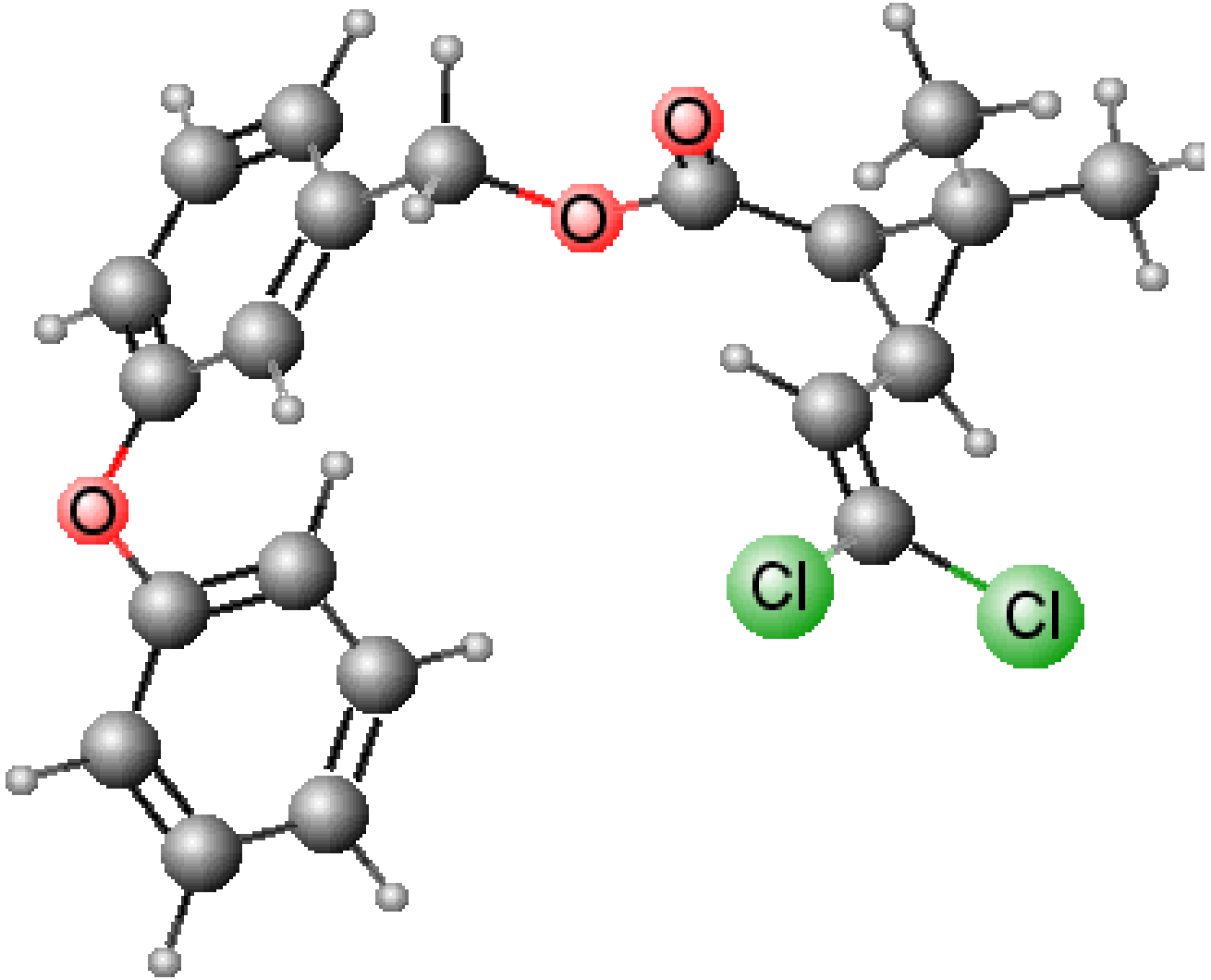
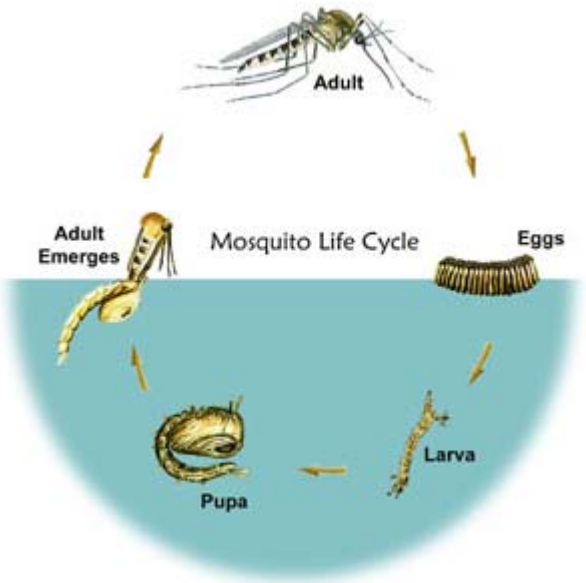
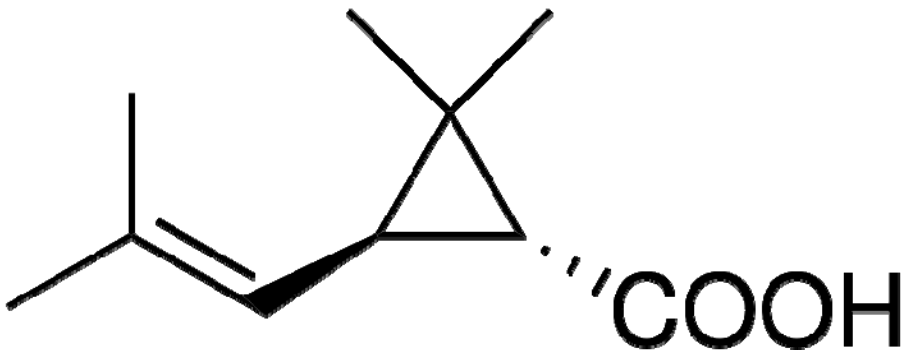
Interesting ~~molecule~~ family of the day

