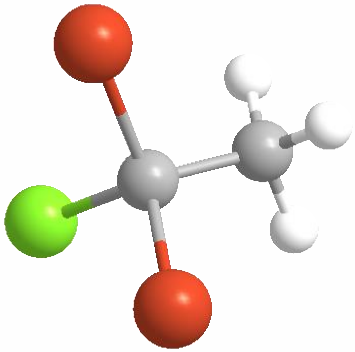
Problem of the Month:

April 2020

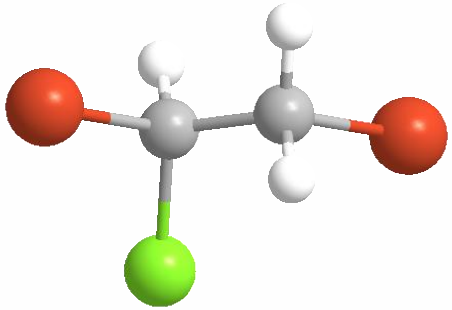
Solution

The molecular formula $C_2H_3Br_2Cl$ only allows a few possible structures

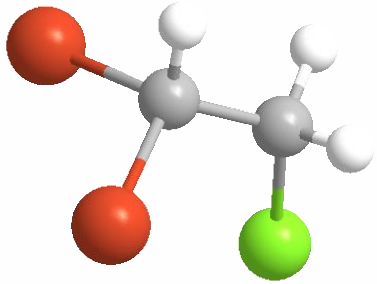
$CBr_2Cl – CH_3$



$CHBrCl – CH_2Br$

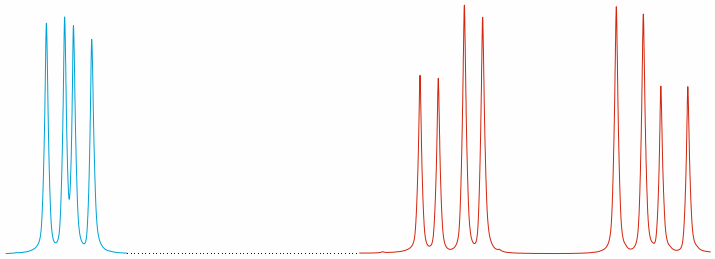


$CHBr_2 – CH_2Cl$



expected, and …

… the real ^{1}H-NMR spectrum

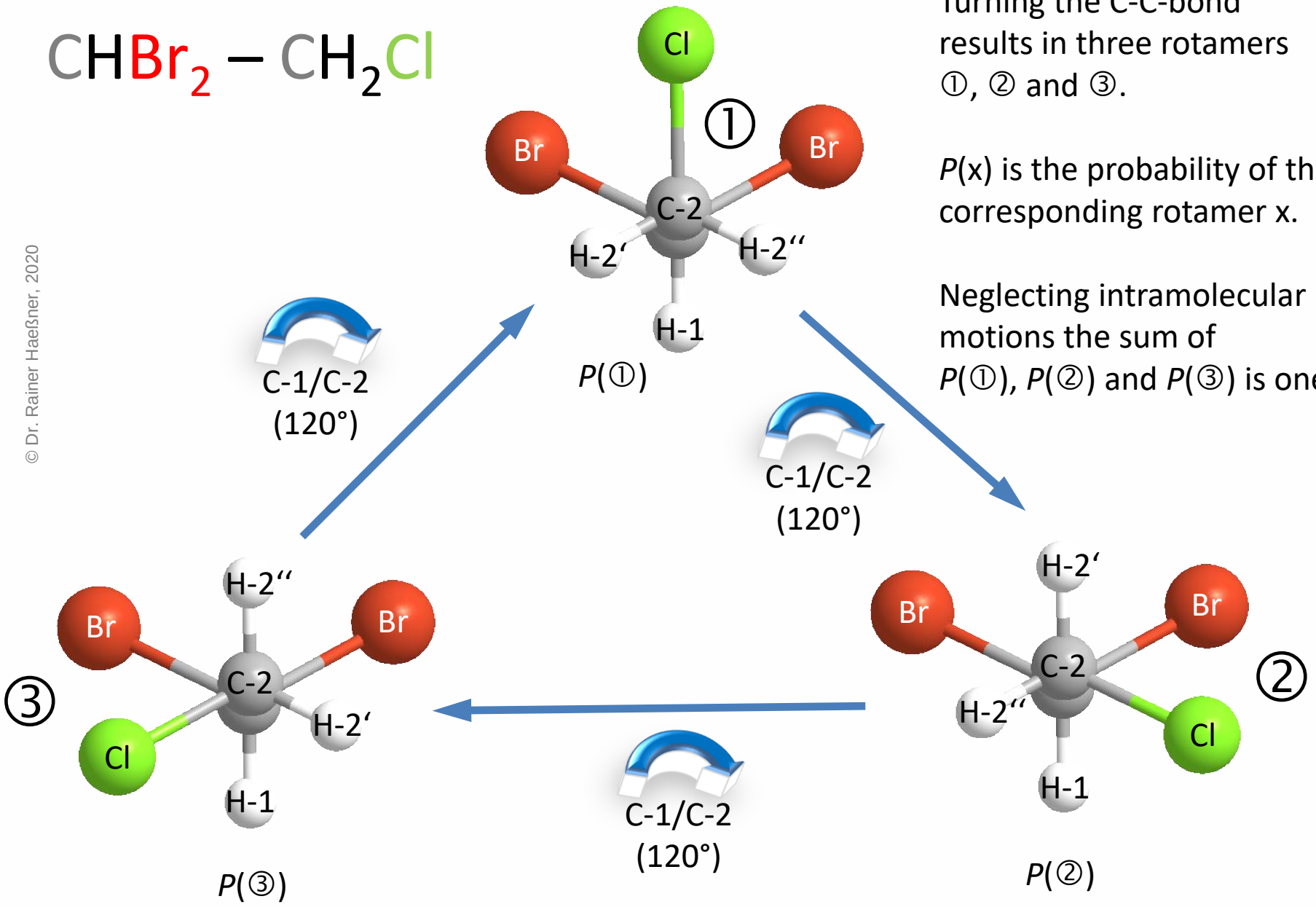


None of the expected NMR spectra correspond to the measured spectrum!

