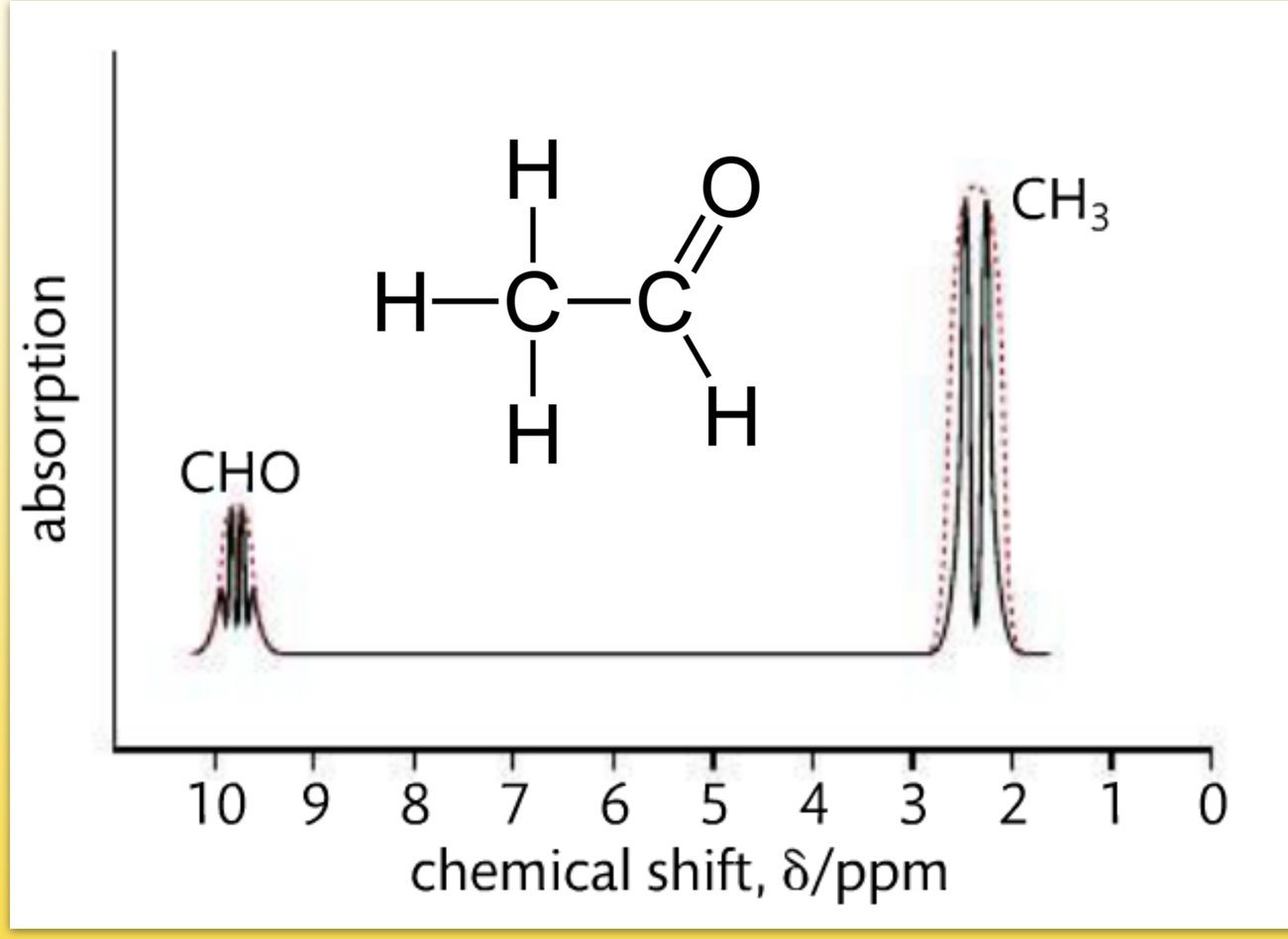
Unit 11
Instrumentation (HL)