- Permethrin

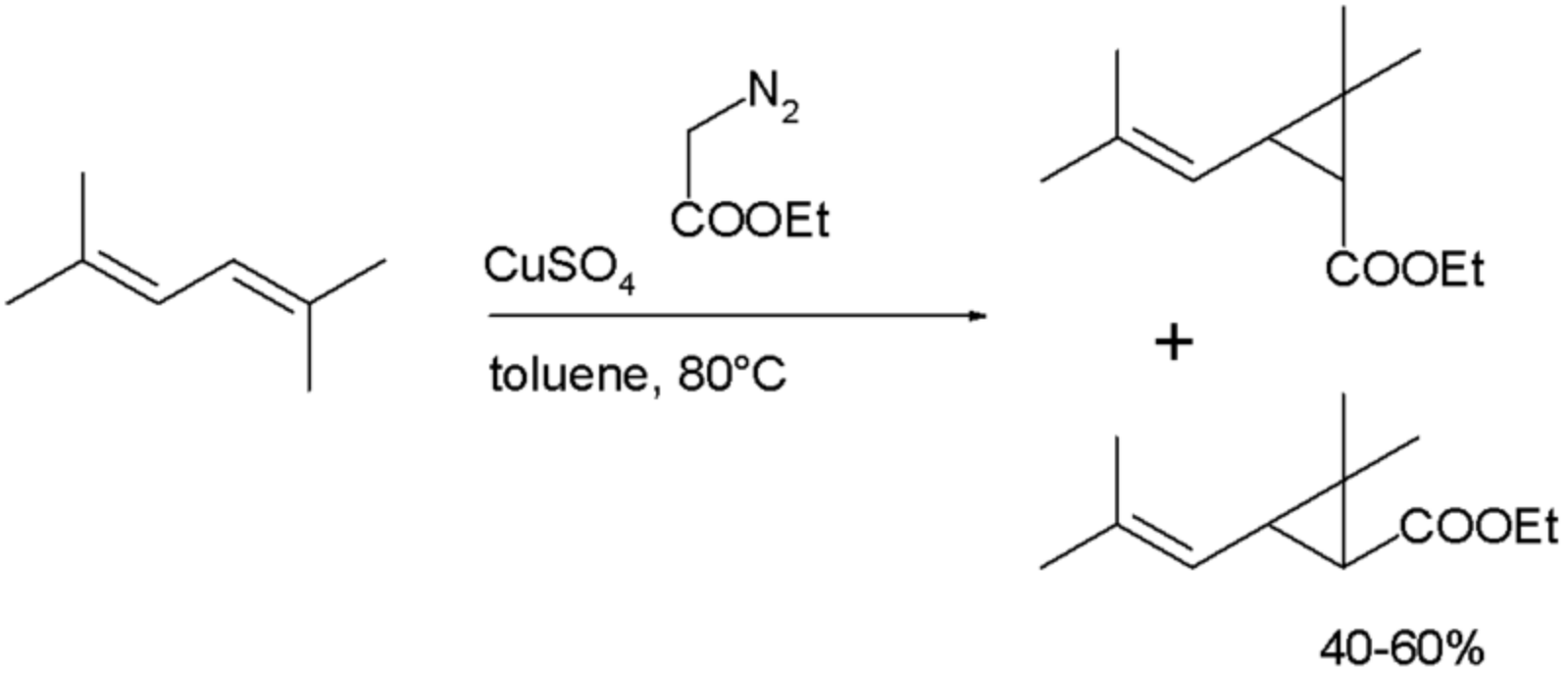


Interesting molecule family of the day





(1R,3R)- or (+)-trans-chrysanthemic acid



Interesting molecule family of the day

Types

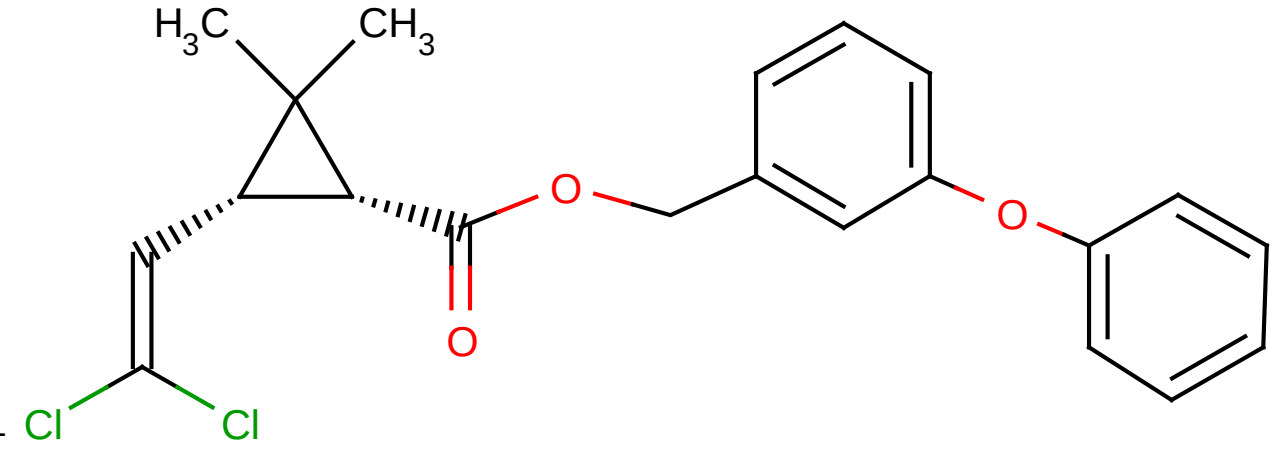
Allethrin, the first pyrethroid synthesized (active ingredient of Raid)
Bifenthrin, active ingredient of Talstar, Capture, Ortho Home Defense Max, and Bifenthrine
Cyfluthrin, an active ingredient in Baygon, dichlorovinyl derivative of pyrethrin
Cypermethrin, including the resolved isomer alpha-cypermethrin, dichlorovinyl derivative of pyrethrin
Cyphenothrin, active ingredient of K2000 Insect spray sold in Israel and the Palestinian territories
Deltamethrin, dibromovinyl derivative of pyrethrin
Esfenvalerate
Etofenprox
Fenpropathrin
Fenvalerate
Flucythrinate
Imiprothrin, FAST ACTING, active ingredient of Raid Ant & Roach Killer
lambda-Cyhalothrin
Metofluthrin
Permethrin, dichlorovinyl derivative of pyrethrin
Prallethrin, active ingredient in Baygon
Resmethrin, active ingredient of Scourge
Silafluofen
Sumithrin, active ingredient of Anvil
tau-Fluvalinate
Tefluthrin
Tetramethrin
Tralomethrin
Transfluthrin, active ingredient in Baygon

Interesting molecule family of the day

- Permethrin
  - insecticide
    - first marketed in 1973
  - agriculture
    - 100 million applications per year
    - cotton, corn, wheat, alfalfa
  - home
    - 18 million applications
    - gardens
    - head lice
  - four *isomers*
    - chiral (mirror), *R* and *S*
    - geometric isomers (*cis* and *trans*)

