

Profil de rotation autour de la C-N du PhenylBr, avec tBu

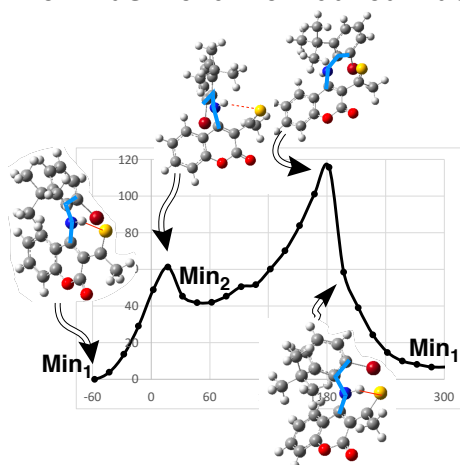


Figure 1: C=S case, rotation of the phenyl. The rotation angle is shown in blue. At -60° Min₁ is obtained. This minimum is here taken as the origin of the energies.

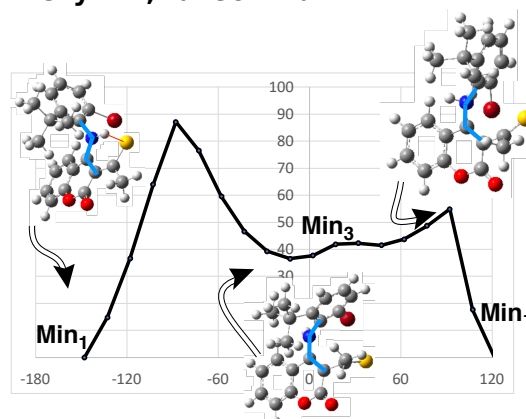


Figure 2: C=S case, rotation of the coumarine. This second rotation angle is also shown in blue. At about -150° , Min₁ is obtained (origin of the energies).

Comment: As we rotate around the phenyl's C-N bond, the angle reaches at $+20^\circ$ a low barrier ($+60$ kJ/mol) that connects to a meta stable plateau at $+40$ kJ/mol. This minimum Min₂ cannot stay still because the barrier to return to Min₁ is low (20 kJ/mol). The second barrier at an angle of 180° is at 120 kJ/mol, the H bond is then restored, it connects to Min₁. According to this computation, there is only one stable isomere, Min₁.

The same occurs for the second rotation, around the coumarine N-C bond (Figure 2): the plateau is at about 40 kJ/mol (Min₃), and the barrier to return to Min₁ is very low (10 kJ/mol).

Conclusion: this system with C=S should have only Min₁ as a stereoisomer. Because even if barriers are low (50 – 90 kJ/mol), the other minima are not stable ($+40$ kJ/mol) compared to Min₁ which is stabilized by the internal H-Bond. Moreover, the barrier to return to Min₁ is always very small. The H-Bond stabilization energy may not be the only reason for the differences because 40 kJ/mol is a bit too large, but it certainly contributes. In the project, we shall evaluate separately the H-Bond contribution, for instance with smaller models.

To note : the low barriers are due to the N-H< inversion which is low in energy. If we freeze the position of the NH toward the C=S< moiety, the barriers are much higher (160 and 240 kJ/mol) and the second min (Min₁* is the enantiomer of Min₁).

