



Concordia
UNIVERSITY

CENTRE FOR RESEARCH IN MOLECULAR MODELING

Special Seminars



January 11, 2005, 2:00 pm
Concordia University SP-S110

Theoretical Study on the Effect of Intramolecular Amino Groups on the C-NO₂ Bond – Amino and Nitro Substitutes of Alkane, Ethene and 1,3-Butadiene

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In this paper it is the first time that the population of nitro group is taken as the ability to absorb electrons (τ) and a criterion for measuring sensitivity of nitro compounds. The larger τ is, the less sensitivity will be. The effect of position and quantity of amino groups on C-NO₂ bonds were studied systematically at B3LYP/6-31G** level. The results indicate that (1) for amino and nitro substitutes of alkanes, the effect of amino group on C-NO₂ bond are inductive effect and spatial effect. When the two groups are separated by more than 2 carbon atoms, these effect are very weak. (2) But for ethylene substituted by amino and nitro groups, amino group at No.1 position weakens C-NO₂ bond, at No.2 position it will strengthen it: the more amino groups are, the shorter C-NO₂ bond will be, the stronger electro-negativity on carbon atom of C-NO₂ bond is, the longer the bond length of C=C is, the more τ is. That is to say, amino group is a very strong donor of electron and in the whole molecule the configuration effect is very large. (3) For amino and nitro substitutes of 1,3-butadiene, effect on C-NO₂ bond occurred by amidos were kin to orientation effect on benzene ring when H-bonds were not formed by H atoms in amino groups and O atoms in nitro groups; but the effect mentioned above would be weakened if H-bonds formed (the stronger H-bonds, the weaker C-NO₂ bond).

Keywords: amino groups, C-NO₂ bond, nitro ability to absorb electrons

Intermolecular Interaction Components from Asymptotically Corrected Kohn-Sham Orbitals

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The symmetry-adapted perturbation theory (SAPT) that has the ability in decomposition of the total interaction energy into physically meaningful components is used to provide a more fundamental understanding of intermolecular forces. This work was motivated by the difficulty of standard SAPT in computing the intermolecular interactions for large energetic dimer systems. SAPT based on Kohn-Sham orbitals (SAPT(DFT)) proves computationally efficient for these large systems, but has been shown to perform poorly for interaction energy components. The deficiencies of SAPT(DFT) result from wrong asymptotical behaviors of commonly used exchange-correlation potentials. To remove the deficiencies, two asymptotic corrections by means of van Leeuwen and Baerends (LB) model potential and Fermi-Amaldi (FA) type potential were applied into three small test systems comprising He₂, (HF)₂ and (N₂)₂ and a set of larger nitramide dimers at several separations. The results showed that when utilizing newly developed frequency-dependent density susceptibilities (FDSD) technique for computing dispersion energy (Misquitta, *et al.*, *Phys. Rev. Lett.* 2003, 91: 033201), the FA asymptotic correction is very effective to circumvent these deficiencies in SAPT(DFT) and yields a good accuracy over the LB correction. The FA corrected SAPT(DFT) approach is capable of correctly predicting all the quantitative trends in binding energies for all test cases and substantially reduces computational cost as compared with the standard SAPT calculations. The successful application of the approach to nitramide dimer demonstrates that it potentially provides a good means to calculate accurately intermolecular forces in larger system such as energetic systems.

Keywords: intermolecular interaction, density functional theory (DFT), symmetry adapted perturbation theory (SAPT), asymptotic correction, frequency-dependent density susceptibilities (FDSD).