Let's take a closer look at one of the structures. Are both protons bound to C-2 really equivalent?

$$CHBr_2 - CH_2Cl$$

$CHBr_2 - CH_2Cl$

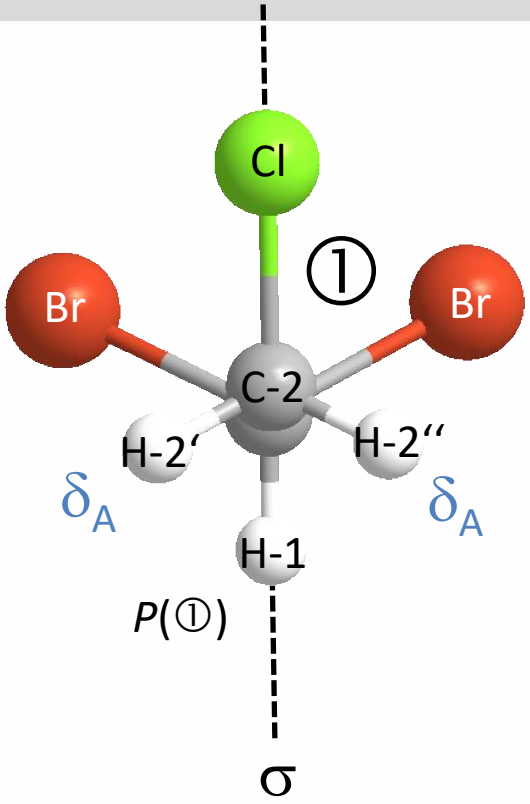


Turning the C-C-bond results in three rotamers ①, ② and ③.

P(x) is the probability of the corresponding rotamer x.

Neglecting intramolecular motions the sum of *P*(①), *P*(②) and *P*(③) is one.

$CHBr_2 - CH_2Cl$



There is a mirror plane in rotamer ①

The chemical shifts of H-2‘ and H-2‘‘ become identical (δ_A).

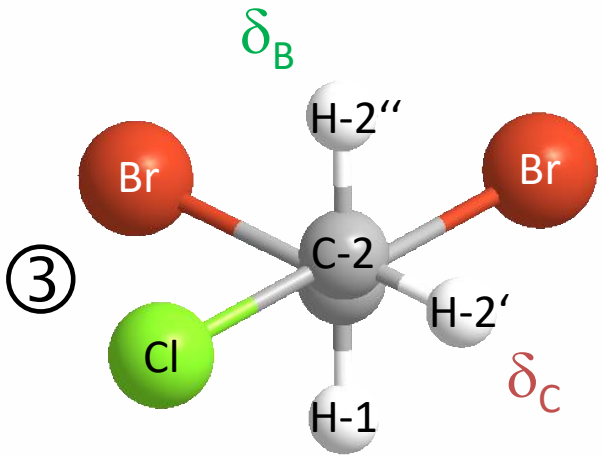
$CHBr_2 - CH_2Cl$

Rotamer ② and rotamer ③ are mirror images.

$P(②) = P(③)$

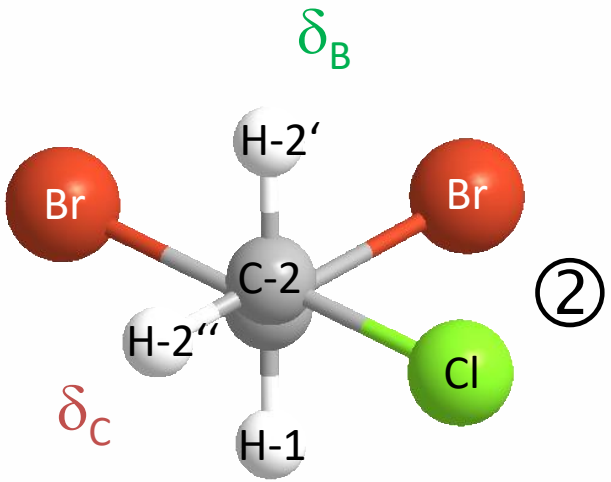
The chemical shifts of H-2‘ in rotamer ② and H-2‘‘ in rotamer ③ are identical (δ_B).

Same for H-2‘‘ in rotamer ② and H-2‘ in rotamer ③ (δ_C).



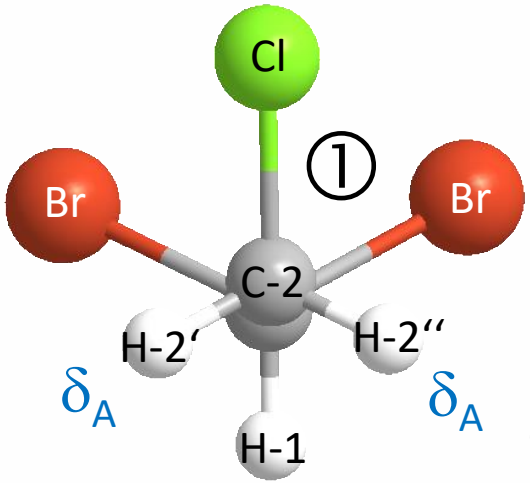
$P(③)$

σ



$P(②)$

$CHBr_2 - CH_2Cl$



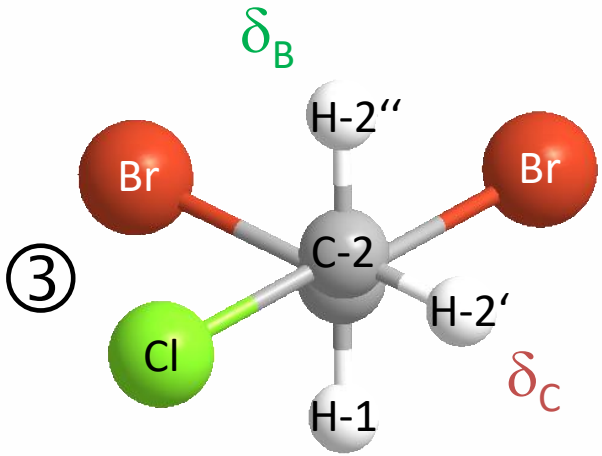
P(①)

$\delta_{H\text{-}2'}$ =

$\delta_A * P(①) + \delta_B * P(②) + \delta_C * P(③)$

$\delta_{H\text{-}2''}$ =

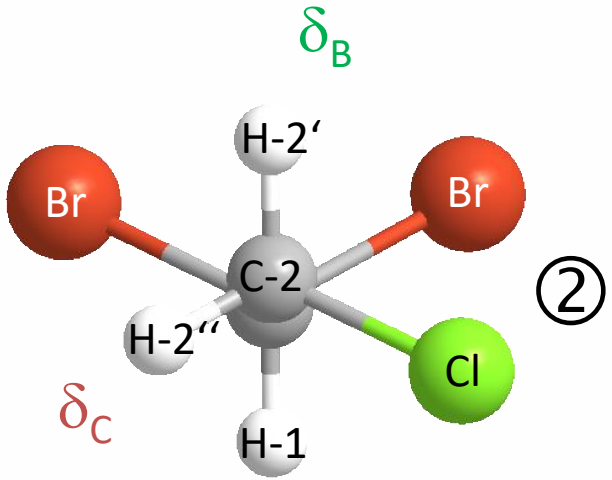
$\delta_A * P(①) + \delta_C * P(②) + \delta_B * P(③)$



P(③)

