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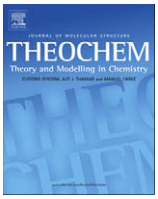

A density functional investigation of 1,3-bis(4-nitrophenyl)urea as anion receptor

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ABSTRACT

The B3LYP/6-311+G(d,p) optimized structures of 1,3-bis(4-nitrophenyl)urea receptor (**1**) and its complexes with halide ions F^-, Cl^-, Br^-, oxygen-containing anions NO_2^-, NO_3^-, HCO_3^-, HSO_4^-, $H_2PO_4^-$, CH_3COO^- and $C_6H_5COO^-$ ions were obtained. Binding energies and thermodynamic properties of binding between the receptor **1** and these anions were determined. Binding energies of receptor **1** are in decreasing orders: $CH_3COO^- > HCO_3^- \sim C_6H_5COO^- > NO_2^- > H_2PO_4^- > NO_3^- > HSO_4^-$ for oxygen-containing anions and $F^- > Cl^- > Br^-$ for halide ions. It was found that the binding energies depend on their hydrogen-bond distances of their binding atoms. It was also found that the complexes of receptor **1** and the studied anions are formed via two-point hydrogen-bonding interactions.

1. Introduction

Anions play an important role in several fields such as biology [1], the environment [2], catalysis [3] and potential medical application [4]. Thus the design of molecular sensors for anion recognition and sensing are interesting of chemists for many years, especially, in the research field of supramolecular chemistry [5]. The major need for designing is both sensitive and selective sensors for anions [6,7]. Hosts containing a variety of donor (D) groups, D–H, such as ureas [8–11], amines [12], amides [13,14] and thioamides [15] have been widely investigated. Urea based receptors have been used more extensively for anion detection [16,17]. Receptors containing one or more urea subunits have been designed and tested for anion recognition and sensing over the past years [18]. Moreover, selectivity is also related to the energy of the receptor-anion interaction; in this sense, strong H-bond interactions are established with anions containing the most electronegative atoms. Recently, 1,3-bis(4-nitrophenyl)urea (**1**) complexes with anions and its X-ray structure with acetate and hydrogen carbonate have been obtained [19]. The complex of receptor **1** with fluoride ion was found to be the most stable complex. Molecular structures of pyrrole derivatives, their interactions with halide ions [20–22] and azophenol thioureas, calix[4]arenes and their complexations with dicarboxylate anions [23,24] were studied by theoretical calculations [20–24].

Although the synthesis and anion binding ability of urea containing nitrophenyl **1** have been developed, the theoretical studies to gain clearer information i.e., geometrical structure, binding energy, molecular orbital and charge transfer, on the origin of molecular recognition affinity have never been considered. In this work, the binding energies and thermodynamic properties of the 1,3-bis(4-nitrophenyl)urea complexes with anions F^-, Cl^-, Br^-, NO_2^-, NO_3^-, HCO_3^-, HSO_4^-, $H_2PO_4^-$, CH_3COO^- and $C_6H_5COO^-$ have therefore been theoretically investigated using the density functional theory method.

2. Computational method

Density functional theory (DFT) has been employed to optimize the structures of 1,3-bis(4-nitrophenyl)urea (**1**) and its complexes with anions F^-, Cl^-, Br^-, NO_2^-, NO_3^-, HCO_3^-, HSO_4^-, $H_2PO_4^-$, CH_3COO^- and $C_6H_5COO^-$. The DFT calculations have been performed using the Becke's three-parameter exchange functional with the Lee–Yang–Parr correlation functional (B3LYP) [25]. All calculations have been performed using the MO computations at the B3LYP/6-311+G(d,p) level of theory [26]. The vibrational frequency computations have been carried out at 298.15 K and 1 atm. Stationary points have been fully optimized and characterized by vibrational frequency calculations, which also provided zero point vibrational energies (ZPVE) [27]. The standard enthalpy ΔH^0_{298} and Gibbs free energy changes ΔG^0_{298} of the reactions have been derived from the frequency calculations at the B3LYP/6-311+G(d,p) level.

