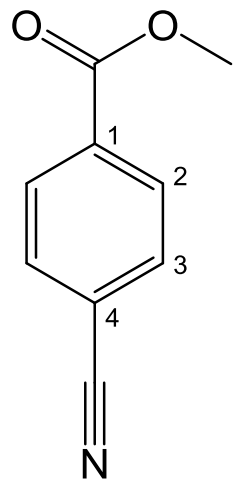


Isonitrile ruled-out

MS



^{13}C-NMR



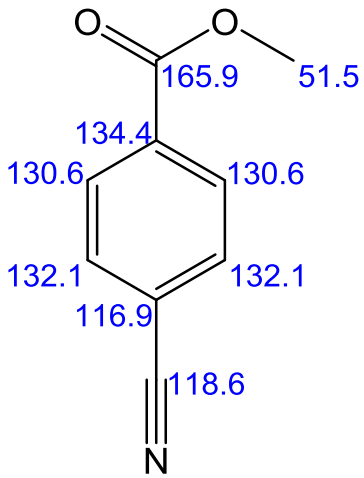
δ_1= 128.5+2+4.3= 134.8 (exp. ~134)

δ_2= 128.5+0.7+1.2= 130.4 (exp. ~130)

δ_3= 128.5+3.5-0.1= 131.9 (exp. ~132)

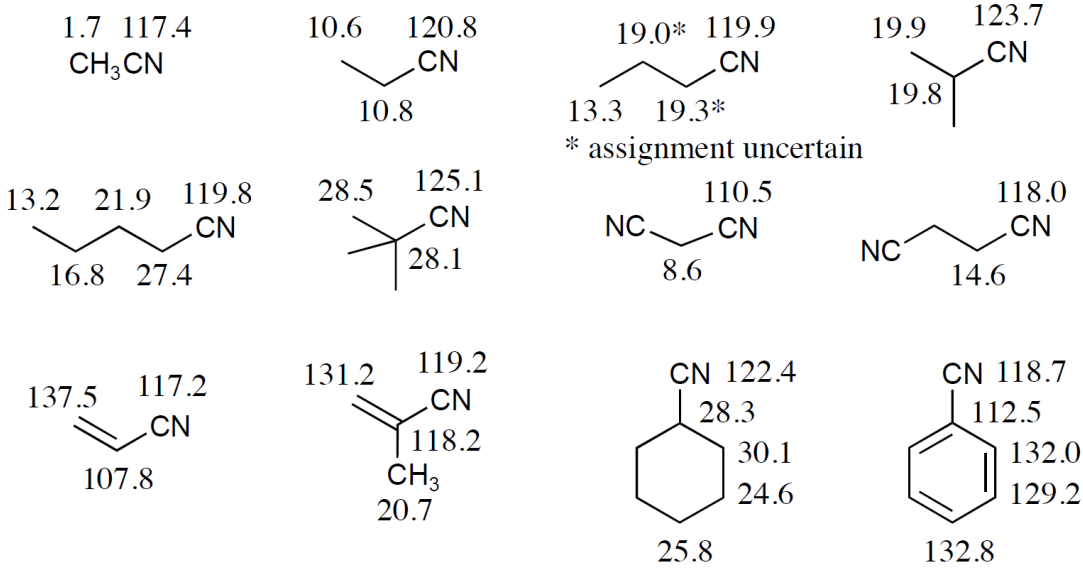
δ_4= 128.5-16+4.3= 116.8 (exp. ~116)

ChemNMR ^{13}C Estimation



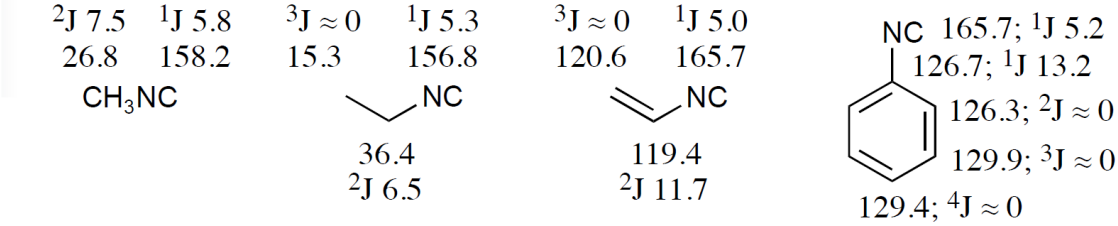
4.9.7 Nitriles and Isonitriles

^{13}C Chemical Shifts of Nitriles (δ in ppm)



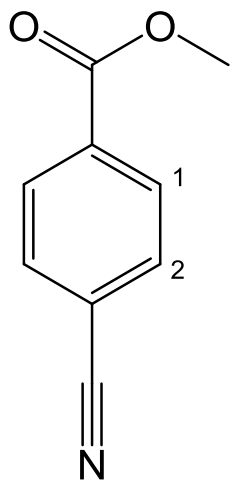
^{13}C Chemical Shifts and ^{13}C–^{14}N Couplings of Isonitriles (δ in ppm, $|J|$ in Hz)

Because of the symmetrical electron distribution around the nitrogen atom, the ^{13}C-^{14}N coupling can be observed in the ^{13}C NMR spectra of isonitriles, leading to triplets with intensities of 1:1:1 (spin quantum number of ^{14}N: I = 1, natural abundance, 99.6%).



Isonitrile ruled-out

^{1}H-NMR



δ_1= 7.34+0.7+0.14 = 8.18 (exp. ~8.14)

δ_2= 7.34 + 0.09 + 0.32 = 7.75 (exp. ~7.74)

ChemNMR ^{1}H Estimation