

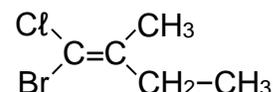


Organic Isomers 2:

E and Z

In Organic Isomers 1, compounds containing double bonds and rings were further identified according to which stereoisomer they were using the *cis/trans*- system. That system is pretty limited. It works when each side of the molecule has one alkyl group and one that's not, but that doesn't cover every case.

Consider the molecule here. It's one possible molecule that could be called 1-bromo-1-chloro-2-methyl-1-butene — the other one would have the chloro and bromo groups reversed — so is this the *cis*- or the *trans*-version? We can't say because *cis/trans*- assumes the double bond bridges the parent chain, and the substituents are separated by the double bond. Neither is true here.



There's a more recent system for naming these compounds: the *E/Z* system. It covers every case that *cis/trans*- does and more. It establishes one high-priority group and one low-priority group on each side of the molecule, and then compares their locations. Priority is established using the Cahn-Ingold-Prelog system.

The Cahn-Ingold-Prelog system uses atomic numbers to determine priority. For the two group on the left side of the double bond in our molecule, chlorine has the atomic number 17, and bromine has the atomic number 35. Bromine's atomic number is higher, so it has higher priority.

What about the groups on the right? To start with, we're only concerned with the atoms that are directly bonded to the carbon in the double bond, but in both cases, it's another carbon, so it's a tie. The atoms involved in the tie are both bonded three more times. We consider those atoms to break the tie. The carbon in the methyl group is one of the atoms in the tie; the first carbon in the ethyl group is the other. The methyl's carbon atom is also bonded to three hydrogen atoms ($Z = 1$). The first carbon atom in the ethyl group is bonded to two hydrogen atoms and the second carbon atom ($Z = 6$). Our choices are, by atomic number, in decreasing order, 1-1-1 and 6-1-1, so the ethyl group has higher priority. (This is a handy rule that can make this analysis go faster: when the choice is between two straight-chain alkyl groups, the longer chain has higher priority.) If we still had a tie, we'd start spreading out through the molecule until there was a difference between the choices.

Some other useful things to know about Cahn-Ingold-Prelog:

- Double and triple bonds are counted as individual bonds to an atom. For example, if we needed to decide what priority an aldehyde group had, $\text{C}(=\text{O})\text{H}$, the three atoms that carbon is bonded to are oxygen, oxygen, hydrogen, so the numbers are 8-8-1.
- If the tie is not broken and you've looked at the whole molecule, that means the tied structures are actually identical, and there is no need for any isomer specification.



Once we've found the high-priority group on each side, we see if they're lined up or not, just as in the *cis/trans*-system. (This newer system isn't any different in that regard; it just uses a more expansive method of selecting which groups to pay attention to.) If the two high-priority groups line up (as in *cis*-), the molecule has the *Z* configuration. If they don't line up (as in *trans*-), the molecule has the *E* configuration. The configuration goes at the start of the molecule name in parentheses. The molecule from the example is (*Z*)-1-bromo-1-chloro-2-methyl-1-butene.

Cycloalkane isomers are also distinguished this way. If one high-priority group is above the ring and the other is below, it's the *E* configuration; otherwise, it's the *Z* configuration.

EXERCISES

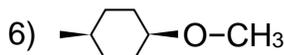
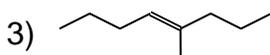
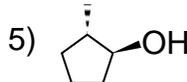
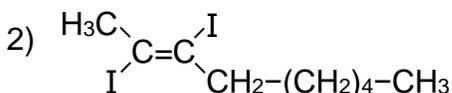
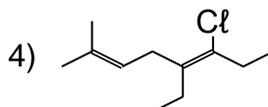
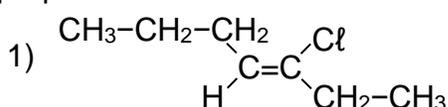
A. 1) Draw the following molecules, then determine whether they are in the *E* or the *Z* configuration.

- | | |
|--|---|
| a) <i>cis</i> -3-methyl-3-heptene | c) <i>cis</i> -2-bromo-2-pentene |
| b) <i>trans</i> -2,3-dichloro-3-hexene | d) <i>trans</i> -1-iodo-3-methylcyclohexane |
- 2) Is it true that *cis*- and *Z* are equivalent and *trans*- and *E* are equivalent?

B. For the following pairs of groups, identify which has higher priority in the Cahn-Ingold-Prelog system, and state what two atomic numbers get compared to make that determination. (E.g., for "chloro; bromo", bromo is higher, 35 vs. 17.) To help you identify the groups, the number of atoms is included for each group.

- | | |
|------------------------------------|--|
| 1) methyl [4 atoms]; iodo [1 atom] | 4) isopropyl [10]; <i>tert</i> -butyl [13] |
| 2) nonyl [28]; octyl [25] | 5) amine [3]; nitro [3] |
| 3) alcohol [2]; methoxy [4] | 6) aldehyde [3]; carboxylic acid [4] |

C. Name the following molecules, specifying isomers with the *E/Z* system where appropriate.



SOLUTIONS

- A: (1)a) *Z* (b) *E* (c) *E* (d) *Z* (2) No, because the systems' priorities are different.
 B: (1) iodo, 53 vs 6 (2) nonyl, 6 vs 1 (3) methoxy, 6 vs 1 (4) *tert*-butyl, 6 vs 1
 (5) nitro, 8 vs 1 (6) carboxylic acid, 8 vs 1
 C: (1) (*Z*)-3-chloro-3-hexene (2) (*E*)-2,3-diiodo-2-nonene (3) (*E*)-4-methyl-4-octene
 (4) (*Z*)-6-chloro-5-ethyl-2-methyl-2,5-octadiene (5) (*E*)-2-methylcyclopentanol
 (6) (*Z*)-1-methoxy-4-methylcyclopentane