Interesting molecule family of the day

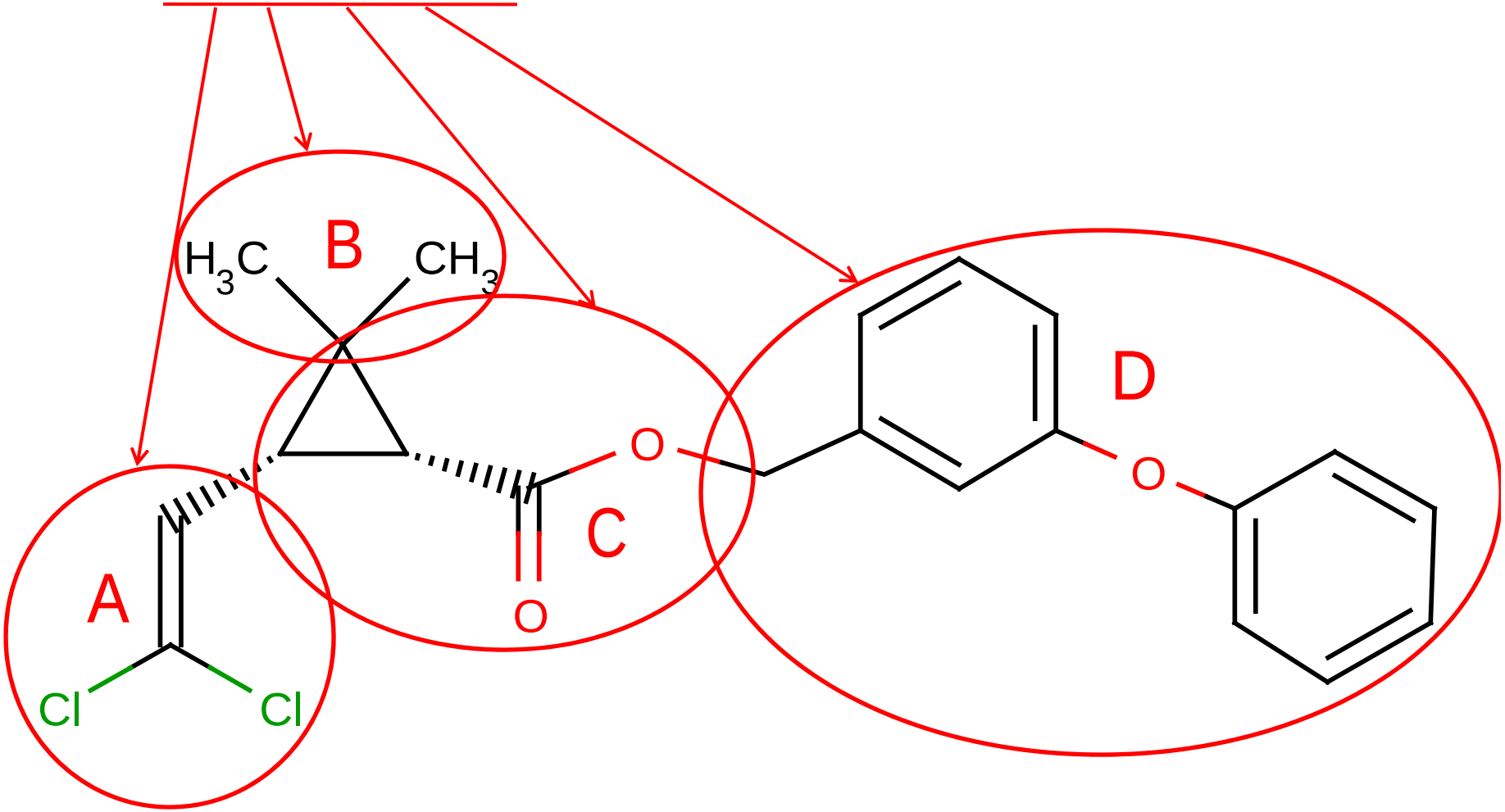
- Permethrin
  - $C_{21}H_{20}Cl_2O_3$
  - mw 391.2 Da
  - T_m 34-35 °C
  - T_b 437.6 °C
  - C_w^{sat} 6 μg L^{-1}
  - K_{aw} 0.000077
  - K_{ow} $10^{6.5}$
  - K_{oc} $10^{5.3}$ L kg^{-1}



- (3-phenoxyphenyl)methyl 3-(2,2-dichlorethenyl)-2,2-dimethylcyclopropanecarboxylate

