

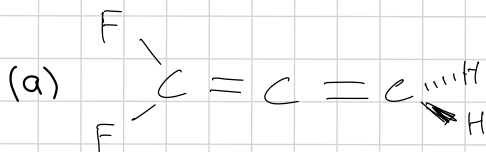
## Jigsaw 3C

1.

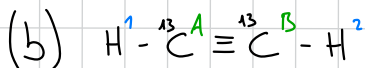
(a) Protons are chemically but not magnetically equivalent for both molecules

(b) Bromines are chemically but not magnetically equivalent

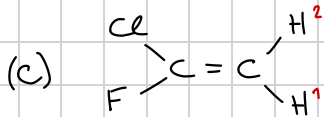
2.



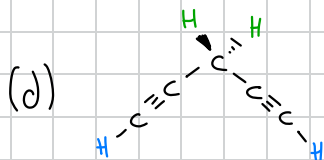
Chemically and magnetically equivalent, because the allene makes the distances between the protons and the fluorine equal.



Chemically but not magnetically equivalent, because the distance between the first H with the  ${}^{13}C^B$  is different than the second H.

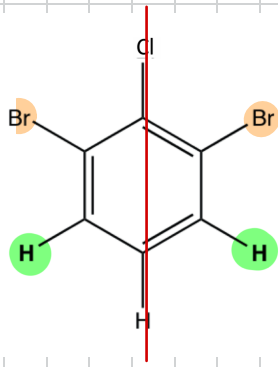


Not chemically and not magnetically equivalent, because the molecule has no symmetry that maps  $H^1$  onto  $H^2$

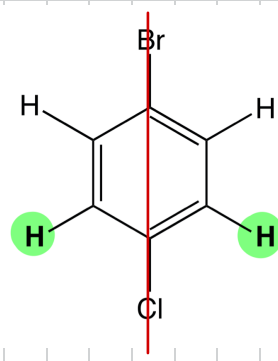


Chemically and magnetically equivalent for each pairs (green and blue, respectively) because the  $^{12}\text{C}$  has 0 spin and therefore no interaction with the  $\text{H}$ 's but not chemically and not magnetically between pairs.

1.



H: \* chemically equivalent  
 \* not magnetically equivalent  
 Br: \* chemically equivalent  
 \* not magnetically equivalent



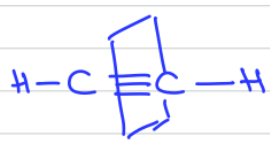
H: \* chemically equivalent  
 \* not magnetically equivalent

2.

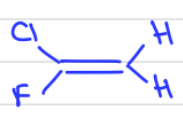
In order to see if the hydrogens were chemically equivalent we had to search for symmetry plane. To see if they are magnetically equivalent, we searched if the J couplings were the same in respect with other atoms. In addition, if it is magnetically equivalent then it is also chemically equivalent.



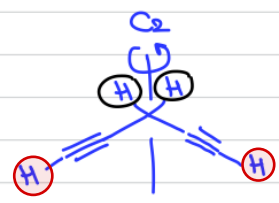
✓ magnetically equivalent  
 ✓ chemically equivalent



✓ chemically equivalent  
 X magnetically equivalent



X magnetically equivalent  
 X chemically equivalent

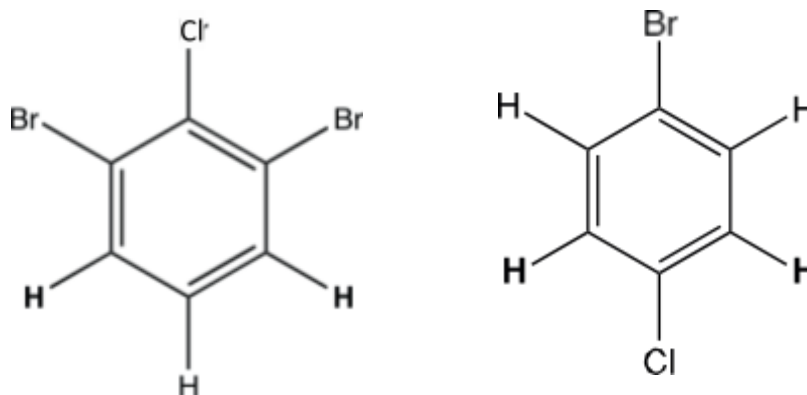


chemically equivalent: \* the red ones are chemically equivalent.  
 \* the black ones are too.  
 \* but black and red are not.  
 magnetically equivalent: \* red ones are not. yes, they are  
 \* black ones are.  
 \* red and black are not.

## Jigsaw 3C

Home Section 3.3 and 3.4. Chemical and magnetic equivalence

1. Are the two bolded protons in the following molecule chemically or magnetically equivalent? What about the two bromine atoms (in the molecule on the left)?

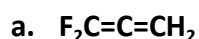


In both molecules, no pair of bold H or Br(left) are magnetically equivalent.

In the first molecule, the 2 bolded protons are magnetically and chemically equivalent because there is a vertical symmetry plane in the molecule passing through the chlorine atom and the center of the cycle. For the same reason, the 2 bromine atoms of the molecule are also chemically and magnetically equivalent.

In the second molecule, the 2 bolded protons are also magnetically and chemically equivalent as there is also a symmetry plane in the molecule. It is passing through the chlorine atom and the bromine atom.

2. For each of the following compounds, determine whether the protons are magnetically or chemically equivalent. Explain why.



In this case there is not C2 but a plane of symmetry

The two protons of the  $\text{CH}_2$  group are both chemically and magnetically equivalent. Indeed, there is a C2 rotational axis along the molecule. Thus, a  $180^\circ$  rotation exchanges the 2 protons without changing the molecule, which means that they are chemically indistinguishable. Their couplings to the carbons and fluorines are identical, so they are also magnetically equivalent.



The two terminal protons are chemically equivalent because the molecule is symmetric

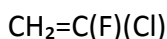
and an inversion center interchanges both ends.

However, they are not magnetically equivalent since each proton is directly bonded to a different  $^{13}\text{C}$  nucleus.

One proton shows a strong  $^1\text{J}(\text{H}-^{13}\text{C})$  coupling with its own carbon, while the other only has a weaker  $^2\text{J}(\text{H}-^{13}\text{C})$  coupling to that same carbon.

As these coupling constants are different, the protons are magnetically non-equivalent.

**c. 1-chloro-1-fluoroethene**



The two vinylic hydrogens of the  $\text{CH}_2$  group are neither chemically nor magnetically equivalent.

The molecule has no symmetry operation that interchanges them because the substituents F and Cl are different.

Each hydrogen experiences a distinct environment (one is cis and the other trans to the fluorine), which leads to different  $^3\text{J}(\text{H}-\text{F})$  coupling constants.

Therefore, they are diastereotopic and not magnetically equivalent.

**d.  $\text{HC}\equiv\text{C}-\text{CH}_2-\text{C}\equiv\text{CH}$**

The two terminal acetylenic protons are chemically and magnetically equivalent. A center of symmetry at the midpoint of the molecule interchanges both ends, giving identical electronics environments and identical couplings. The two hydrogens of the  $\text{CH}_2$  are also chemically and magnetically equivalent, since a  $\text{C}_2$  axis through the  $\text{CH}_2$  connects them. Both sides of the molecule are the same, so their environments and couplings are identical.