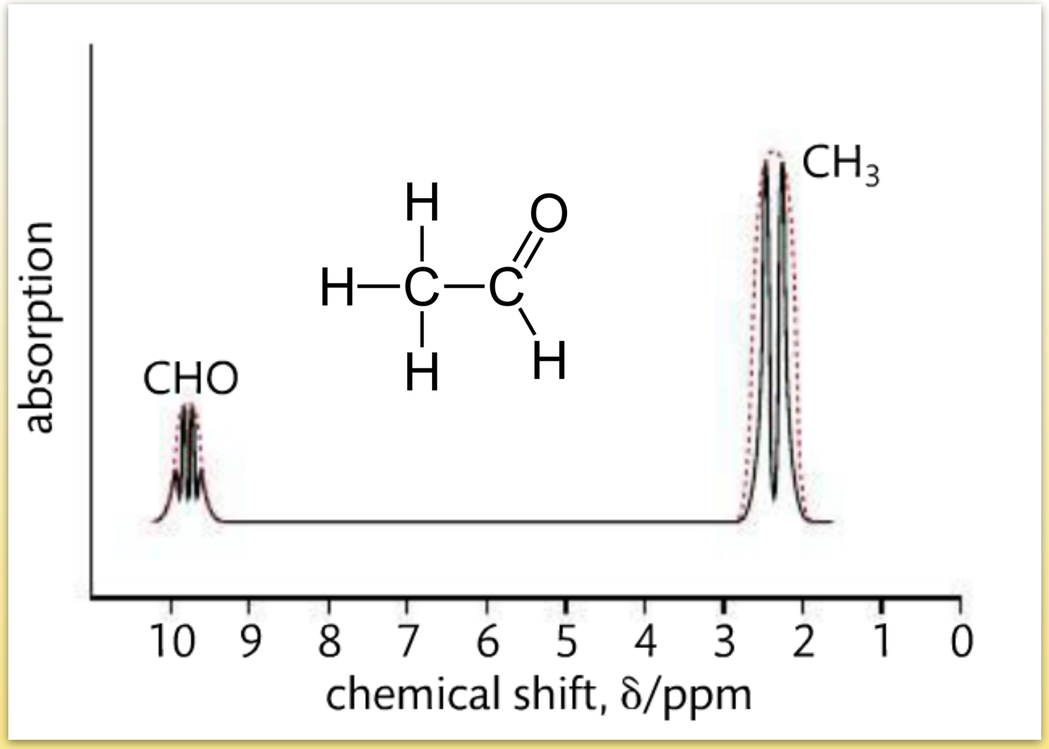
High Resolution NMR and X-ray Diffraction

21.1 High-resolution ^{1}H NMR

- High-resolution reveals more about structure
- Single peaks (shown earlier) are split into smaller parts (multiple peaks)
  - Effective magnetic field modified by the magnetic field produced by neighboring protons.
- ***Spin-Spin coupling!***



21.1 High-resolution ^{1}H NMR



- CHO proton split due to CH_3 protons.
- 2 possible orientations for each proton (2^3 combinations).
- 4 different local magnetic fields.
- 4 signals: 1, 3, 3, 1 intensities.

External magnetic field				
		↓↑↑	↓↓↑	
		↑↓↑	↓↑↓	
	↑↑↑	↑↑↓	↑↓↓	↓↓↓
	All protons aligned with external magnetic field.	Two protons with and one against external magnetic field.	One proton with and two against external magnetic field.	All protons against external magnetic field.

21.1 High-resolution ^1H NMR

- EXAMPLE: Predict the splitting pattern produced by a neighboring -CH_2- group.

There are 2^2 different combinations.

	↓↑	
↑↑	↑↓	↓↓
Both protons aligned with external magnetic field.	One proton aligned with and one against external magnetic field.	Both protons aligned against external magnetic field.

Three lines are produced with relative intensities of 1, 2, 1.

21.1 High-resolution ^{1}H NMR

- Splitting patterns can be deduced from Pascal's triangle.

