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Theoretical study for a complex of 1,2,5-thiadiazole with formic acid

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ABSTRACT

Ab initio and DFT calculations have been performed on a complex of 1,2,5-thiadiazole with formic acid. Fifteen local minima of the complex are found using the MP2/6-31G method. In the ten planar structures, 1,2,5-thiadiazole and formic acid connect by two non-covalent bonds, such as O—H···N, C—H···O, C—H···N and S···O, to form ring structures, and the other five structures contain only one non-covalent bond. The three stable structures with the lowest total energies are examined at the HF/6-311++G(2d, 2p), MP2/6-311++G(2d, 2p) and B3LYP/6-311++G(2d, 2p) theory levels. The first and second stable structures contain intermolecular O—H···N/C—H···O and S···O/O—H···N interactions, respectively. Their binding energies by MP2 corrected BSSE and ZPE are −7.0 to −7.2 kcal/mol, which indicate a great stabilization of the complex. The NBO analysis has revealed that the $n(N) \rightarrow \sigma^*(O—H)$ interaction gives the strongest stabilization to the complex and the lone pairs of carbonyl oxygen in formic acid play an important role in the weak intermolecular interactions in the complex.

1. Introduction

Compounds containing a 1,2,5-thiadiazole ring have received much attention, due to their potential use as fungicides, herbicides, polymer materials [1], fluorescent materials [2] and organic conductors [3,4]. From viewpoint of crystal engineering, the peripheral S and N atoms are expected to form short intermolecular heteroatom contacts, which can result in unique molecular networks [5]. For example, one-dimensional supramolecular tape structures connected by short intermolecular S···N heteroatom interactions at the 1,2,5-thiadiazole rings were observed in the crystal of benzobis(1,2,5-thiadiazole) derivatives [6]. In addition, multidimensional structures achieved by intermolecular S···S and/or S···N interactions contribute to stabilizing the metallic state at low temperature in the solid state of organic conductors and superconductors [7]. Therefore, development of building blocks involving intermolecular heteroatom interactions is challenging for controlling molecular aggregations and designing crystal structures. Such type of molecular building block, however, is not extensively investigated to date. Theoretical studies of intermolecular heteroatom interactions are still very rare, while those of hydrogen-bonded complexes have been an active area of research for last several years [8]. Some works have been reported for intermolecular S···S interactions in tetrathiafulvalene molecules [9], intermolecular S···X (X = O, N and S) interactions in protein structures [10] and statistical analysis of intermolecular S···O and S···N interactions using a structural database [11]. Our final goal is to control molecular arrangements of functional molecules containing 1,2,5-thiadiazole rings using weak non-covalent bonds. With this in mind, we focus our attention on a complex of 1,2,5-thiadiazole with formic acid, and we have performed fundamental theoretical studies of the system to clarify a non-covalent binding pattern of the 1,2,5-thiadiazole moiety. Formic acid is the simplest organic acid with two attractive interaction sites on its carboxylic part. In crystal engineering, carboxylic parts are the most important building blocks for designing crystal structures. The tools for constructing functional supramolecular architectures using robust and directional non-covalent bonds are called "*supramolecular synthons*" [12]. A number of possible stable geometries are considered for the complex of 1,2,5-thiadiazole with formic acid, where various types of non-covalent interactions are supposed between two components of the molecule. If the results of the theoretical study reveal the strong stability and directionality of the complex, 1,2,5-thiadiazole moieties can be applied to novel supramolecular synthons. Furthermore, a significant amount of work on the structures of formic acid clusters has been published [13,14], whereas 1,2,5-thiadiazole clusters like the complex in this study have never been reported in the literature to date.

In this paper, we report the structures and properties of the complex of 1,2,5-thiadiazole with formic acid, which may be useful to the study of molecular clusters and molecular design in supramolecular systems.

2. Computational details

All calculations were performed with the GAMESS [15]. The structures of the studied monomers and complexes were fully

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optimized at the Hartree–Fock (HF) method, second-order Møller–Plesset perturbation method (MP2) [16,17] and density functional theory (DFT) method with the exchange potential of Becke [18] and correlation functional of Lee, Yang and Parr (B3LYP) [19]. The 6-31G and 6-311++G(2d, 2p) basis sets were used in this work. The 1,2,5-thiadiazole molecule was adapted to C_{2v} symmetry and the other structures have C_s symmetry. The obtained binding energies of the complexes were corrected for both basis set superposition error (BSSE) by the Boys–Bernardi full counterpoise method [20] and for zero-point vibrational energy (ZPE). The harmonic frequency analyses have been carried out and all the optimized geometries have no imaginary frequency. The natural bond orbital (NBO) analysis [21] has been carried out using the NBO version 3.1 [22] as implemented in Gaussian 03 [23]. All molecular graphics were drawn using MacMolPlt [24].

