Effect of Intermolecular Hydrogen Bonding on the Nuclear Quadrupole Interaction in Imidazole and its Derivatives as Studied by *ab initio* Molecular Orbital Calculations

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Ab initio Hartree-Fock molecular orbital calculations were applied to the crystalline imidazole and its derivatives in order to examine systematically the effect of possible N–H · · · N type hydrogen bonding on the nuclear quadrupole interaction parameters in these materials. The nitrogen quadrupole coupling constant (QCC) and the asymmetry parameter (η) of the electric field gradient (EFG) were found to depend strongly on the size of the molecular clusters, from single molecule, to dimer, trimer and to the infinite molecular chain, i.e., crystalline state, implying that the intermolecular N–H · · · N hydrogen bond affects significantly the electronic structure of imidazole molecule. A certain correlation between the QCC of ^{14}N and the N–H bond distance R was also found and interpreted on the basis of the molecular orbital theory. However, we found that the value of the calculated EFG at the hydrogen position of the N–H group, or the corresponding QCC value of ^{2}H, increases drastically as R^{-3} when R is shorter than about 0.1 nm, due probably to the inapplicability of the Gaussian basis sets to the very short chemical bond as revealed in the actual imidazole derivatives. We suggested that the observed N–H distances in imidazole derivatives should be re-examined.

Key words: Hydrogen Bond; Nuclear Quadrupole Interaction; Molecular Orbital; Imidazole.