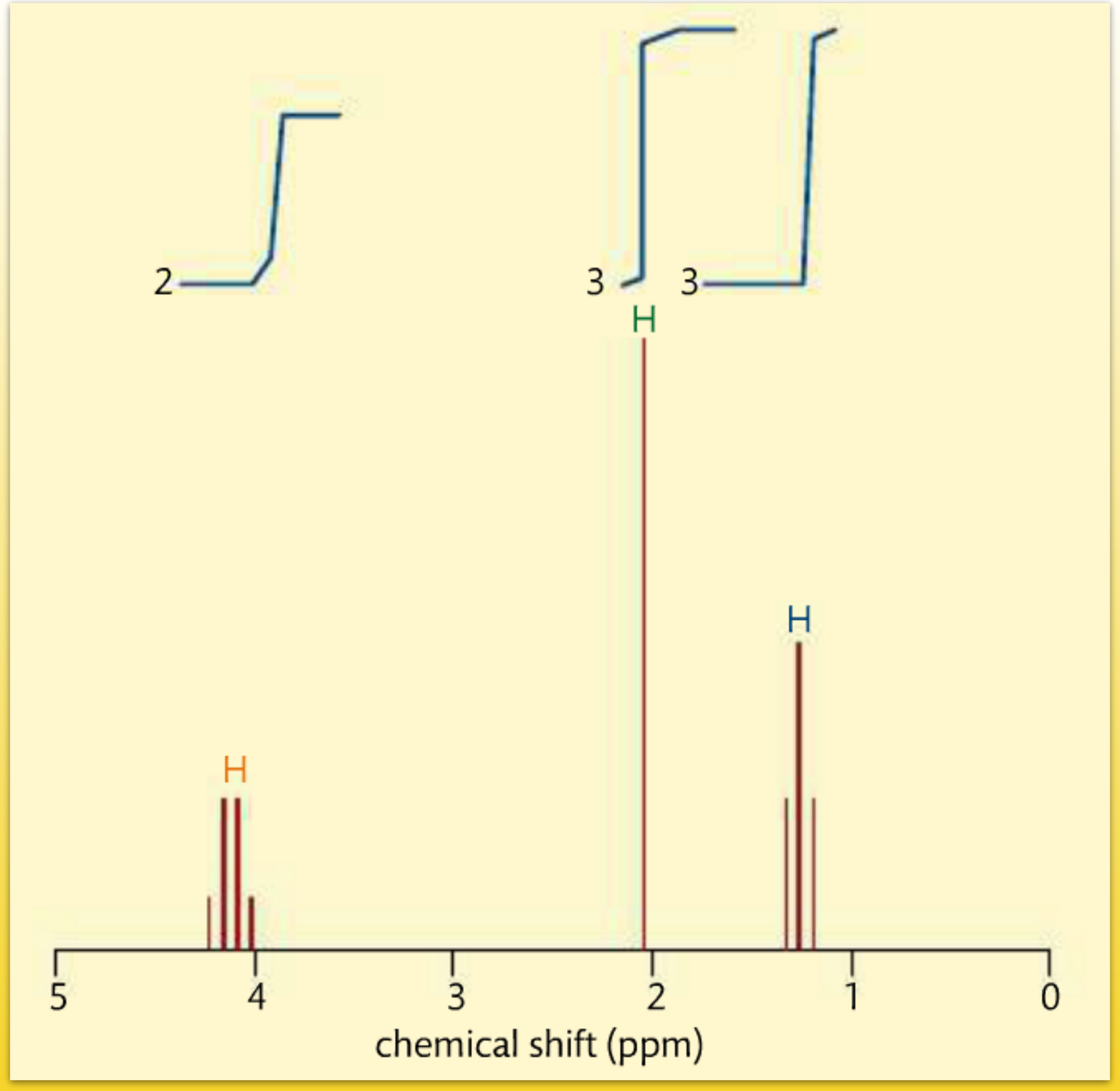
Number of chemically equivalent protons causing splitting	Splitting patterns with relative intensities
0	1
1	1 1
2	1 2 1
3	1 3 3 1
4	1 4 6 4 1

- Protons bonded to the **same** atom don't interact with each other.
- Protons on non-adjacent carbon atoms do not generally interact with each other
- the O-H single peak in ethanol does not split unless the sample is pure (rapid exchange of protons between ethanol molecules)