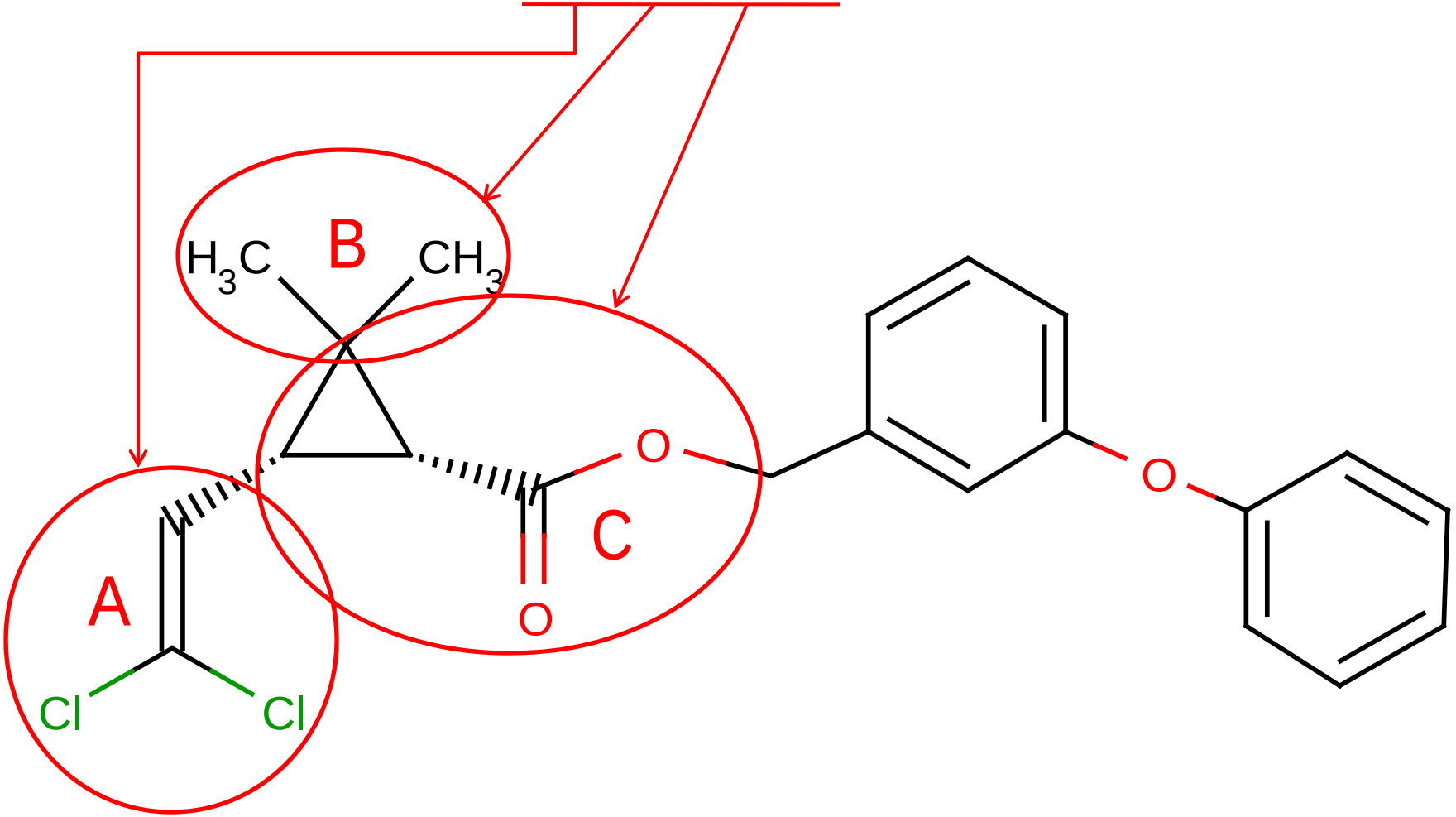
Interesting molecule family of the day

- Permethrin
  - (3-phenoxyphenyl)methyl 3-(2,2-dichlorethenyl)-2,2-dimethylcyclopropanecarboxylate



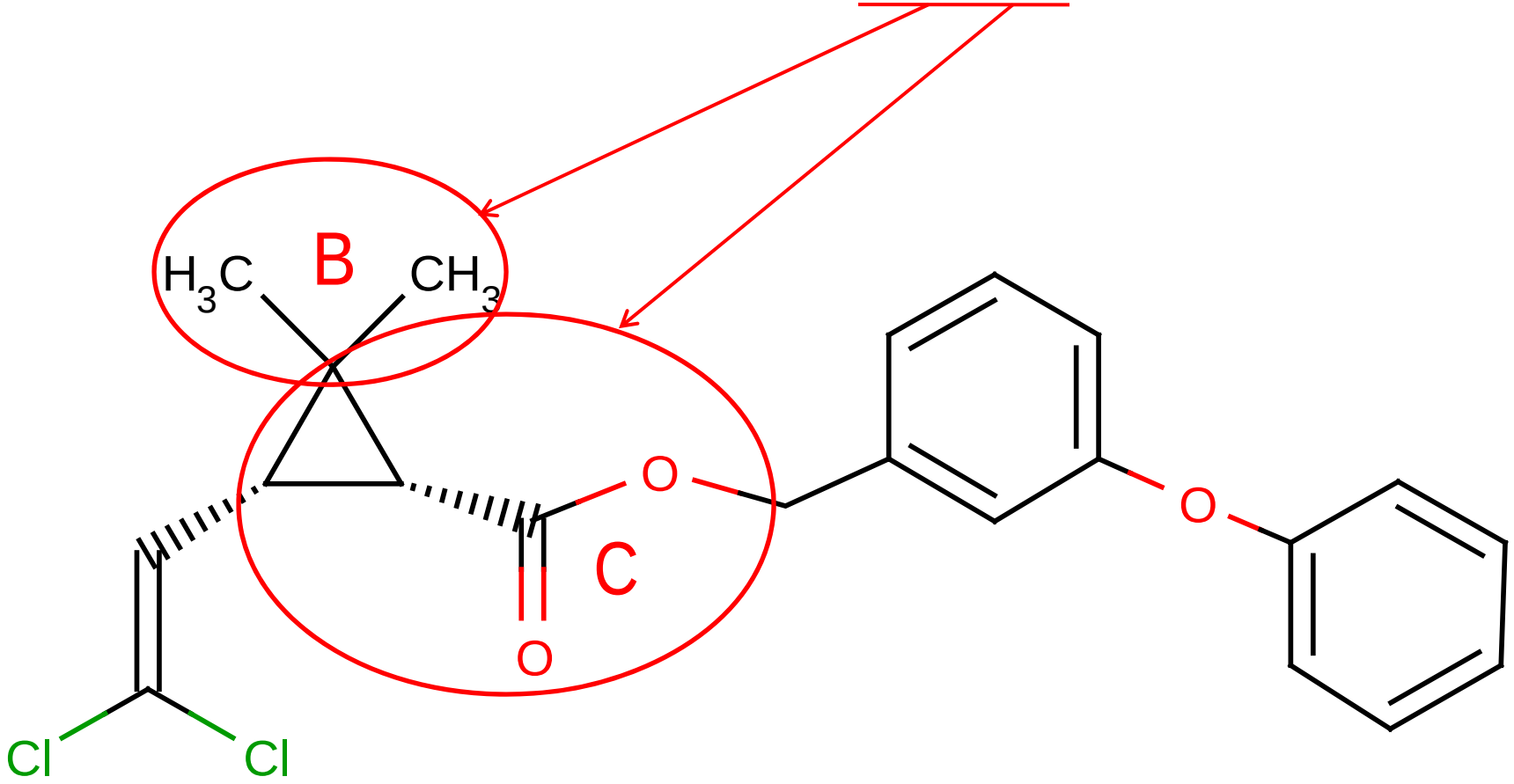
Interesting molecule family of the day

- Permethrin
  - (3-phenoxyphenyl)methyl 3-(2,2-dichlorethenyl)-2,2-dimethylcyclopropanecarboxylate



Interesting molecule family of the day

- Permethrin
  - (3-phenoxyphenyl)methyl 3-(2,2-dichlorethenyl)-2,2-dimethylcyclopropanecarboxylate



Interesting molecule family of the day

The human cost of spraying – Non-toxic measures would spare suffering

In its May 30 editorial, "Grave new world," the *Daily Camera* endorsed adulticiding (spraying for adult mosquitoes) in the fight against mosquitoes carrying West Nile Virus. It also asked those with multiple chemical sensitivities to make reasonable accommodations for the good of the community.

Putting aside for a moment the editorial's casual brush-off of the devastating effects chemical spraying would have on people like me, let me be clear that there is *no scientific evidence* that adulticiding is effective in fighting West Nile virus.

What is known is that synthetic pyrethroid pesticides such as permethrin are neurotoxins, capable of producing symptoms including tremors, poor coordination, headaches and loss of memory. Laboratory tests have also shown permethrin to cause immune and endocrine system damage, chromosome aberrations in human cells and lung and liver tumors in mice. While the Environmental Protection Agency has classified permethrin as a "possible carcinogen," research to determine its long-term effects on humans is still being conducted, and the evidence against pesticides continues to mount.