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The natural bond orbital (NBO) analysis implemented in Gaussian 03 program [28] is applied through a series of intermolecular interactions under the above system to evaluate the NBO charges. All calculations were performed with the Gaussian 03 program [28]. The MOLDEN 4.2 program [29] was utilized to display the molecular structure, monitor the geometrical parameters and observe the molecular geometry convergence via the Gaussian output file. The molecular graphics of all related species were generated with the MOLEKEL 4.3 program [30].

3. Results and discussion

3.1. Molecular structures and energies

The B3LYP/6-311+G(d,p) optimized structures of the receptor **1** and its complexes with anions F^-, Cl^-, Br^-, NO_2^-, NO_3^-, HCO_3^-, HSO_4^-, $H_2PO_4^-$, CH_3COO^- and $C_6H_5COO^-$ and their binding free energies are shown in Fig. 1. It was found that the molecular symmetries of the receptor **1** and its complexes with F^-, Cl^-, Br^-, NO_2^-, NO_3^- and $C_6H_5COO^-$ ions are C_{2v} point group but its complexes with HCO_3^-, HSO_4^-, $H_2PO_4^-$ and CH_3COO^- belong to C_s, C_s, C_2 and C_s symmetries, respectively. The selected geometrical parameters for the receptor **1** and its complexes with anions are shown in Table 1. Geometrical parameters of the B3LYP/6-311+G(d,p)-optimized molecule for the complexes with HCO_3^- and CH_3COO^- ions were found to be somewhat different from their corresponding X-ray crystallographic data [19]. It was found that each of these structures of the complexes were formed via two-point hydrogen-bonds.

Relation between the binding free energy (ΔG) of the receptor **1** with anionic guests and their hydrogen-bond distances is shown in Fig. 2(a). It shows that trends on correlation between the binding energies of the receptor **1** with these anions and their hydrogen-bond distances are linearly related depending on anionic type; the above and bottom lines in Fig. 2(a) are for the halide and oxygen-containing anions, respectively. The linear relations for the halide and oxygen-containing anions can be confirmed with the correlation coefficients of 0.992 (r^2, above line) and 0.887 (bottom line), respectively. Due to the thermodynamic formula $\Delta G = -RT \log K$, the negative binding free energy ($-\Delta G$) has to correlate with the log K of the association process and its correlation coefficient must approach to unity. The plots of the negative binding free energy against the experimental values of log K [19] of the systems of two halide ions (top) and of oxygen-containing anions (bottom) are shown in Fig. 2(b) and the weak correlation between $-\Delta G$ and Log K for the system of the oxygen-containing anions ($r^2 = 0.518$) was obtained. Nevertheless, the system of the two halide ions could not be concluded because only two data points were applied.

The hydrogen-bond distances for the halide complexes are within the range of 1.520–2.306 Å and the oxoanionic complexes are within the range of 1.697–2.269 Å. Their hydrogen-bond characteristics should be remarked by their complexation according to the different binding ions. Hydrogen-bond characteristics of the complexes with the halide ions and the oxygen-containing ions are as NH···X, (X = F^-, Cl^- or Br^-) and NH···O, respectively. It was found that the calculated hydrogen-bond distances of the complexes with $HCO_3^-$and CH_3COO^- ions are somewhat different from their corresponding X-ray data [19]; the bond distances of the $HCO_3^-$and CH_3COO^- are 1.729 and 1.697 Å for computation and 1.913 and 1.819 Å for experiment, respectively. This may be caused by the difference of their molecular strain, electrostatic and polarity environments. Moreover, the counter ion such a tetrabutyl ammonium ion which is included in the X-ray structure was not included in the structure optimization. The binding energies, enthalpies and Gibbs free energies of the complexations between the receptor **1** and the anions obtained from the B3LYP/6-311+G(d,p) calculations are listed in Table 2. In the halide system, the **1**/F^- is the most stable complex ($\Delta E = -79.62$ kcal/mol) which is in good agreement with the experiment as reported by Boiocchi group [19]. It was concluded that the complexation abilities of these complexes strongly depend on both intermolecular hydrogen-bond distance and the type of anion. For the system of oxoanionic complex, relative stabilities are in decreasing order: **1**/CH_3COO^- > **1**/HCO_3^- ~ **1**/$C_6H_5COO^-$ > **1**/NO_2^- > **1**/$H_2PO_4^-$ > **1**/NO_3^- >