Example #2

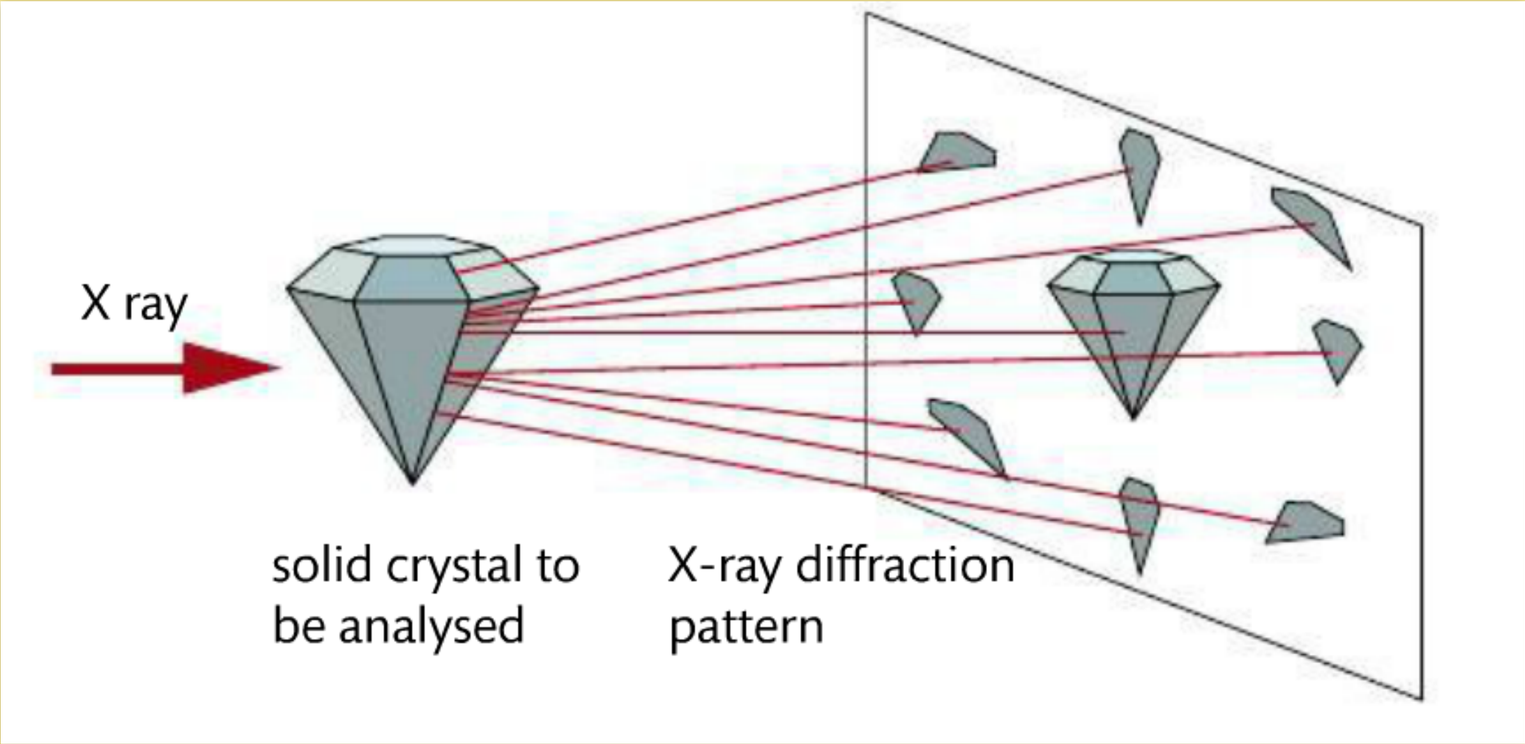
- Empirical formula C_2H_4O

a) Deduce the molecular formula
b) Draw possible structures of molecules
c) Use Table 27 to identify a structure which is consistent with the ^1H NMR and account for the number of peaks and the splitting patterns.



X-ray diffraction

- What's the most direct way to perceive an object?
- Shine a light on it!
- Visible light's way too big (large wavelength) to do that so…..
- We use X-rays (10^{-9} m)
- X-rays passing through a crystalline solid scatter in an orderly way
- A diffraction pattern results