3. Results and discussion

We have found at least 15 local minima for the complex of 1,2,5-thiadiazole with formic acid at the MP2/6-31G level. Harmonic frequency analyses indicated that the obtained structures are true minima. Fig. 1 shows the optimized planar structures of the complex with their total energies. The structural optimizations were also performed on non-planar structures, which are π-stacking complexes with parallel molecular planes and T-shaped complexes with perpendicular molecular planes. They, however, converged on any structure listed in Fig. 1 during the optimization. In the ten structures in Fig. 1, 1,2,5-thiadiazole and formic acid molecules connect by two non-covalent bonds to form ring structures, and the other five structures contain only one non-covalent bond. Relative energy of structure XV to I is 18.1 kcal/mol. Various types of non-covalent bonds, such as

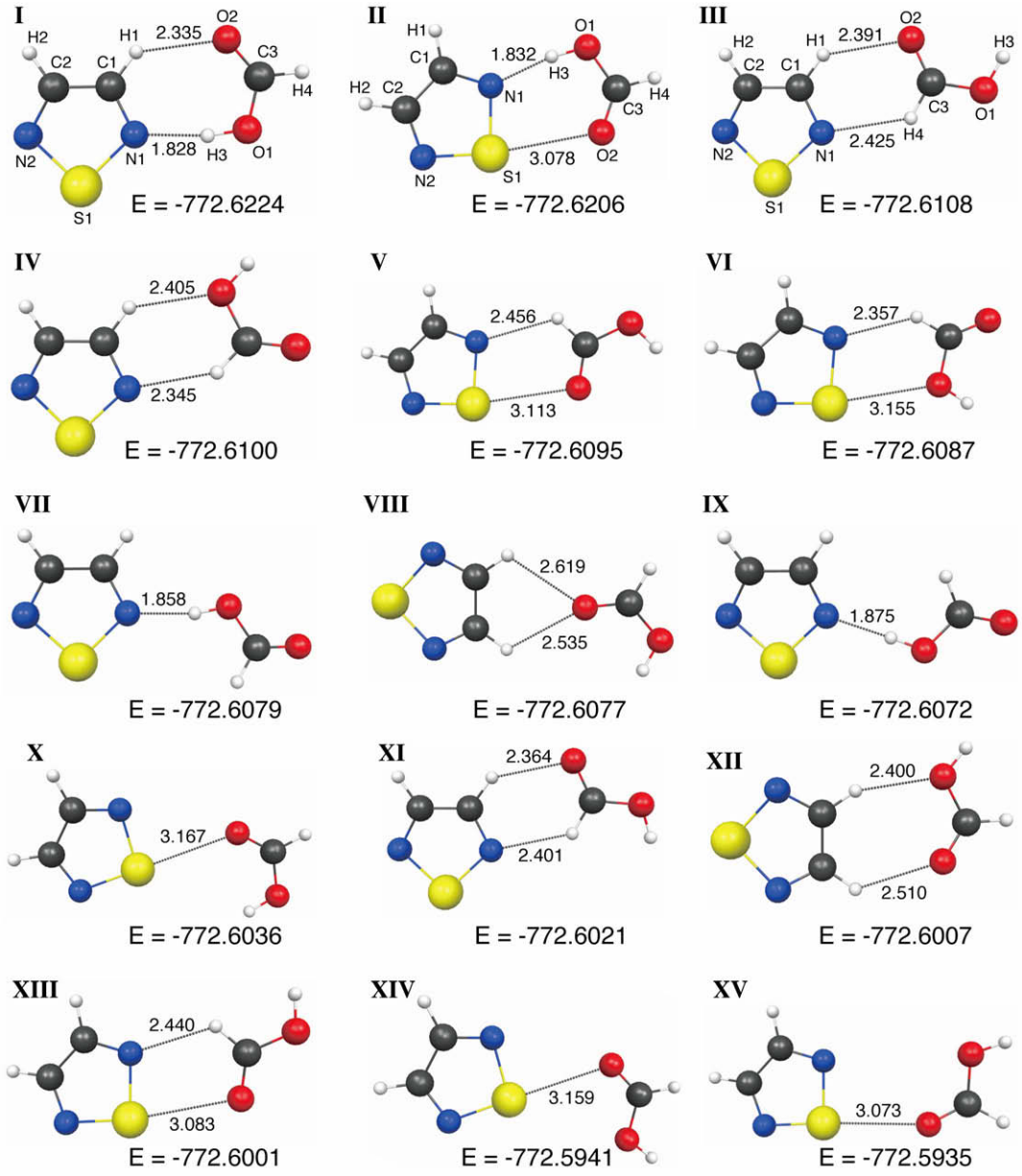

Fig. 1. The optimized planar structures for the complex of 1,2,5-thiadiazole with formic acid at the MP2/6-31G level with their total energies (hartree), intermolecular distances (Å) and atomic numbering schemes for I, II and III.