Boulder Daily Camera, June 13, 2004

Interesting molecule family of the day

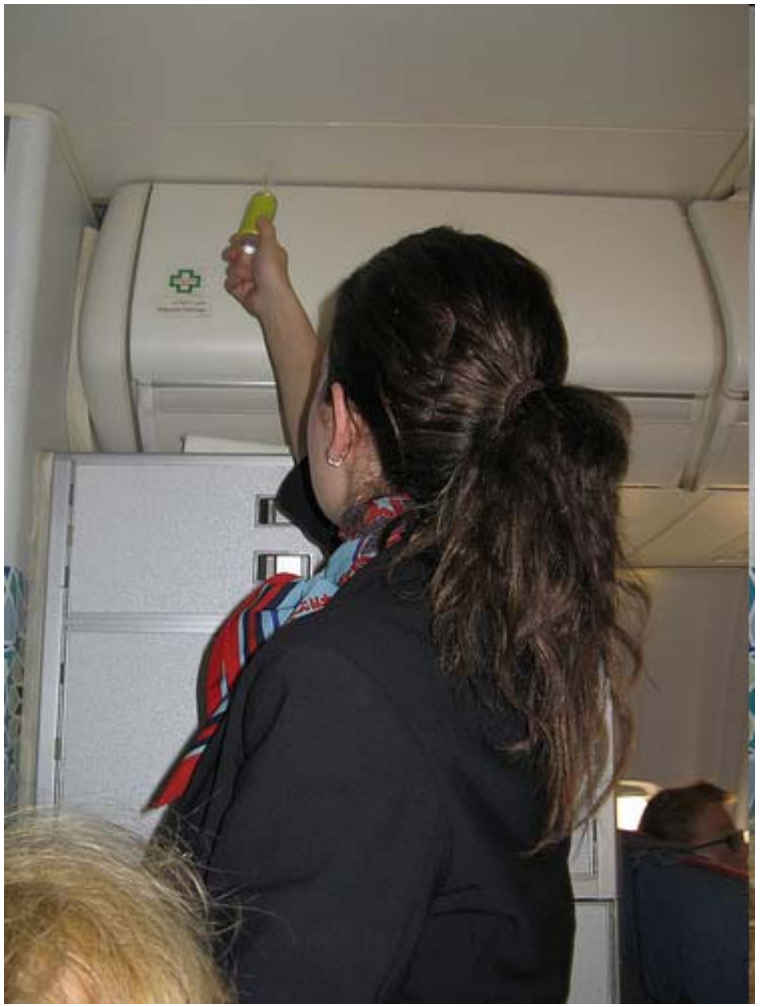
Insect Shield® Pro Calf-Length Sock

Bugs bite toes too. These socks protect all ten of them. Arch support, Coolmax™ foot bed, and moisture wicking make these socks seriously comfortable. **Insect Shield repellent lasts 70 washings.** ExOfficio clothing field-tested and approved by the African Wildlife Foundation.

Price: $14.00

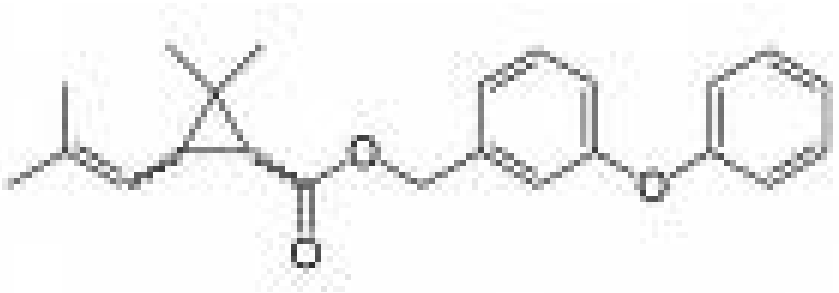
Interesting molecule family of the day

A cloud of insecticide containing DDT descends on passengers in this circa 1955 photo. Although banned in the US in 1972, DDT was sprayed in US aircraft until 1989.



Last week!

Interesting molecule family of the day



d-phenothrin (trade name: Sumithrin)

Interesting molecule family of the day

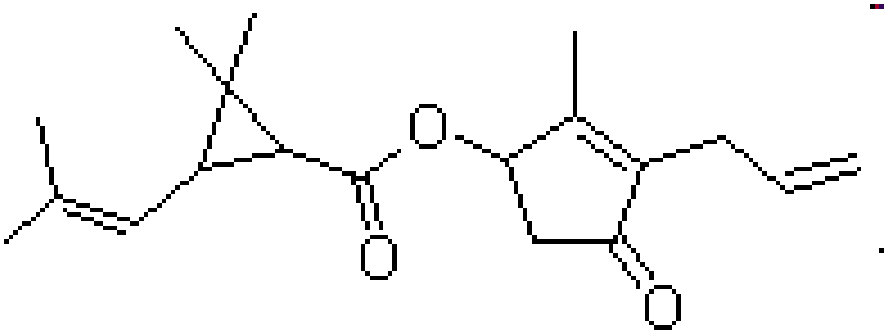
American Airlines

As of July 2008, American Airlines' flights arriving in Barbados and Jamaica are residually sprayed. Flights arriving in China may be residually sprayed or sprayed in-flight. American Airlines is currently exempt from spraying on flights arriving in India. Flights arriving in Trinidad/Tobago and Uruguay are sprayed while passengers and crew are still on board, and flights arriving in Panama are sprayed after people have left the plane. American Airlines serves destinations in South Africa that stop en route in Dakar (DKR) so they must be sprayed inflight prior to arrival.

DELTA USES A MINT BASED PESTICIDE FREE COMPOUND

AIR VS RESIDUAL SPRAY, IN FLIGHT OR BETWEEN FLIGHTS

Interesting molecule family of the day



10% d-allethrin

Precautions

•Hazards to humans and domestic animals—Caution: Avoid prolonged inhalation or contact with skin. Avoid contact with eyes or clothing. Do not touch lit end of coil. Do not use indoors. Wash hands after use and before eating or smoking. Cover any exposed food to avoid contamination. Do not place in direct contact with flammable objects, materials or surfaces.

•First aid: Call a poison control center or doctor for treatment advice. Have the product container or label with you when calling a poison control center or doctor, or going for treatment.

•If inhaled: Move person to fresh air. If person is not breathing, call 911 or an ambulance, then give artificial respiration, preferably mouth-to-mouth, if possible.

•If on skin or clothing: Take off contaminated clothing. Immediately rinse skin with plenty of water for 15-20 minutes.