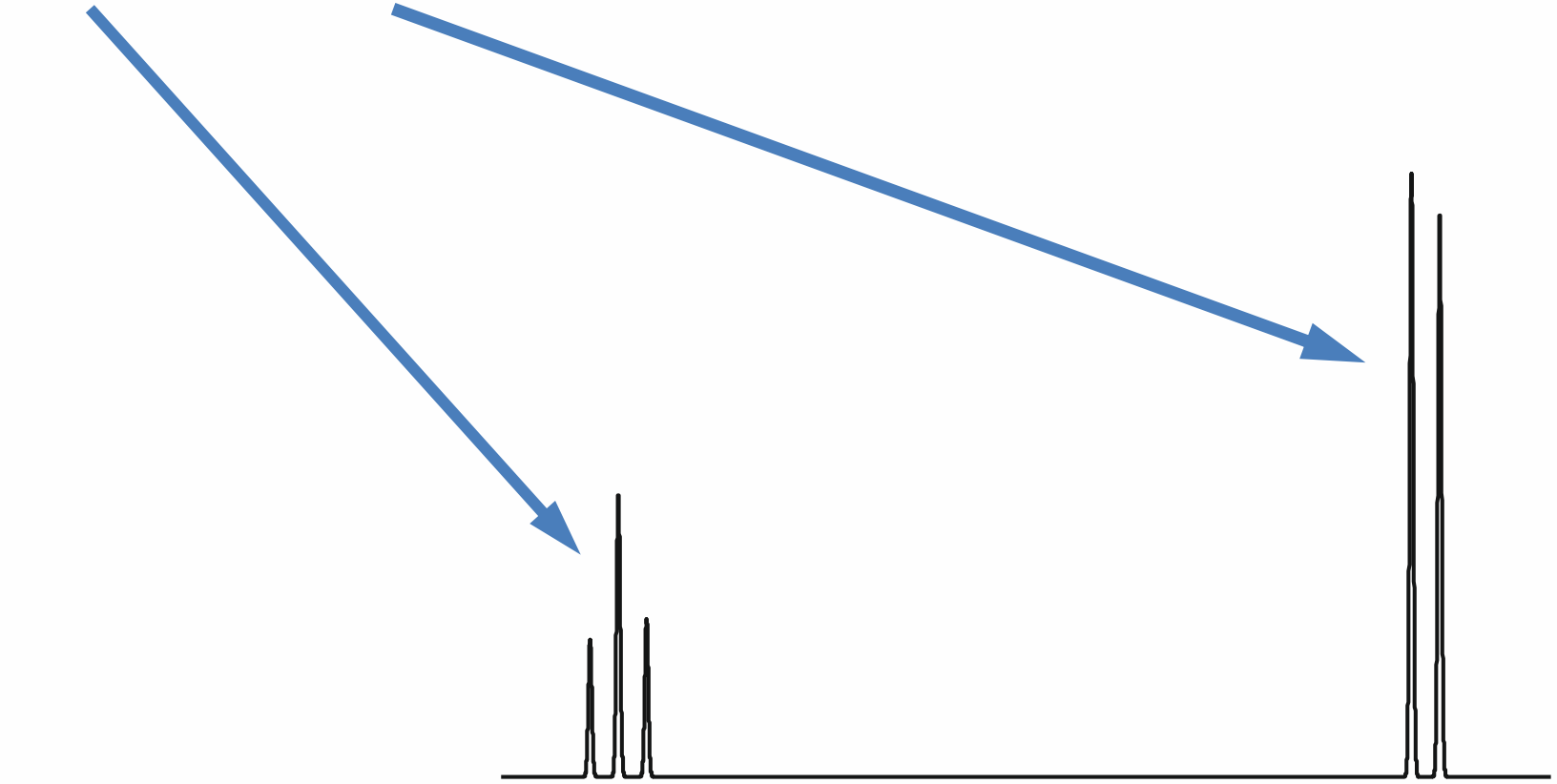
with $P(②) = P(③)$

$$\delta_{H\text{-}2'} = \delta_{H\text{-}2''}$$



P(②)

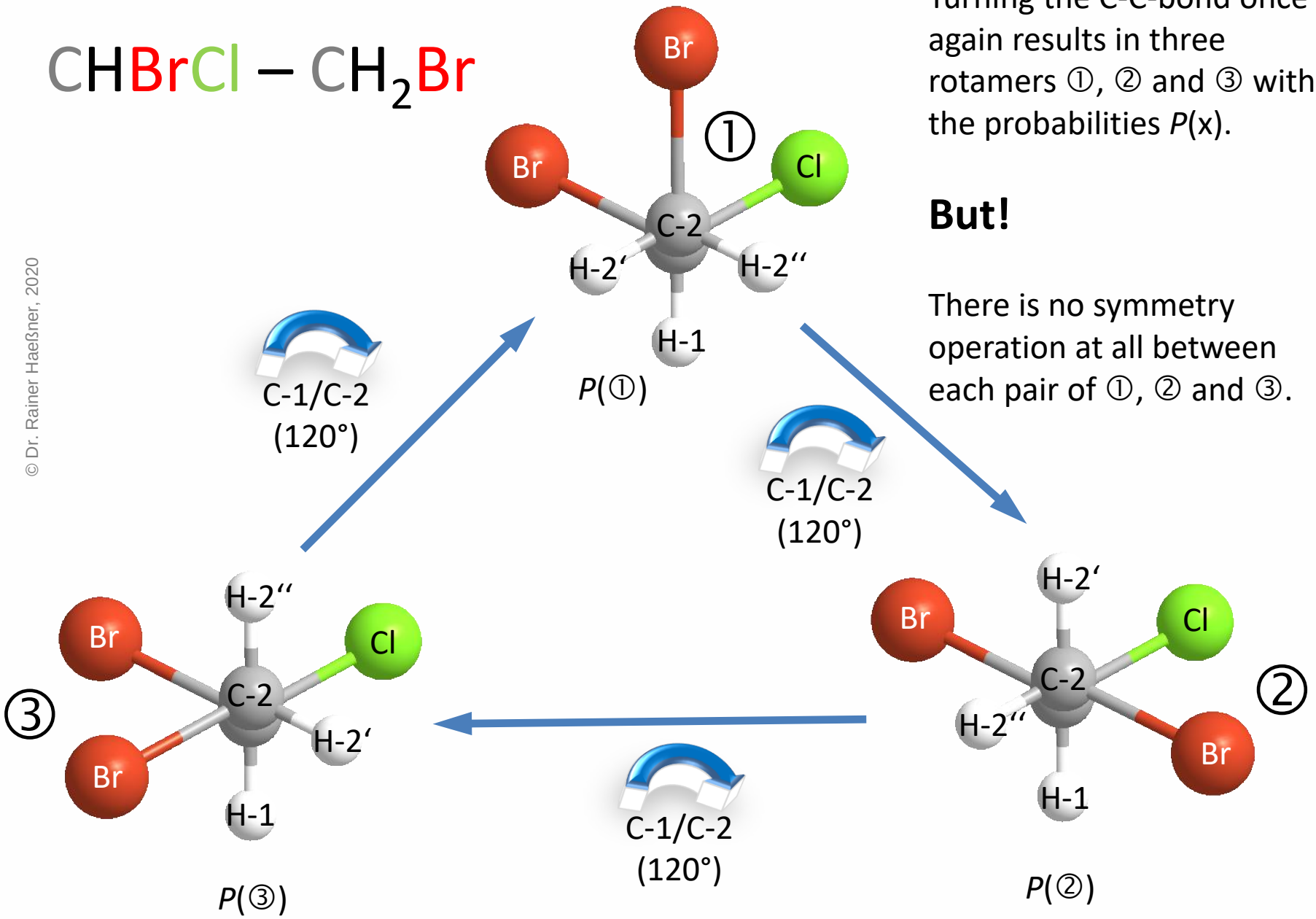
$CHBr_2 - CH_2Cl$



expected ^{1}H-NMR spectrum

What about the two protons bound to C-2 in this compound?

