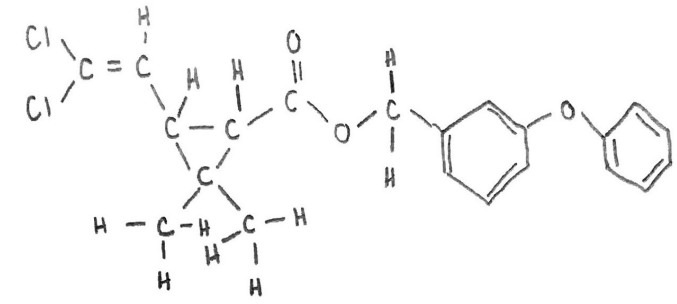
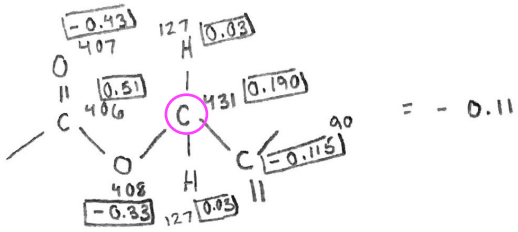
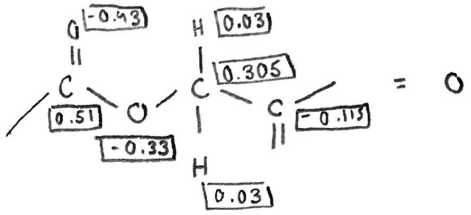
PERMETHRIN



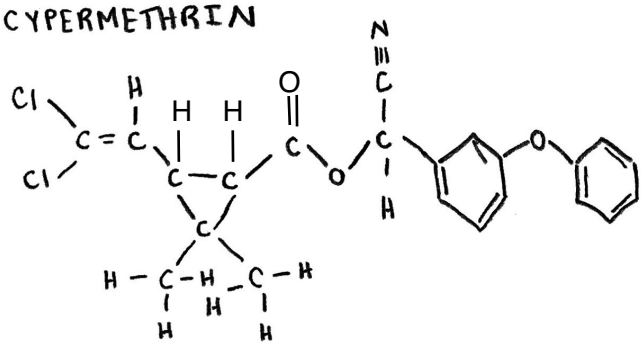


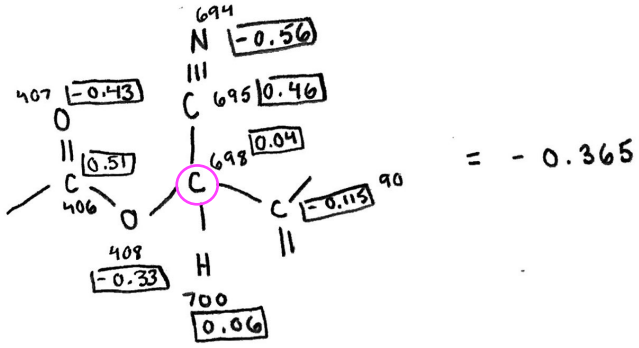


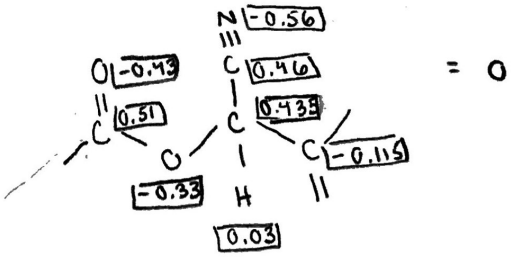
The circled C is that of an ethyl ester, #431, but we have to account for it being adjacent to an aromatic ring instead of an alkane chain.

The C of a CH2 in an alkane chain (#81 Alkane CH2) has a charge of -0.12, while a CH2 adjacent to an alkane chain and an aromatic ring (#94 Ethyl benzene) has a charge of -0.005. The difference is +0.115 going from the chain to the ring, therefore we need to add 0.115 to the charge of the C. Then the total charge becomes 0.

CYPERMETHRIN







For cypermethrin, we need to adjust the C of the alkyl nitrile group for 1) being adjacent to an aromatic ring and 2) being adjacent to an ethyl ester group.

1) The aromatic ring adjustment is the same that we applied above (difference between #81 and #94), +0.115

2) The difference between #431 (an ethyl ester C) and #81 (a regular alkane chain CH2) is +0.31.

Adding these adjustments yields +0.425, which is 0.06 higher than the 0.365 difference in the molecule.

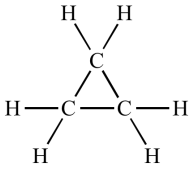
The charge of the H connected to this C is ambiguous. If it is an H of an alkyl nitrile group, #700, it has a charge of 0.03. If it is considered the H of an ethyl ether group, #127, it is 0.06.

Therefore I will distribute the remaining -0.06 difference between the C and the H atoms, giving the final total shown above.

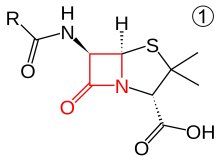
The same adjustments as in cypermethrin were made in cyfluthrin.

Main decision: Should I replace the 91 with 13 or the 3 with 89?

- 91 is the cyclopropane C
- 13 is the alkane C
- 3 is the C of C=O
- 89 is the C of beta-lactam N-C=O



cyclopropane



beta-lactam

Bonds:
3-91 --> 3-13 / 89-91 (they have the same parameters)

Angles:
4-3-91 --> 4-3-13 (4-89-13 DNE)
91-3-20 --> 13-3-20 (20-89-91 DNE)
13-91-13 --> 13-91-91
3-91-91 --> 47-91-91
3-91-46 --> 13-91-46
21-47-21 --> 21-13-21
20-13-19 --> 13-13-19
48-13-19 --> 13-13-19

Dihedrals:

Choosing to replace 91 with 13

4-3-91-91 --> 4-3-13-13 or ~~4-89-91-91~~?
4-3-91-46 --> ~~4-89-91-46~~ 4-3-13-46
20-3-91-46 --> ~~0-89-91-0~~ 20-3-13-46
91-3-20-13 --> 13-3-20-13
91-91-47-47 --> 13-13-47-47
46-91-47-47 --> 46-13-47-47
46-47-91-46 --> 46-13-47-46
46-47-91-91 --> ~~46-13-47-47~~ 0 13 47 46
13-91-13-46 --> 13-13-13-46
20-3-91-91 --> ~~0-89-91-0~~ 20-3-13-13
48-13-20-3 --> 13-13-20-3
48-20-48-48 --> 13-20-48-48