X-ray diffraction

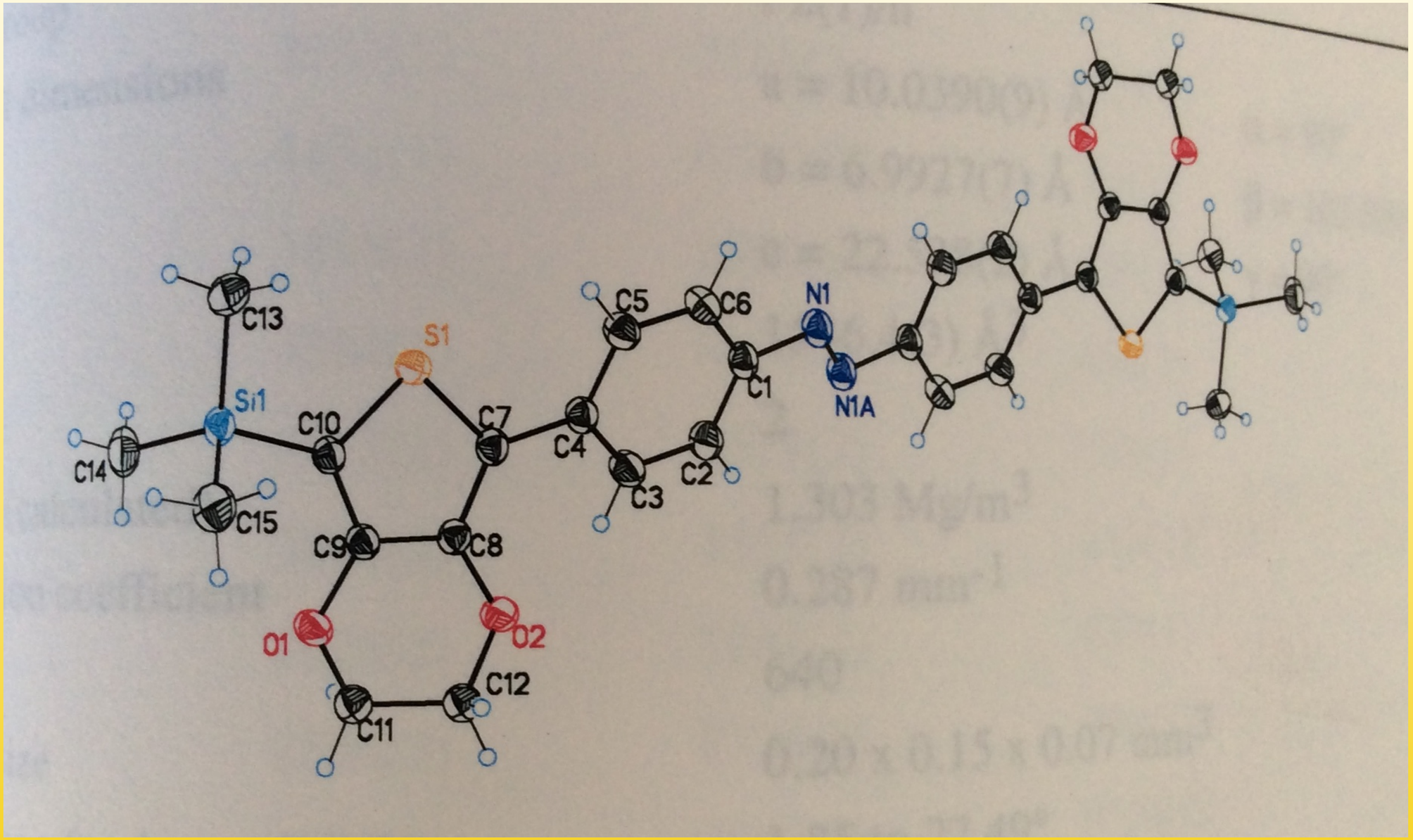


Table A-2. Bond lengths [Å] for BEDOT-AB-TMS_2

Bond	Bond distance (Å)	Bond	Bond distance (Å)
Si1-C14	1.8575(18)	C6-H6A	0.9500
Si1-C13	1.8611(15)	C7-C8	1.377(2)
Si1-C15	1.8672(18)	C8-C9	1.4189(19)
Si1-C10	1.8690(15)	C9-C10	1.368(2)
S1-C10	1.7300(15)	C11-C12	1.521(3)
S1-C7	1.7327(14)	C11-H11A	0.9900
O1-C9	1.3761(17)	C11-H11B	0.9900
O1-C11	1.446(2)	C12-H12A	0.9900
O1-C11'	1.464(6)	C12-H12B	0.9900
O2-C8	1.3682(16)	C11'-C12'	1.455(6)
O2-C12'	1.4269(19)	C11'-H11C	0.9900
O2-C12	1.456(2)	C11'-H11D	0.9900
N1-N1#1	1.253(3)	C12'-H12C	0.9900
N1-C1	1.4287(18)	C12'-H12D	0.9900
C1-C6	1.387(2)	C13-H13A	0.9800
C1-C2	1.393(2)	C13-H13B	0.9800
C2-C3	1.380(2)	C13-H13C	0.9800
C2-H2A	0.9500	C14-H14A	0.9800
C3-C4	1.402(2)	C14-H14B	0.9800
C3-H3A	0.9500	C14-H14C	0.9800
C4-C5	1.400(2)	C15-H15A	0.9800
C4-C7	1.4635(19)	C15-H15B	0.9800
C5-C6	1.387(2)	C15-H15C	0.9800
C5-H5A	0.9500		

Symmetry transformations used to generate equivalent atoms: #1 – x + 1, – y +2, – z.

X-ray diffraction

- By mapping electron density with monochromatic x-rays, a picture of the molecules structure can be shown.
- Sample must be in the solid state - only orderly structures give ordered diffraction patterns
- First applications were for inorganic crystals, but has now been expanded to organic molecules

Anthracene