$CHBrCl - CH_2Br$

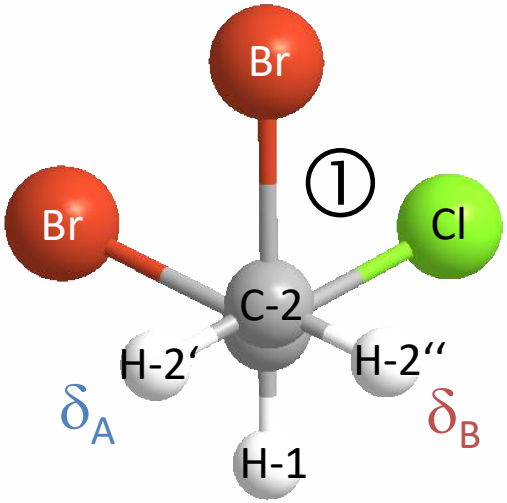


Turning the C-C-bond once again results in three rotamers ①, ② and ③ with the probabilities *P*(x).

But!

There is no symmetry operation at all between each pair of ①, ② and ③.

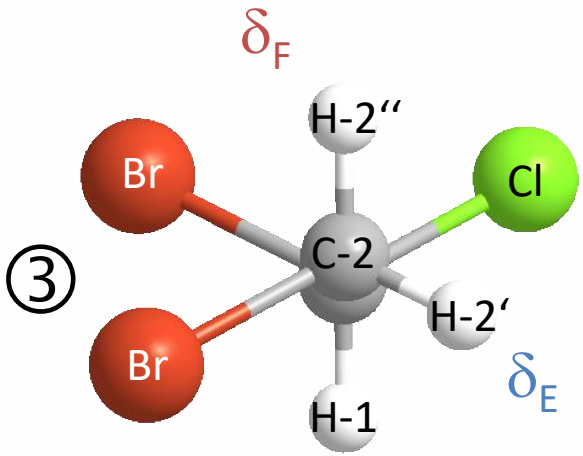
$CHBrCl - CH_2Br$



P(①)

Proton H-2‘ has a different chemical environment in each of the rotamers, resulting in three different chemical shifts δ_A, δ_C and δ_E

The same is true for proton H-2“, resulting in three different chemical shifts δ_B, δ_D and δ_F

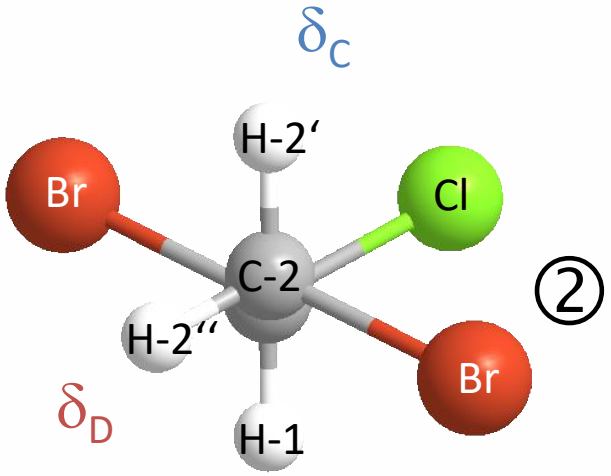


P(③)

as default we expect

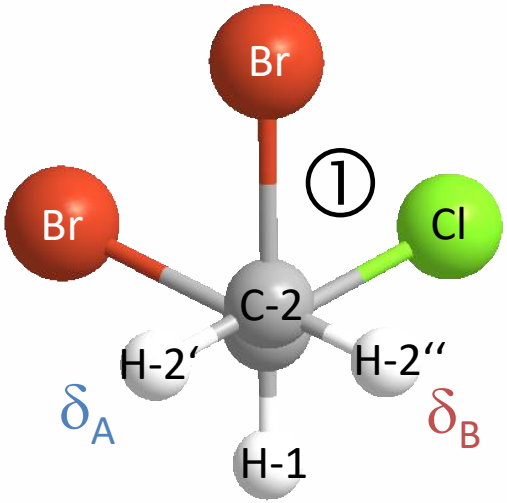
$$P(①) \neq P(②) \neq P(③)$$

$$\delta_A \neq \delta_C \neq \delta_E \neq \delta_B \neq \delta_D \neq \delta_F$$



P(②)

$CHBrCl - CH_2Br$



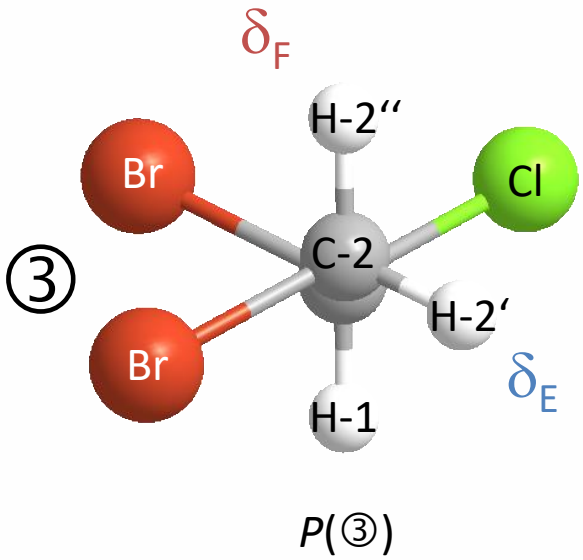
$\delta_{H\text{-}2'} =$

$\delta_A * P(①) + \delta_C * P(②) + \delta_E * P(③)$

$P(①)$

$\delta_{H\text{-}2''} =$

$\delta_B * P(①) + \delta_D * P(②) + \delta_F * P(③)$

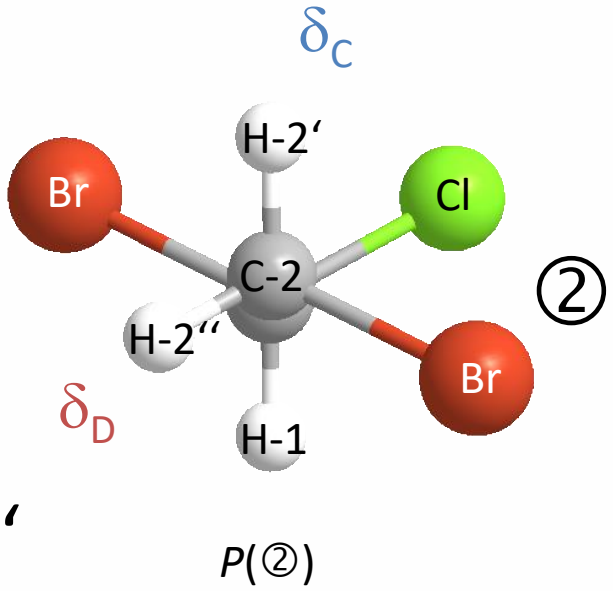


$P(③)$

The averaged chemical shifts of proton H-2‘ and H-2“ depend on nine different factors.

