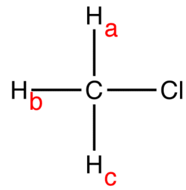
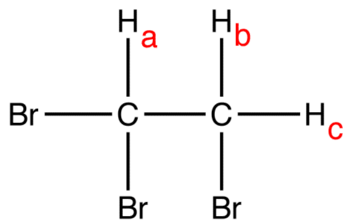
14.8: The n+1 Rule Applies Only to First-Order Spectra

The (n+1) Rule, an empirical rule used to predict the multiplicity and, in conjunction with Pascal's triangle, splitting pattern of peaks in ^{1}H and ^{13}C NMR spectra, states that if a given nucleus is coupled (see spin coupling) to n number of nuclei that are equivalent (see equivalent ligands), the multiplicity of the peak is n+1. eg. 1:



1

The three hydrogen nuclei in 1, H_a, H_b, and H_c, are equivalent. Thus, 1H NMR spectrum of 1 H_as only one peak. H_a, H_b, and H_c are coupled to no hydrogen nuclei. Thus, for H_a, H_b, and H_c, n=0; (n+1) = (0+1) = 1. The multiplicity of the peak of H_a, H_b, and H_c is one. The peak H_as one line; it is a singlet. eg. 2:



2

There are two sets of equivalent hydrogen nuclei in 2:

- Set 1: H_a
- Set 2: H_b, H_c

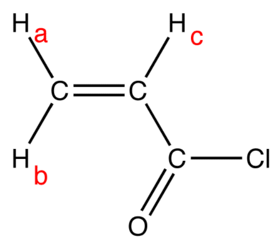
Thus, the 1H NMR spectrum of 2 H_as two peaks, one due to H_a and the other to H_b and H_c.

The peak of H_a: There are two vicinal hydrogens to H_a: H_b and H_c. H_b and H_c are equivalent to each other but not to H_a. Thus, for H_a, n=2; (n+1) = (2+1) = 3. The multiplicity of the peak of H_a is three. The peak H_as three lines; from the Pascal's triangle, it is a triplet.

The peak of H_b and H_c: There is only one vicinal hydrogen to H_b and H_c: H_a. H_a is not equivalent to H_b and H_c. Thus, for H_b and H_c, n=1; (n+1) = (1+1) = 2. The multiplicity of the peak of H_b and H_c is two. The peak H_as two lines, from the Pascal's triangle, it is a doublet.

To determine the multiplicity of a peak of a nucleus coupled to more than one set of equivalent nuclei, apply the (n+1) Rule independently to each other.

eg:



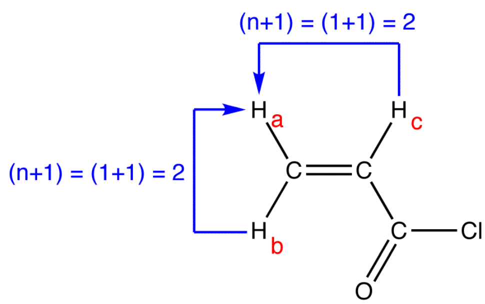
3

There are three set of equivalent hydrogen nuclei in 3:

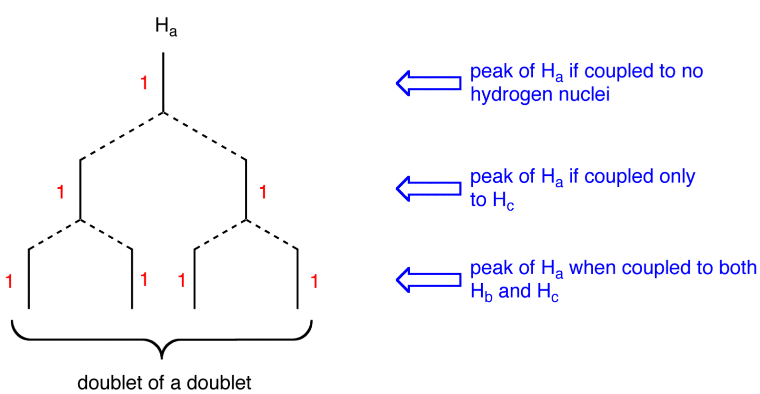
- Set 1: H_a
- Set 2: H_b
- Set 3: H_c

	H_a	H_b	H_c
H_a		geminal; coupling occurs	vicinal; coupling occurs
H_b	geminal; coupling occurs		vicinal; coupling occurs
H_c	vicinal; coupling occurs	vicinal; coupling occurs	

peak of H_a:

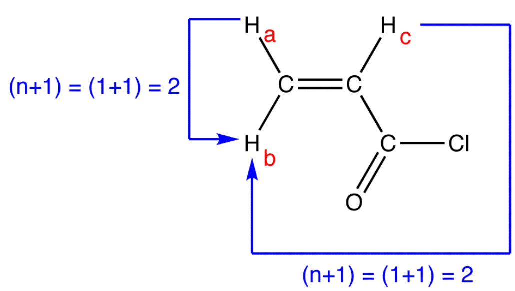


multiplicity of the peak of $H_a = 2 \times 2 = 4$. To determine the splitting pattern of the peak of H_a, use the Pascal's triangle, based on the observation that, for alkenyl hydrogens, $J_{cis} > J_{gem}$.

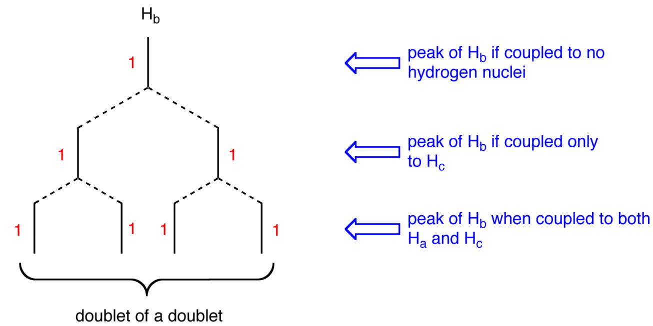


The peak of H_a is a doublet of a doublet.

peak of H_b:

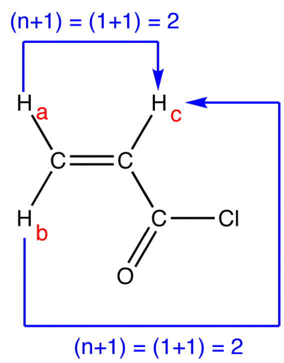


multiplicity of the peak of $H_b = 2 \times 2 = 4$. To determine the splitting pattern of the peak of H_b, use the Pascal's triangle, based on the observation that, for alkenyl hydrogens, $J_{trans} > J_{gem}$.

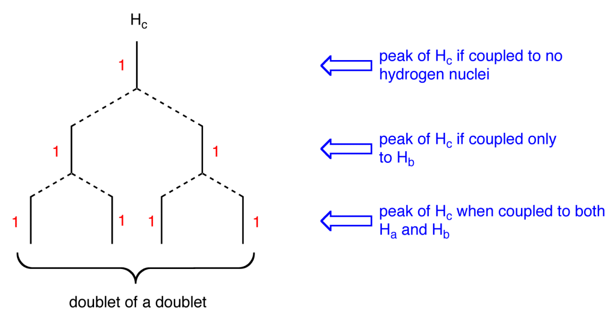


The peak of H_b is a doublet of a doublet.

peak of H_c:



multiplicity of the peak of $H_c = 2 \times 2 = 4$. To determine the splitting pattern of the peak of H_c, use the Pascal's triangle based on the observation that, for alkenyl hydrogens, $J_{trans} > J_{cis}$.



The peak of H_c is a doublet of a doublet.