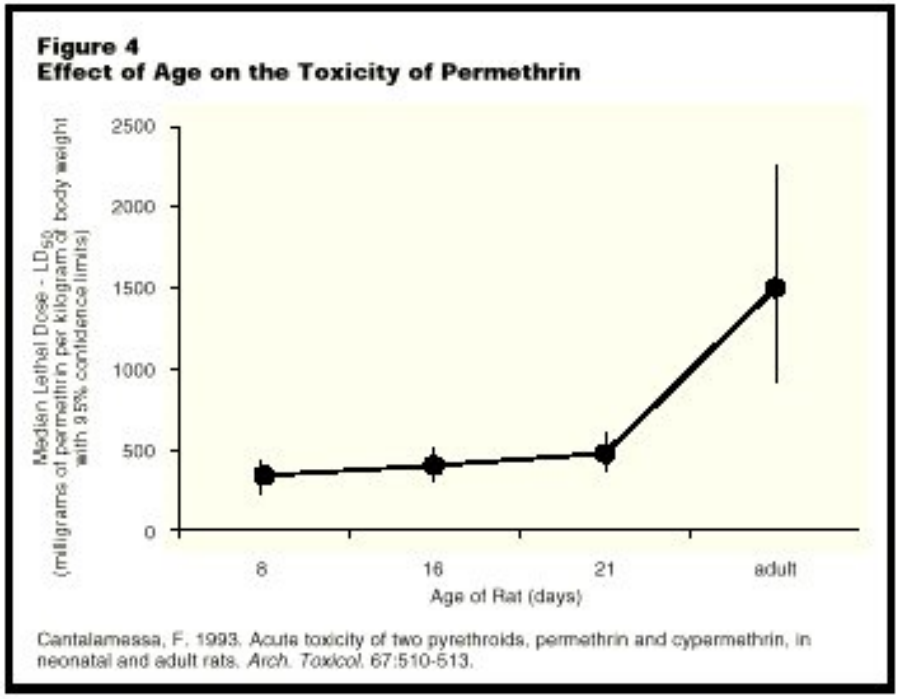
•If in eyes: Hold eye open and rinse slowly and gently with water for 15 -20 minutes. Remove contact lenses, if present, after the first five minutes, then continue rinsing eye.

•Physical or chemical hazards: Use with caution to avoid fire hazard.

•Environmental hazards: This pesticide is highly toxic to fish. Do not apply directly to water. Drift from treated areas may be hazardous to organisms in adjacent aquatic sites. Do not contaminate water when disposing of equipment washwaters.

Interesting molecule family of the day

- Permethrin
  - cancer classification: possible human carcinogen (EPA)
  - neruotoxin
  - oral reference dose (RfD) (IRIS)
    - 0.05 mg kg^{-1} d^{-1}
    - DDT for comparison: 0.0005 mg kg^{-1} d^{-1}
  - *cis* isomer ten times more toxic than *trans*



Permethrin is more toxic (the LD_{50} is lower) to young rats than to adult rats.

"It appears children may be more sensitive to permethrin than adults. Permethrin is almost 5 times more acutely toxic to 8-day-old rats than it is to adult rats."

Vapor Pressure

$$\ln p^* = -\frac{\Delta_{12}H}{RT} + \frac{\Delta_{12}S}{R}$$

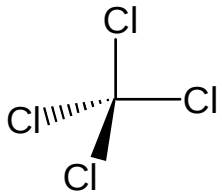
- Entropy of melting (solid to liquid)
  - Myrdal and Yalkowsky:

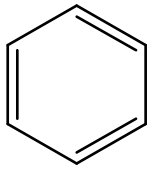
$$\Delta_{fus}S(T_m) = 56.5 + 9.2\tau - 19.2\log\sigma$$

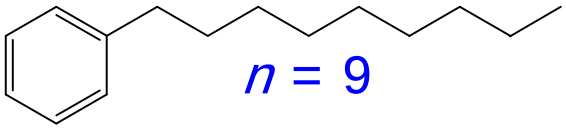
τ: effective number of torsional bonds

σ: rotational symmetry number

- does not work well for small spherical or H-bonding molecules





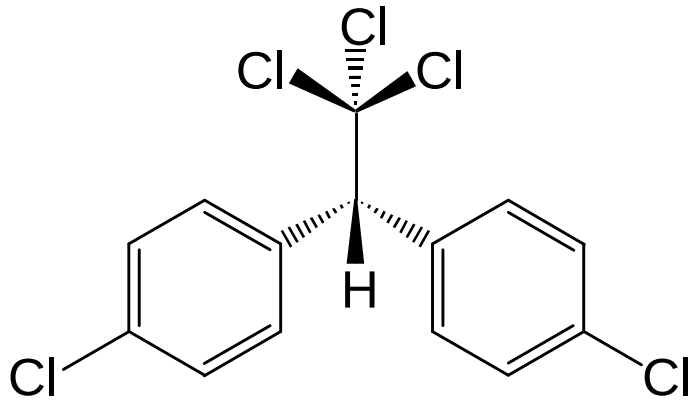


NOT A GOOD WAY TO ESTIMATE OR PREDICT!

Vapor Pressure Estimation

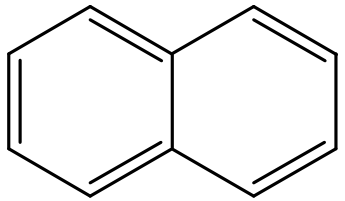
- Estimating the entropy of melting: carbon tetrachloride and naphthalene

$$\Delta_{fus} S(T_m) = 56.5 + 9.2\tau - 19.2 \log \sigma \qquad \text{(Eqn. 4-39)}$$



DDT

1,1,1-trichloro-2,2-bis(4,4'-dichlorodiphenyl)ethane

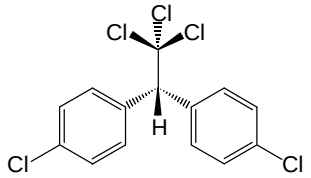


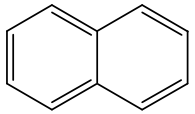
naphthalene

Vapor Pressure Estimation

- Estimating the entropy of melting:
  DDT and naphthalene

$$\Delta_{fus}S(T_m) = 56.5 + 9.2\tau - 19.2\log\sigma$$ (Eqn. 4-39)



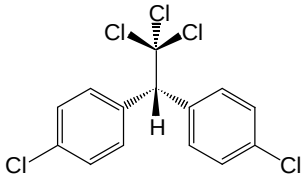


τ	?	?
σ	?	?

