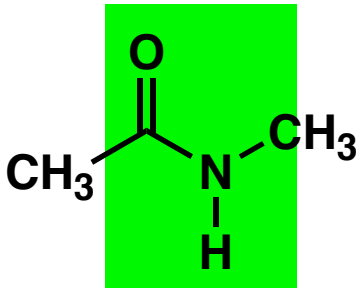
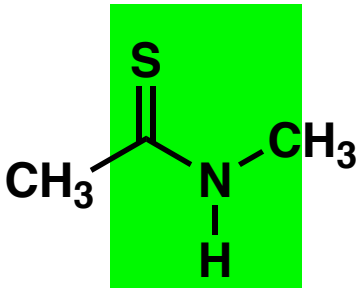
Discussion Problem

The amide functional group joins α-amino acids into peptides and proteins. Replacement of the amide's oxygen atom with sulfur results in an analogous functional group known as the thioamide. The geometry of the amide and thioamide groups reveals delocalized electronic structure. In particular, the nitrogen atom of amides and thioamides is planar, not pyramidal. Moreover, the atoms contained within the green rectangle lie in a plane. Based on this information, (a) draw the second best resonance contributor for each of these functional groups. (b) For which functional group, an amide or a thioamide, is the 2nd best resonance contributor more important? Why? (c) Given the geometric description above, what hybrid orbitals on nitrogen are used in amide and thioamide bonding? (d) Draw a picture that shows the orbitals involved in the amide's delocalized bonding.

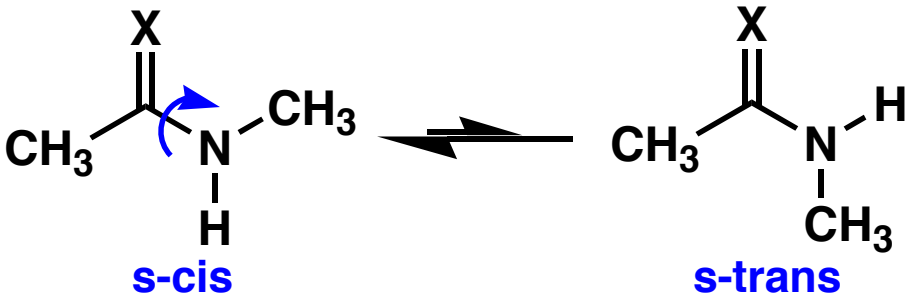


amide (peptide bond)



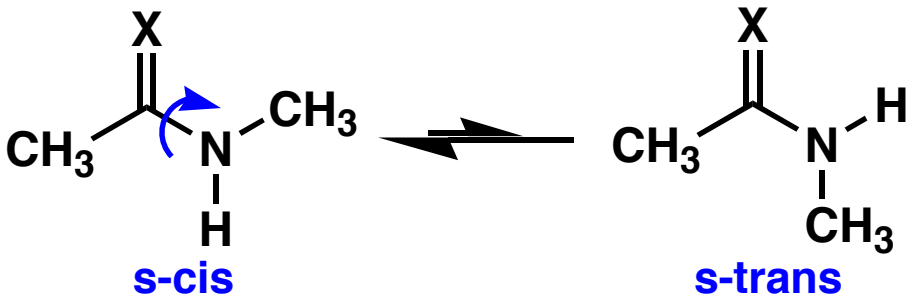
thioamide

Discussion Problem Continued



The amide and thioamide groups exist in two planar forms known as the *s-cis* and *s-trans* conformations. These two conformations are interconverted by a 180˚ rotation about the C-N bond as indicated below. The transition state for this interconversion process occurs at a rotation angle of 90˚. (e) Using a Newman projection viewed down the C-N bond, show the geometry of the transition state including the orientation of the p-orbitals on the nitrogen, carbonyl carbon, and X atoms. (f) Does resonance delocalization contribute much stability to the transition state for either the amide or the thioamide? Explain.

Discussion Problem Continued



Draw a potential energy diagram for the *s-cis* to *s-trans* interconversion (only draw one diagram but put both the thioamide and amide on this diagram). Be sure to show (1) the relative energies of the *s-cis* state for the amide vs. the thioamide, (2) the relative energies of the transition state for the amide vs. the thioamide, and (3) the energies of the *s-trans* states for the amide and thioamide relative to the corresponding *s-cis* states. (h) Based on your diagram, predict whether the rate of rotation around the C-N bond is <u>slower</u> for an amide or thioamide.