

Structural stability, NH₂ inversion and vibrational assignments of 2,4,6-trichloroaniline and 2,3,5,6-tetrachloroaniline

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Abstract

The structural stability of aniline, 2,4,6-trichloroaniline and 2,3,5,6-tetrachloroaniline was investigated by DFT-B3LYP and ab initio MP2 and MP4(SDQ) calculations with the 6-311G** basis set. From the calculations the three molecules were predicted to exist predominantly in a symmetric *near-planar* structure. The NH₂ inversion barrier was estimated from the MP2/6-311G** level of theory to be about 9.6 kJ/mol for aniline, 5.9 kJ/mol for the trichloro and 4.6 kJ/mol for the tetrachloro derivatives. The line intensities of the ring breathing and the C—Cl stretching modes were shown to have a great dependence on the number of chlorine atoms on the benzene ring. The relative change in Raman line intensity of the C—Cl stretching mode was explained on the basis of the inductive effect of the chlorine atoms on the benzene ring. The vibrational frequencies were computed at the DFT-B3LYP level and the infrared and Raman spectra for each molecule were calculated. Complete vibrational assignments were made on the basis of normal coordinate analyses and potential energy distributions for the two chloroanilines.

Keywords: Ab initio MP2; MP4(SDQ) and DFT-B3LYP calculations; Vibrational spectra and assignments; Aniline; 2,4,6-trichloroaniline; 2,3,5,6-tetrachloroaniline