usually the result is

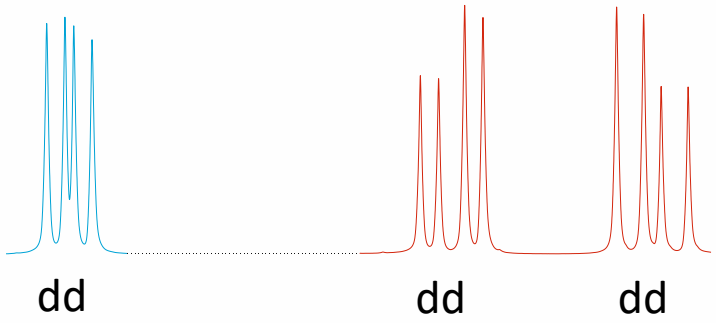
$$\delta_{H\text{-}2'} \neq \delta_{H\text{-}2''}$$

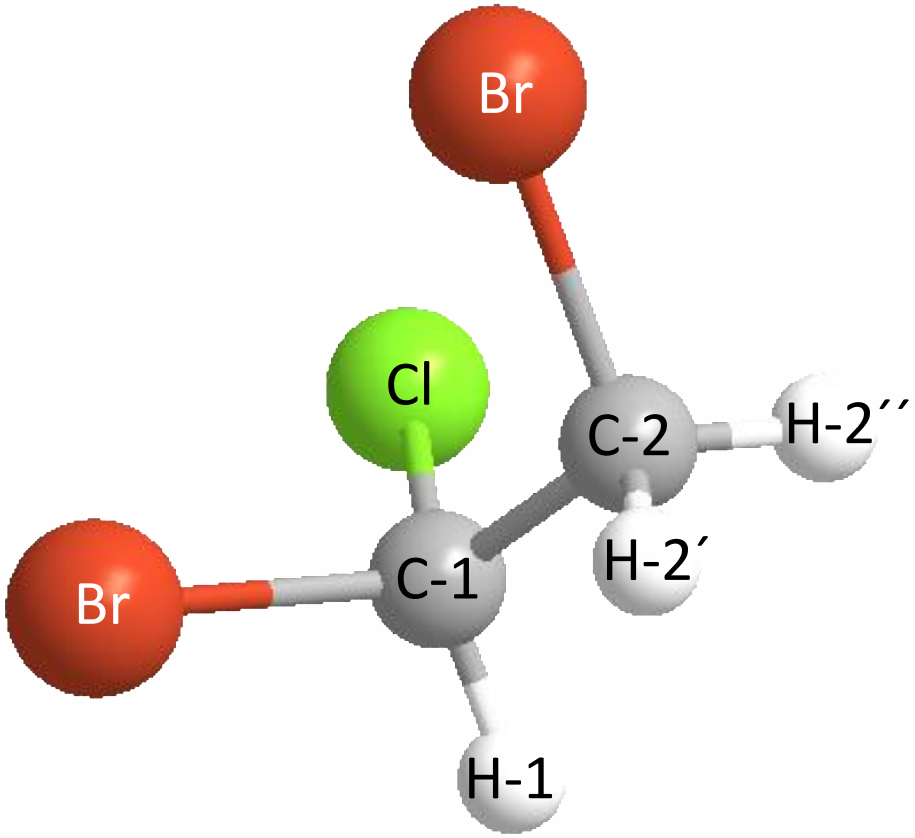


$P(②)$

$CHBrCl - CH_2Br$

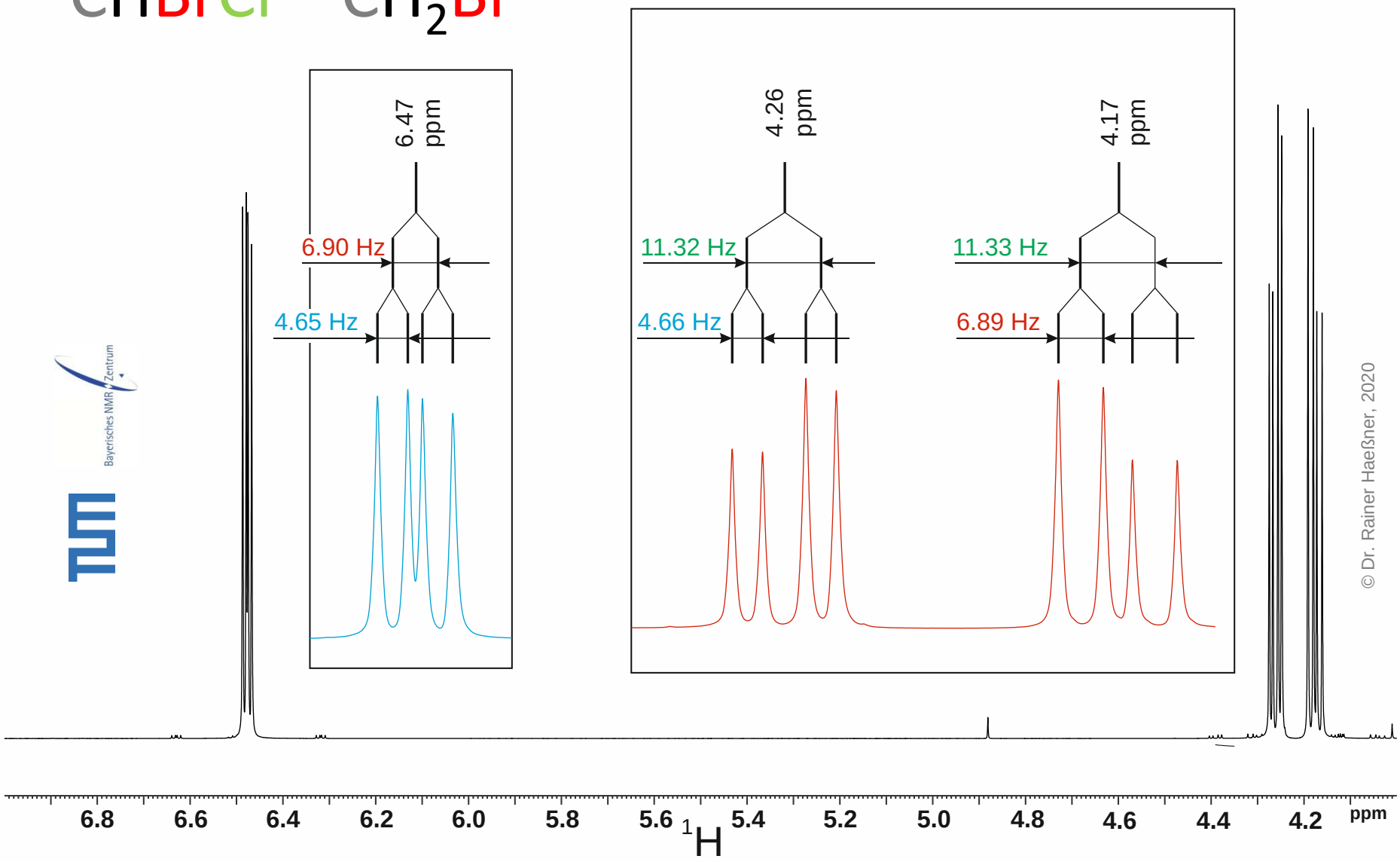
if $\delta_{H\text{-}1} \neq \delta_{H\text{-}2'} \neq \delta_{H\text{-}2''}$
each of the three proton signals
appears as doublet of doublets