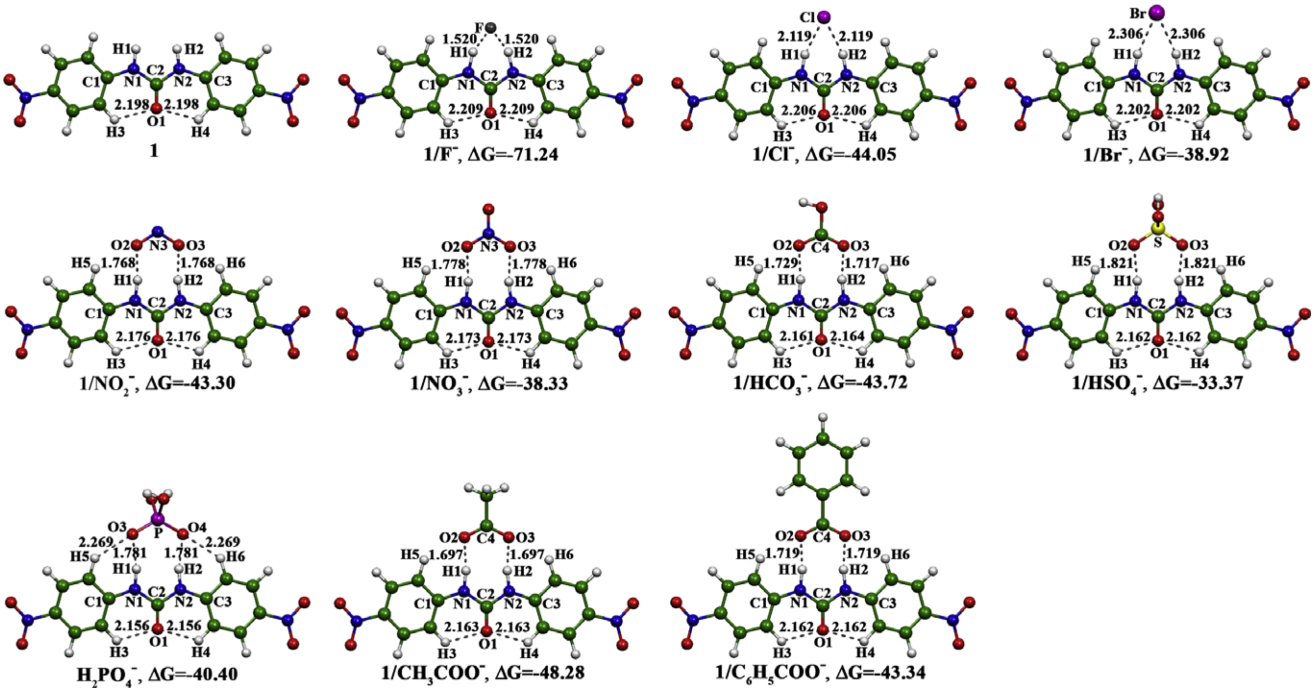

Fig. 1. The B3LYP/6-311+G(d,p) optimized structures of the receptor **1** and its complexes with anionic guests. The hydrogen-bond distances and binding free energies (ΔG) are in angstrom and kcal/mol, respectively.