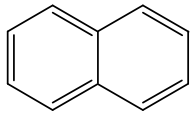
τ= number of nonterminable sp3 + 0.5 nonterminate sp2 + 0.5 (ring systems)-1

Vapor Pressure Estimation

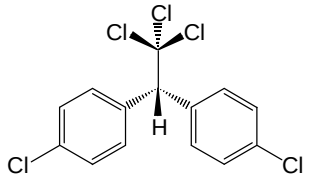
- Example: DDT and naphthalene
  - τ, torsional bond number

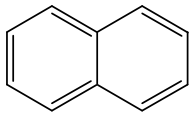


$$\tau = \sum\left(1+0.5(0)+0.5(2)\right)-1=1$$ (1 *SP3*, 2 *RING*)



$$\tau = \sum\left(0+0.5(0)+0.5(1)\right)-1=0$$ (1 <u>independent</u> *RING*)

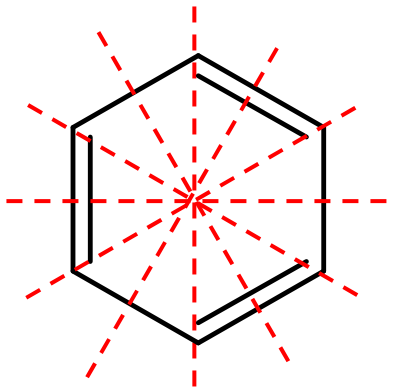




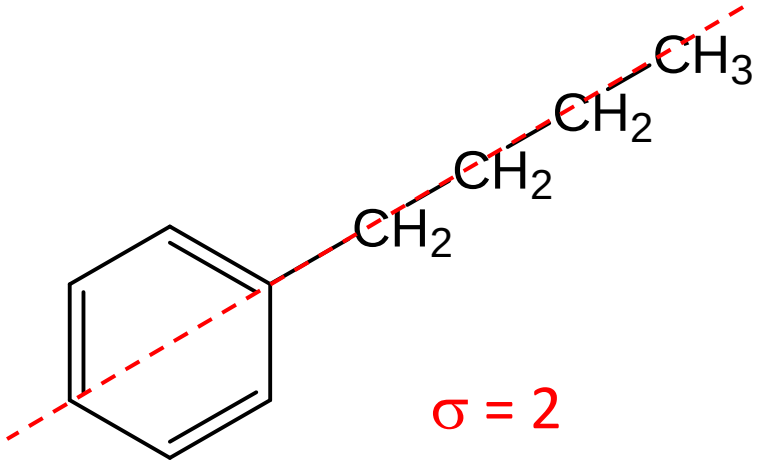
τ	1	0
σ	?	?

Vapor Pressure Estimation

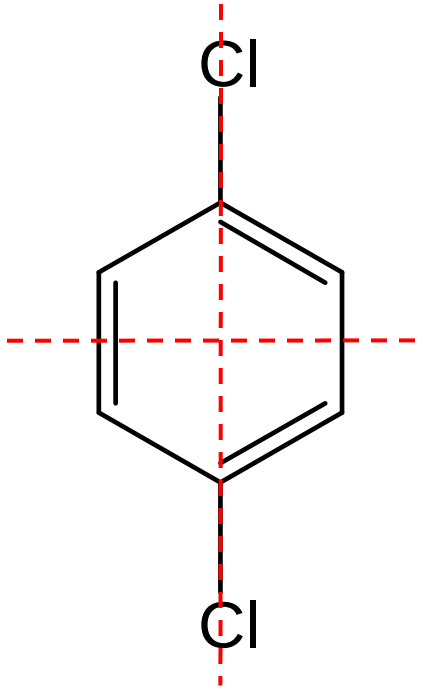
- Example: carbon tetrachloride and naphthalene
  - σ, rotational symmetry number (p. 126)
    - number of indistinguishable orientations for the compound
    - axes of rotational symmetry
      - σ = 1 for a compound with no rotational symmetry
    - each axis adds σ = 2 (Table 4.5)
    - see Dannenfelser et al. (1993)



σ = 12



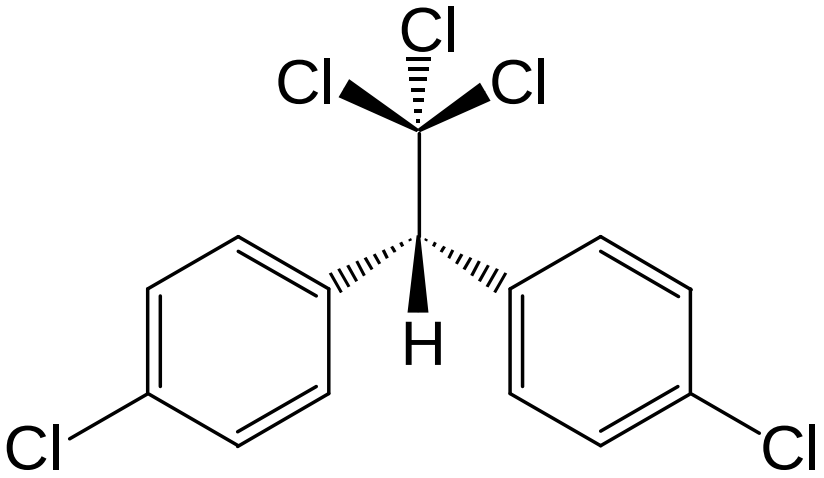
σ = 2



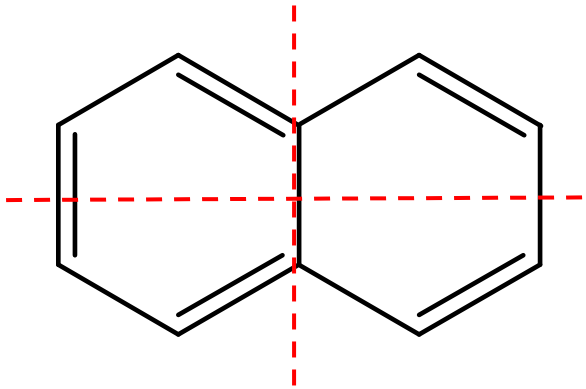
σ = 4

Vapor Pressure Estimation

- Rotational symmetry



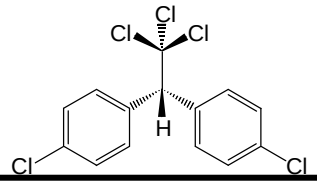
$\sigma = 1$

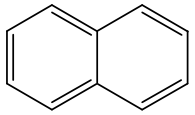


$\sigma = 4$

Vapor Pressure Estimation

- Example: carbon tet and naphthalene





τ	1	0
σ	1	4

$$\Delta_{fus}S(T_m) = 56.5 + 9.2\tau - 19.2\log\sigma$$

$$\Delta_{fus}S(T_m) = 56.5 + 9.2(0) - 19.2\log(4)$$

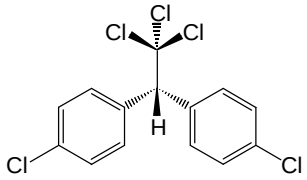
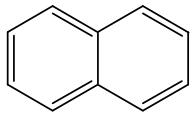
$$\Delta_{fus}S(T_m) = 44.9\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

