Computational and Theoretical Chemistry 988 (2012) 19–26

Contents lists available at SciVerse ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

Halogen bonding of substituted iodobenzenes with potential solvent molecules: A comparison of binding energies

Geoffrey B. Piland, Paul G. Jasien *

Department of Chemistry & Biochemistry, California State University, San Marcos, San Marcos, CA 92096, United States

ARTICLE INFO

Article history:
Received 14 February 2012
Accepted 20 February 2012
Available online 27 February 2012

Keywords:
Halogen bonding
Intermolecular interactions
Solvation
Computational

ABSTRACT

Results of a series of MP2 calculations on the halogen bonding interactions of a variety of oxygen and chlorine containing Lewis bases with iodobenzene, monofluoroiodobenzenes, pentafluoroiodobenzene, and p-iodophenol are reported. The O-containing bases, for the most part, gave binding energies that correlated with basicity, but there were exceptions. The calculated values for the binding energy were on the order of 1 kcal/mol for the Cl bases, but varied from 1 to 8 kcal/mol for O bases. The effect of higher order correlation effects (MP4 and CCSD) on the energies was relatively minor. Calculations using a PCM to simulate solvent showed that in all cases, this effect lowers the binding energy of the halogen bond even though the computed halogen bond distance decreased. This work also compared multiple binding sites on the p-iodophenol system in complexes with H_2O; two hydrogen bonding, one π bonding, and the halogen bonding site to the iodine atom. It was found that although the halogen binding yields a significant BE of about 1–2 kcal/mol, this value is far below the hydrogen bonding sites.

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1. Introduction

It is well documented that intermolecular interactions play a crucial role in determining the properties of molecular aggregates. The best known of these intermolecular interactions is the hydrogen bond, which occurs when a slightly electron deficient hydrogen atom bonded to an electronegative atom interacts with an accessible electron pair on another species. Over the past few decades an analogous interaction involving halogen atoms has become better characterized [1]. In this so-called halogen bonding interaction, a halogen atom (most commonly Br or I) bonded to a more electronegative atom/group develops an electron deficient region along the sigma bond axis. This region has been called the σ-hole [2] and shows a positive enough electrostatic potential to interact with a negatively charged region associated with a lone pair of electrons. The interaction is often represented by XY–B, where Y represents the halogen atom and B represents the Lewis base providing the electron pair. A detailed analysis of the interaction more than a decade ago by Lommerse et al. [3] concluded that the halogen bonding interaction “is mainly due to electrostatic effects, but polarization, charge-transfer, and dispersion contributions all play an important role”. More recently [4], the results of Atoms In Molecules (AIMs) theory has been used to analyze the bonding in a number of small halogen bonded systems and compare this interaction with that of hydrogen bonded systems. Lu et al. [5], also examined the halogen bonding in a series of bromobenzene adducts with S, N, and O bases using AIM theory and concluded that the stronger halogen bonds are more covalent in nature, while the weaker ones are purely electrostatic.

The halogen bonding interaction has been associated with a wide range of molecular properties. Work by Auffinger et al. [6] investigated the role that halogen bonds may play in stabilizing inter- and intramolecular interactions that can affect ligand binding and molecular folding. Examples of the application of this idea to biological problems are evidenced in the computational work on rational drug design by Lu et al. [7] that used a QM/MM ONIOM methodology and the experimental work of Himmel et al. [8] that investigated the influence of iodine containing molecules on HIV-1 Inhibitors. Recently, from the results of quantum chemical calculations, it has been hypothesized that the activity of iodothyronine deiododinase activity may actually be a result of halogen bonding through an iodine atom [9].

Although biological applications of halogen bonding are intriguing, perhaps the area of material and crystal engineering has seen the most practical applications of halogen bonding in molecular design. This general area has been reviewed by Metrangolo et al. [1,10]. One specific application of this rational molecular design includes the possibility of tuning non-linear optical properties by using halogen bonding [11,12]. One of these reports [11] stated that the halogen bonding interaction of the solvent is so significant that it reverses the direction of the molecular dipole moment in some molecules.

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* Corresponding author.
E-mail address: jasien@csusm.edu (P.G. Jasien).

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doi:10.1016/j.comptc.2012.02.021

There have been a large number of computational studies of the halogen bonding phenomenon. Two of these have previously been noted [3,4]. Another study [13] done about a decade ago systematically investigated the relationship of the halogen bond binding energy (BE) to the number of electronegative substituents on the halogen donor molecule. This clearly established the sensitivity of BE to the substitution pattern on the halogen donor. Riley and Merz [14] investigated the effect of the solvent environment using the Polarizable Continuum Model (PCM) [15]. They found that the BE of halobenzene complexes with formaldehyde showed interactions on the order of less than 2 kcal/mol and that the BE increases on going from Cl to Br to I. Furthermore they reported that the presence of solvent decreases the binding energy in all cases studied. Lu et al. [16] also investigated solvent effects using PCM to calculate the BE of some halogen bonded complexes of C_2H_3I and C_6F_5I with a variety of Lewis bases, including H_2O and NH_3. Consistent with the previously discussed investigation by Riley and Merz [14], this work also noted a decrease in BE in a solvent environment.