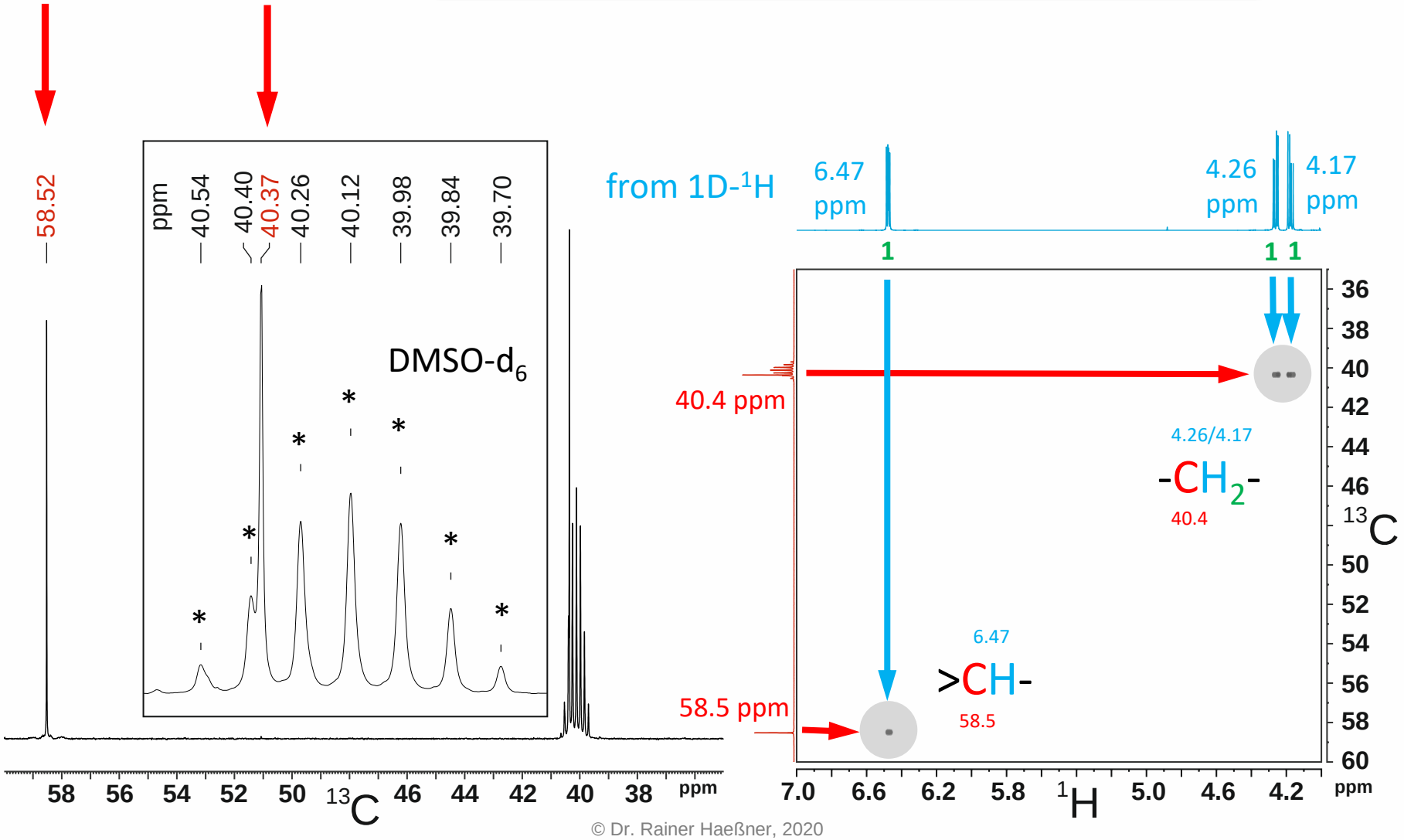


$CHBrCl - CH_2Br$

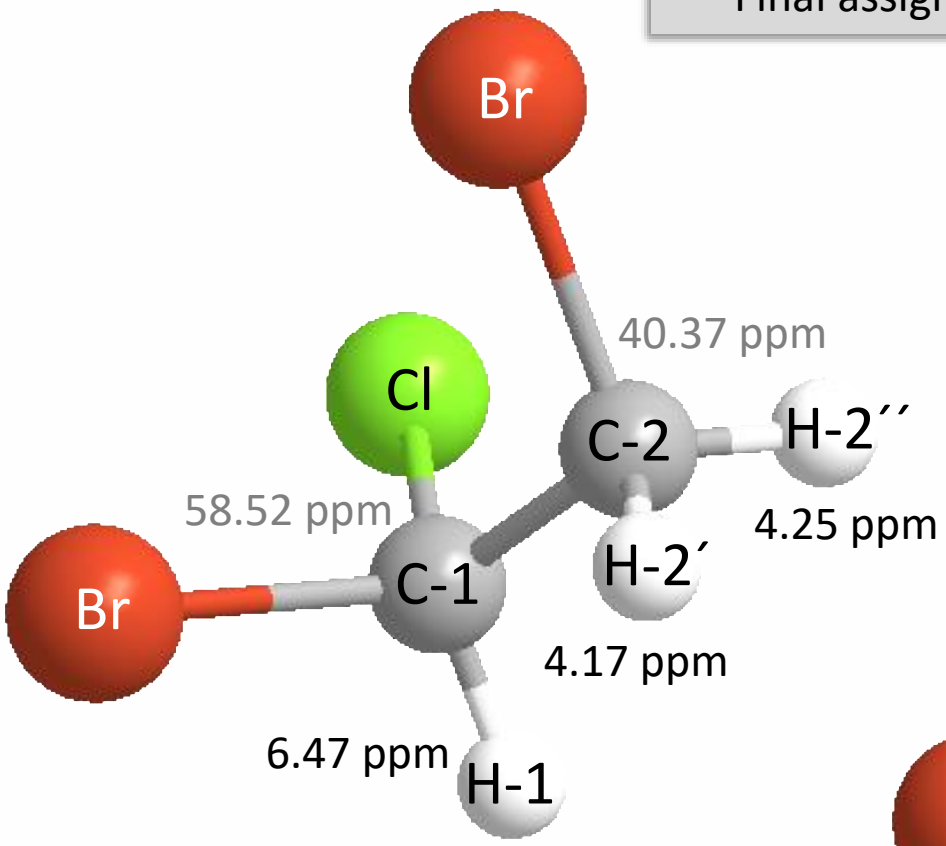
^1H NMR spectrum recorded at 600.4 MHz

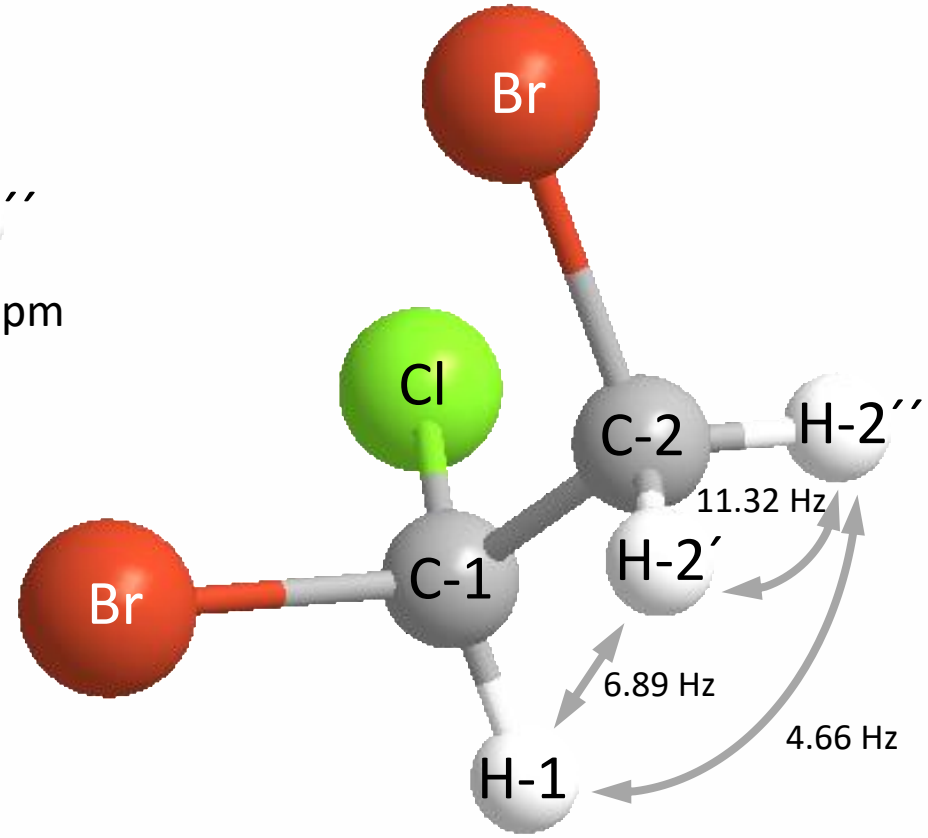