$\Delta_{fus}S$ (J mol^{-1} K^{-1})	65.7	44.9

Measured (table 4.5) 71.6 62.7

Vapor Pressure Estimation

- Example: DDT and naphthalene

$\Delta_{fus}S$ (J mol^{-1} K^{-1})		
Reid et al.	56.5	56.5
Myrdal et al.	74.9	44.9
measured	71.6	52.7

Vapor Pressure Estimation

- Solids

$$\ln \frac{p_{iS}^*}{p_{iL}^*} = -(6.80 + 1.1\tau - 2.3\log\sigma)\left(\frac{T_m}{T} - 1\right)$$

  - Remember rules for $\Delta_{fus}S(T_m)$
    - spherical, symmetric compound ~14 J mol^{-1} K^{-1}
  - Still need p_L^*
    - data from CRC or…
    - estimate using ln p^* relationships

Vapor Pressure Estimation (4.35)

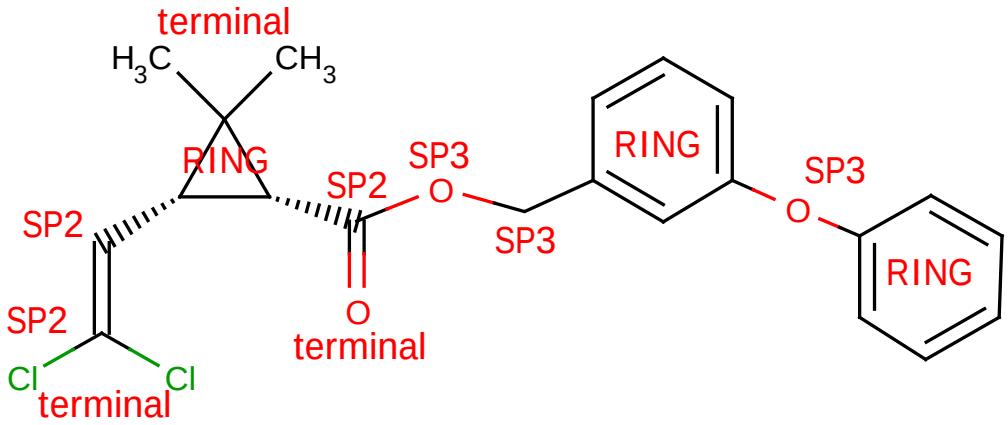
- Example: permethrin
  - determine the vapor pressure at 25°C using only T_b, T_m
  - T_m = 34-35 °C = 307 K
  - T_b = 437.6 °C = 710.8 K

$$\ln p_{iL}^{*}\ (\text{bar}) \approx -(21.2 + 0.3\tau + 177 HBN)\left(\frac{T_b}{T} - 1\right) + (10.8 + 0.25\tau)\ln\left(\frac{T_b}{T}\right)$$

$$\tau = \sum\left(SP3 + 0.5SP2 + 0.5RING\right) - 1$$

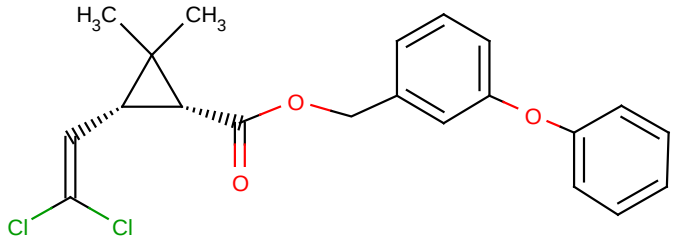
$$\tau = \sum\left(3 + 0.5(3) + 0.5(3)\right) - 1 = 5$$

$$HBN = 0$$



Vapor Pressure Estimation

- Example: permethrin
  - T_b = 437.6 °C = 710.8 K



$$\ln p_{iL}^{*}\ (\text{bar}) \approx -(21.2 + 0.3(5) + 177(0))\left(\frac{710.8}{298.2} - 1\right) + (10.8 + 0.25(5))\ln\left(\frac{710.8}{298.2}\right)$$

$$\ln p_{iL}^{*} = -20.95$$

$$p_{iL}^{*} = 8.0 \times 10^{-10}\ \text{bar}$$

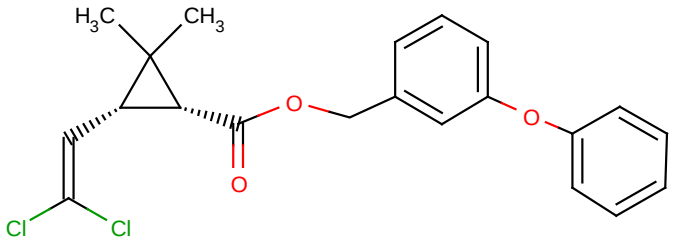
  - this is the vapor pressure of permethrin as a *subcooled liquid*

Vapor Pressure Estimation (4.40)

- Example: permethrin
  - T_m = 34-35 °C = 307 K

$$\ln \frac{p_{iS}^*}{p_{iL}^*} = -(6.80 + 1.1\tau - 2.3\log\sigma)\left(\frac{T_m}{T} - 1\right)$$

  - $\tau = 5$
  - $\sigma = 1$ (no rotational symmetry)

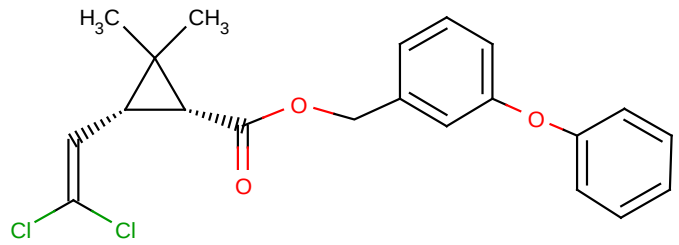


Vapor Pressure Estimation

- Example: permethrin
  - T_m = 34-35 °C = 307 K

$$\ln \frac{p_{iS}^*}{p_{iL}^*} = -\left(6.80 + 1.1(5) - 2.3\log(1)\right)\left(\frac{307}{298} - 1\right)$$

$$\ln \frac{p_{iS}^*}{p_{iL}^*} = -0.37$$



$$\frac{p_{iS}^*}{p_{iL}^*} = 0.69$$

$$p_{iS}^* = 0.69\, p_{iL}^* = 0.69\left(8.0 \times 10^{-10}\ \text{bar}\right)$$

$$\boxed{p_{iS}^* = 5.5 \times 10^{-10}\ \text{bar}}$$

p_S^* = 4.5×10^{-10} bar

Kidd and James (1991) *The Agrochemicals Handbook*