

The most stable conformation in alkyloxy moieties is gauche

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Generally it is assumed and has been confirmed that the most stable conformation of flexible chains like alkyl groups is all-trans. Using quantum chemical calculations, unexpectedly we found in compounds of different chemical structure containing alkyloxy moieties that the most stable conformation of the latter is not all-trans, but it contains a gauche conformation. This result can be obtained by calculations with semi-empirical or DFT methods and it was confirmed by calculations with high level ab initio calculations using the MP2 method. Depending on the specific compound and the applied method, the energy difference between the all-trans conformer and the gauche conformer is in between 0.3 to 9.5 kJ/mole. In the gauche conformation an open five-membered ring is formed in which the distance between the O atom and the adjacent H atom is smaller than the van der Waals radii (Fig. 1). With increasing polarity of the H atom, this distance becomes smaller and the energy differences of the all-trans and gauche conformers increase. The formation of weak hydrogen bonds between the oxygen atom and the adjacent hydrogen can explain this effect¹.

Despite the relatively small energy related to this effect, its occurrence has been observed in the solid state. The different clearing temperatures of liquid crystalline isomers in certain cases can be explained by formation of gauche conformers with lower length-to breadth ratio. In compounds with several O atoms in the chains the effect can produce predominant conformers stable in the liquid as well as in the solid state.

References

1. G. R. Desiraju, Th. Steiner, *The Weak Hydrogen Bond*, Oxford Publications 2006

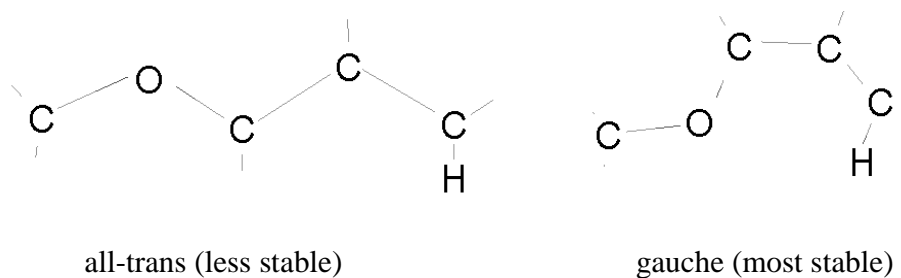


Fig. 1 Methyl-propylether