Both DFT and MP2-based studies have contributed to a more detailed understanding of the halogen bond. Lu et al. [17] published a computational study that examined the affects of higher order correlation on the BE of the halogen bond, as well as a comparison with a number of DFT functionals. From CCSD(T) results, they concluded that "halogen bonding interactions are fairly sensitive to the inclusion of higher-order electron correlation effects that lead to a repulsive correlation with respect to those at the MP2 level." In addition, these authors showed that the choice of density functional greatly influenced the calculated outcome. Some of these functionals performed well compared to the MP2 results, but a number of others seemed to disproportionately favor the H-bonded structure over the halogen bonded, resulting in a failure to locate the halogen bonded minimum.

Donald et al. [18] looked at the effects of σ-hole tuning on a large number of halomethane-like systems containing heavy atom Group 14 atoms. In another study, Romaniello and Lelj [19] investigated halogen bonding using a DFT methodology combined with effective core potentials (ECPs). They concluded that relativistic effects are important for describing the geometry and BE even for third row atoms. In addition, based on their analysis using TD-DFT to calculate the C_6 van der Waals coefficient, they concluded that for the systems studied, the dispersion energy represented only a small contribution to the total BE.

A number of recent experimental studies have centered around using NMR shifts to elucidate the properties of halogen bonded systems. Experimental work by Cavallotti et al. [20] used ^{19}F NMR shifts in conjunction with DFT calculations to investigate radical complexes. The spectra showed significant downfield shifts indicative of halogen bonding. A more recent combined experimental ^{19}F NMR and computational study [21] has concluded that C–I–π halogen bonding is significant in perfluoroiodopropanes with toluene with an enthalpy of formation for the complexes determined to be slightly less than 3 kJ/mol. Sarwar et al. [22] used ^{19}F NMR titrations to extract the association constants and ΔG° values for complexation of various fluorinated iodoalkanes and iodoarenes with a variety of O and N bases. They further examined how these ΔG° values correlated with calculated quantities from B3LYP calculations. Lastly, in their study of Group 10 metal fluoride complexes that form halogen bonds, Beweries et al. [23] used ^{19}F NMR titrations to determine the ΔH° and ΔS° values for the halogen bonding complexes in these metal containing systems.

Using optical methods, Fan et al. [24] performed a detailed analysis of the $I^{(2)}$ CARS spectra of perfluoroiodoalkanes with pyridine. They measured both the shifts of the ring-breathing mode of pyridine and the equilibrium constant for halogen binding in a number of systems. Another experimental study by Roper et al. [25] combined X-ray and computational methods to examine various halogen bonded structures. This investigation looked at several di- and triiodofluorobenzenes interacting with appropriate Lewis bases to elucidate the effect of cooperativity in the structure of these complexes.

The current work builds on the previous computational studies in trying to quantify the BE in halogen bonding systems. Herein, computational results are reported for complexes of various unsubstituted and fluoro-substituted iodobenzenes with a range of Lewis bases. These bases include: $CHCl_3$, CCl_4, DMSO, acetone, dimethyl ether, methanol, and H_2O, which are meant to model a variety of potential solvent molecules The wide range of systems done at the same calculational level provides a much-needed comparison among the diverse systems. The effect of higher order correlation and basis set superposition error (BSSE) are examined systematically, as is the effect of solvent on a number of complexes. Lastly, a direct comparison of the BE for halogen and hydrogen bonding sites on the same molecule is made.

2. Methodology

All calculations were run using the Gaussian 09 [26] for Windows software. The basis sets used were the CEP-121G basis sets of Stevens et al. [27,28] These basis sets use effective core potentials for all atoms (except H). The core potential for iodine is based on relativistic calculations and therefore included contraction of the core electrons due to relativistic effects. The use of valence basis sets generated via the same procedure for all atoms will decrease the chances of imbalances in representing the different atoms. Previous studies have used ECPs to only represent the iodine atom, while using an all-electron basis set for the other atoms. It should be noted that as implemented in the Gaussian program, the *cep-121g* basis set option for all second and third row atoms, is a 211 contraction, as opposed to the originally proposed 121 contraction. The basis sets used are all of triple zeta quality. The basis set for iodine that is used is the originally proposed 41 contraction of the sp Gaussian functions. To this was added an extra set of uncontracted sp functions with exponent 0.031 (even-tempered) to yield an overall triple-zeta quality basis set. The diffuse nature of the sp set should be appropriate to describe the polarizability of the iodine atom in the halogen bonded systems. Standard polarization functions were added to all atoms with d function exponents of 0.80 for C, O, N, F, 0.292 for I, 0.65 for S, and 0.75 for Cl. The H atom basis set was augmented with p functions with exponent 1.10. The overall basis set was shown to give almost identical results for geometry, BE, and BSSE at the MP2 level to those of a Lu et al. [16] for $C_6F_5I–NH_3$ and $C_6F_5I–OH_2$ using the triple zeta quality aug-cc-pVDZ-PP basis set.

Due to the shallowness of the potential for the intermolecular interactions, all geometry optimizations were done at the MP2 level using the *tight* criteria for convergence. In some cases the maximum and/or rms displacements were not fully converged, however, the force and energy change criteria were always met. Zero point energy (ZPE) evaluations and verification of all stationary points as minima were done by calculating the vibrational frequencies. This was done via analytical differentiation for most systems, but some of the larger systems required two-point finite differencing of first derivatives.

The effect of higher order correlation was assessed for a number of the systems in this work. Single point MP4(SDTQ) and CCSD(T) calculations were performed at the optimized MP2 geometries. The systems examined included both Cl ($CHCl_3$) and O (H_2O) bonded complexes. The analysis of higher order electron correlation also included an evaluation of BSSE at these levels as will be discussed in detail later.

Although it has become common to perform calculations using DFT methods on weakly-bonded systems, the MP2 level calculations

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