^{13}C assignment
(one of the carbon signals is a little bit hidden)



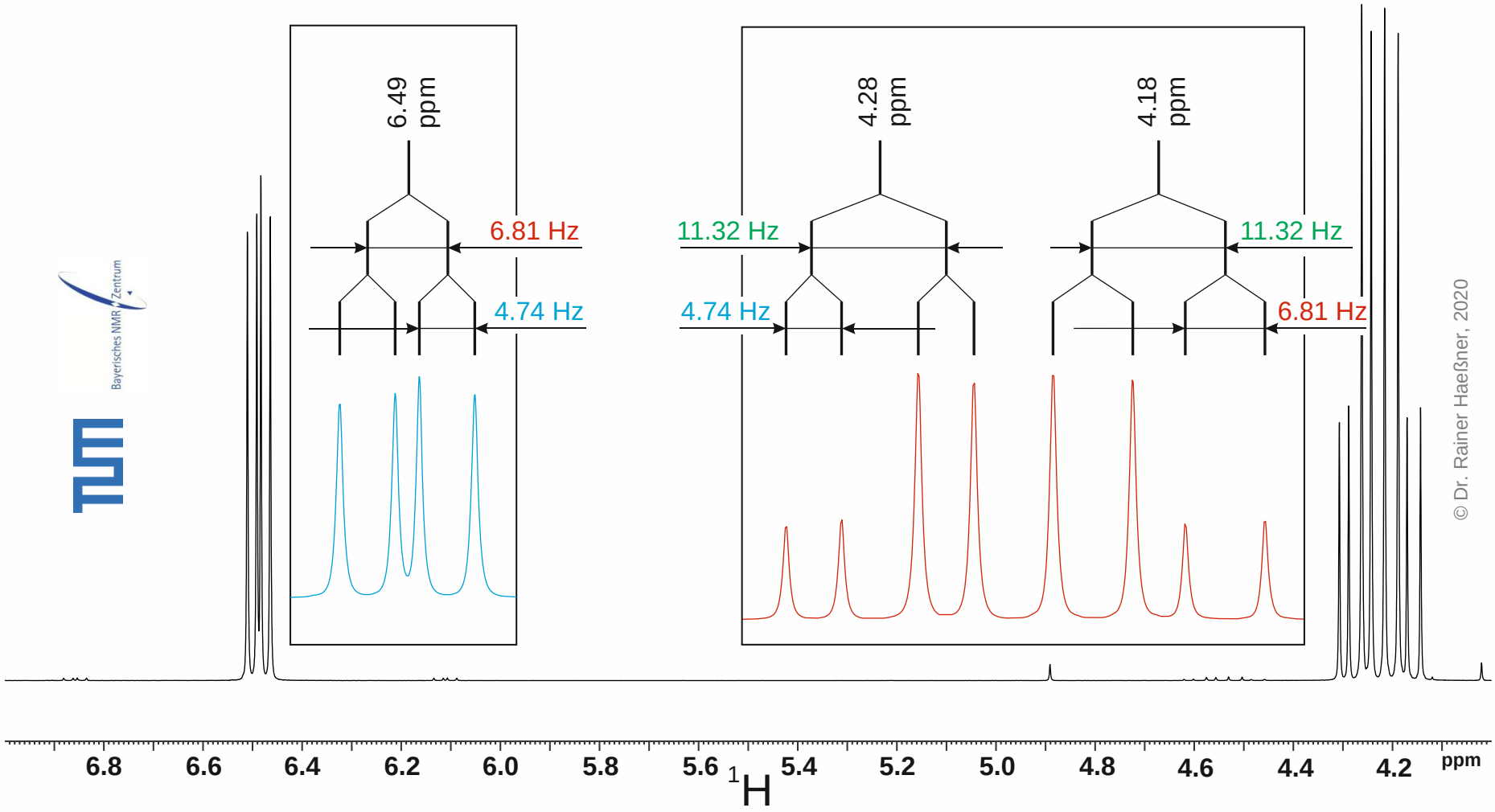
Final assignment (H-2‘ and H-2‘‘ might be reversed)

