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QUANTUM-CHEMICAL STUDY OF THE EFFECTS OF NONCOVALENT INTERACTIONS ON THE NUCLEAR MAGNETIC SCREENING CONSTANTS OF PYRIMIDINE BASE ASSOCIATES

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The effects of weak noncovalent interactions on the nuclear magnetic screening (NMS) constants (σ ^{1}H), (σ ^{13}C) and charge distribution (q_t) on atoms in van der Waals model associates of unsubstituted and substituted pyrimidines and substituted uracil are considered. The NMS constants were calculated by the UB3LYP/6-31G(*d*,*p*) with GIAO functions. The correlation dependences of the ^{1}H and ^{13}C σ constants on the charge q on atoms whre constructed. It were shown that they can be represented as polynomials that include the terms that are linear and quadratic relative to the charge. The relations obtained in this way are similar in form and close in magnitude to the coefficients of the known Buckingham and Augspurger functions that describe the electric field effects on the nuclear magnetic screening constants. It was found that the coefficients in these polynomials have a definite physical sense in that they characterize nuclear magnetic screening and the "screening polarizability" tensor in the unperturbed molecule and associate, respectively. The NMS constants and charge distribution in pyrimidine base associates and accordingly the coefficients that reflect their values in polynomials depend on the form, size, and composition of the associate and can vary significantly depending on the position of the pyrimidine base in the associate.

Keywords: nuclear magnetic screening, van der Waals associates, pyrimidine bases, quantum-chemical calculations, screening polarizability, stacking interactions, electric fields, charge distribution.

INTRODUCTION

Today active research is under way to study the structure and properties of highly organized natural, biological, and synthetic supramolecular systems such as helices [1, 3], rosettes [4], rods [5], clusters [5-8], layers or ribbons [9, 10], nanotubes [11, 12], including chiral nanotubes [3, 13], and nanodisks [14]. These structures are of great interest in view of their unique physicochemical properties, which are often not exhibited by their separate molecular blocks, such as, e.g., charge transfer processes in the stack structures of aromatic molecules, including those of pyrimidine bases; dramatic changes in the tautomer forms of pyrimidine bases if there are several stacking interactions in nucleic acid helices; and drug intercalation effects and their influence on the properties of biomolecules.

Design of supramolecular assemblies and nanostructures having preset specific physicochemical properties is based on the cluster formation mechanism; in this mechanism, an important role is played by the cooperative effects of all

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