Theoretical Study on Amines: aniline, N-methylaniline, p-methylaniline and p-methyl-N-methylaniline

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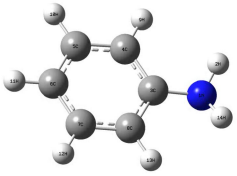
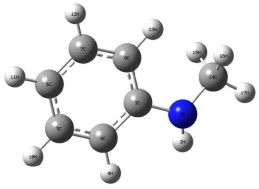
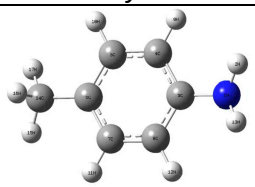
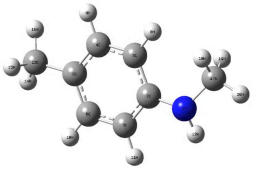
The acetylation of amines is one of the most frequently used transformations in organic synthesis as it provides an efficient and inexpensive means for protecting amino groups in a multistep synthetic process. Geometric parameters of reactants: aniline,N-methylaniline,p-methylaniline[1]and p-methyl-N-methylaniline were performed in the gas phase using the DFT/B3LYP density functional quantum mechanical method and was adopted the 3-21+G* basis set. Enthalpies of formation were determined using the AM1 method. The table lists the energies, lengths and angles values obtained. Steric effects caused by the additional methyl group might be responsible of an increase of the energy of N-methylaniline compared to aniline and an increase of the energy of p-methyl-N-methylaniline compared to p-methylaniline.

Amines Structures	Bond Lengths	Bond Angles	Energies kcal mol^{-1}
 Aniline	C_3-C_4 = 1.42 Å C_4-H_9 = 1.09 Å C_3-N = 1.39 Å N-H_2= 0.99 Å	C_3-N-H_2 = 114.22 º C_4-C_3-N = 120.71 º C_3-C_4-H_9= 120.13 º C_3-C_4-C_5= 120.29 º	20.38
 N-methylaniline	C_3-N = 1.40 Å C_{14}-N = 1.43 Å C_{14}-H_{17} = 1.12 Å N-H_2= 0.99 Å	C_3-N-C_{14} = 118.92 º C_8-C_3-N = 122.09 º N-C_{14}-H_{15}= 113.27 º C_3-N-H_2= 112.83 º	24.08
 p-methylaniline	C_3-N = 1.40 Å C_6-C_{14} = 1.48 Å C_{14}-H_{15} = 1.12 Å N-H_2= 0.99 Å	C_6-C_{14}-C_{17} = 110.98 º C_4-C_3-N = 120.80 º C_7-C_6-C_{14}= 120.63 º C_3-N-H_2= 114.09 º	15.71
 p-methyl- N-methylaniline	C_{17}-N = 1.43 Å C_2-N = 1.41 Å C_5-H_{13} = 1.48 Å N-H_{12}= 0.99 Å	C_2-N-C_{17} = 118.83 º H_{19}-C_{17}-N = 113.30 º C_4-C_5-C_{13}= 120.74 º C_2-N-H_{12}= 112.73 º	16.50

References

1. Altun, A.; Gölcük, K.; Kumru, M. Structure and vibrational spectra of p-methyl aniline: Hartree-Fock, MP2 and density functional theory studies. *J. Mol. Struct. (Theochem)*. **2003**, *637*, 155–169.