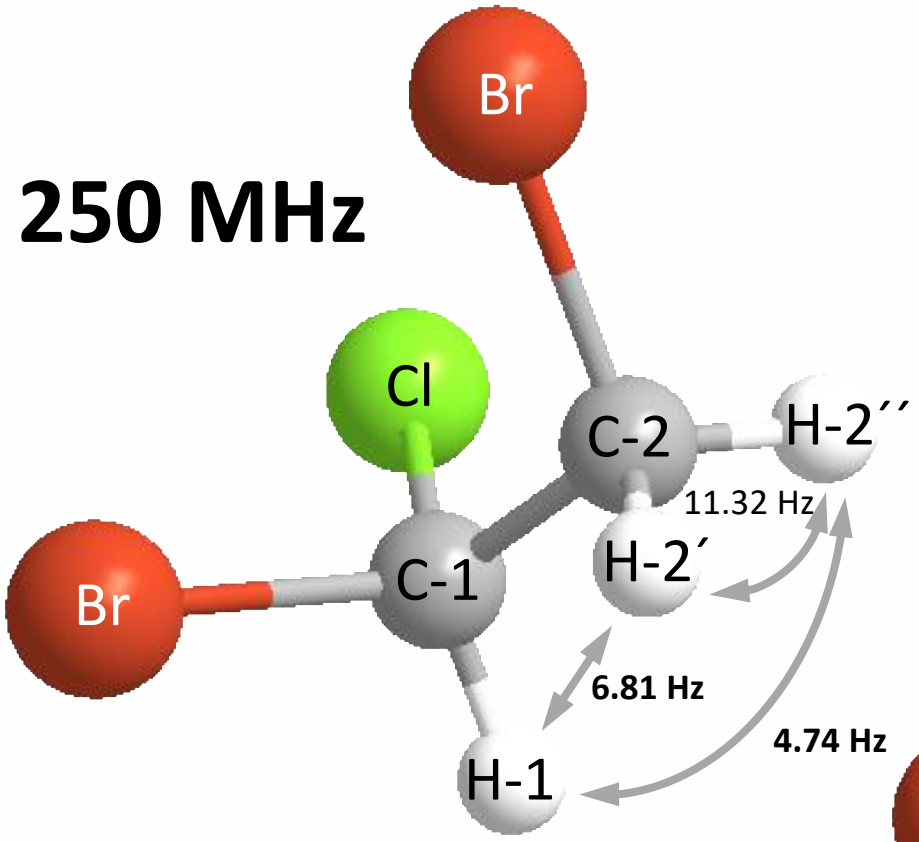


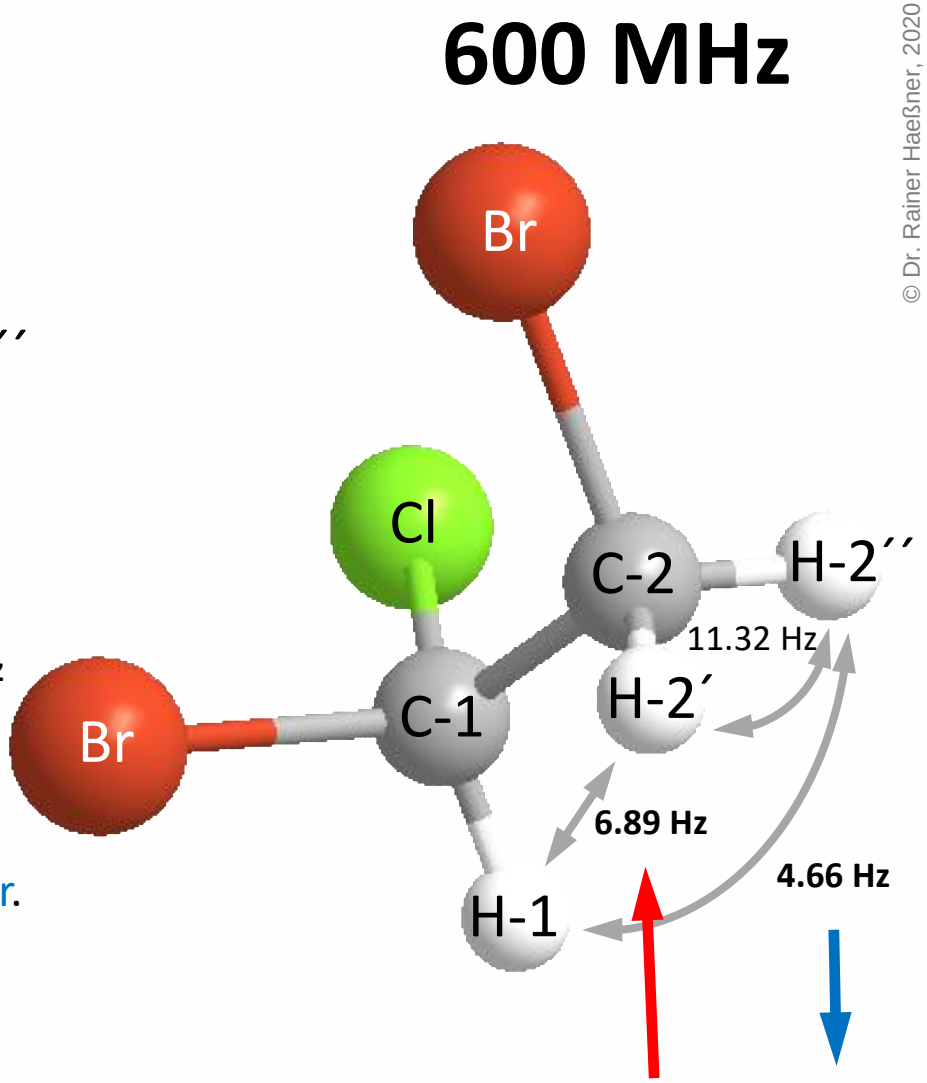


But … wait a minute!

Let‘s analyze the same ^{1}H-NMR measured at 250 MHz







Increasing the magnetic field one coupling constant becomes larger, another one smaller.

Coupling constants shouldn‘t depend on the magnetic field!

It might be a good idea to investigate the value of the coupling constants at more than just two different magnetic fields.