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Halogen bonding in self-assembling systems: A comparison of intra- and interchain binding energies

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ABSTRACT

Calculations using the M06-2X and ωB97-XD density functionals with a triple-zeta quality polarized basis sets have been used to investigate the binding energies in a series of halogen bonded complexes of $C_2F_4I_2$ with $NC(CH_2)_nCN$ ($n = 0–2$). Results for complexes with monomer ratios from 1:1 to 3:3 indicate a near constant binding energies per halogen bond of ~8 kJ/mol, ~13 kJ/mol, and ~14 kJ/mol for $n = 0–2$, respectively, indicating no observable cooperative effects in the linear halogen bonding. Results from calculations on the stacking energy of the linear chains for systems up to 3:3 indicated that these binding energies were comparable to those for the linear halogen bonds. The strong stacking interaction is hypothesized to be due to favorable electrostatic forces between the F atoms on $C_2F_4I_2$ with either adjacent H atoms on $NC(CH_2)_2CN$, or the C—C π-hole on NCCN. The stacking interactions showed a significant cooperative effect, as well as a synergistic effect with the linear halogen bonds as demonstrated by a shortening of the I···N distances in the component chains. Binding energies for all 1:1 complexes of $C_2F_4I_2$ and $C_4F_8I_2$ with $NC(CH_2)_nCN$ ($n = 0–4$) show a strong linear correlation with the ΔESP between the positive σ-hole on the I atom and the negative region around the N atom lone pair.

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 interactions is the hydrogen bond (HB), which occurs when a slightly electron deficient H atom bonded to an electronegative atom interacts with an accessible electron pair on another species. Over the past few decades, interactions involving halogen atoms have become of increasing interest as an analogous interaction to HBs [1–4]. In the former intermolecular interaction, a halogen atom (most commonly Br or I) bonded to a more electronegative atom/group develops an electron deficient region along the σ-bond axis. This region has been called the σ-hole [5,6] and shows a quite positive electrostatic potential (ESP), sufficient to interact strongly with a negatively charged region associated with a lone pair of electrons. This interaction has been called a halogen bond (XB) and is often represented by RX—Y, where X represents the halogen atom and Y represents the Lewis base providing the electron pair. Unlike the HB, which can often be found in non-linear conformations, the position of the σ-hole oriented 180° to the RX bond axis generally restricts the XB to an almost perfect linear arrangement. This geometric restriction has been the topic of a number of proposed explanations [7–10].

Theoretical aspects of the XB interaction, along with various applications have been recently reviewed [4,6]. Although most of the theoretical studies detailed thus far have dealt with small systems, a soon to be published review explicitly discusses applications to biochemical systems [11]. Early work by Auffinger et al. [12] investigated the role that XBs play in stabilizing inter- and intramolecular interactions that affect ligand binding and biomolecular conformation. Subsequent studies have discussed examples of potential roles of XBs in a variety of other systems [13–16]. These biochemical examples of XBs are an important area of application and a number of research groups have investigated the necessary form of the classical potential to incorporate the XB into force field-based methods [17,18].

Another area of research that illustrates the importance of the XB is in materials and crystal engineering, which has been pioneered by the group of Metrangolo [2] and led to a number of practical applications of halogen bonding in molecular design [19–26]. The work most relevant for this current report is that of Metrangolo et al. [19] on diiodo-perfluorocarbon/dicyano-alkyl containing layered solids. These complexes form linear chains that adopt an all trans-conformation, which provides the potential for a regular array and hence facile crystallization. These spontaneously self-assembling systems have been characterized using diffraction techniques [19], which provided detailed structural information on both intra- and inter-chain morphology.

Paralleling the experimental advances in systems with XBs are detailed theoretical analyses focusing on two basic questions. The first pertains to the computational methods needed to accurately describe dimeric XB systems [4,6,27–33]. A variety of XB systems have been used as benchmarks for assessing the accuracy of binding energy (BE)

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predictions for various theoretical methods. Two of these sets are the XB18 and XB51 systems proposed by Kozuch and Martin [30]. These systems tended to be small, so that various methods could be compared with the benchmark CBS/CCSD(T) results. Recently, Oliveira et al. [34] have examined a sample of 202 complexes and proposed the use of vibrational spectroscopy as a more robust indicator of the strength of the XB than simply the BE. A second major area of theoretical study has addressed the question of the nature of the XB interaction with respect to the contribution of electrostatic, polarization, charge transfer (CT), and dispersion effects [35–42]. Although potentially providing additional insight into the nature of the XB, the limitations of partitioning the energy in this manner have been very succinctly discussed by Clark [43].

Although many 1:1 adducts of halogen bonded systems have been computationally investigated, a number of studies have examined more extended systems with an eye toward elucidating cooperative effects [44–50]. These effects in XB systems may significantly increase the BE in the linear chains and provide an important energetic impetus for self-assembly. From a simple electrostatic point of view, systems of dipolar compounds would be expected to show a significant cooperative effect, which can be attributed to a dipole-induced dipole effect. On the other hand, some systems that have been studied computationally do not seem to show large cooperative effects in the BE [46]. A study by Roper et al. [48] combined X-ray and computational methods to examine various halogen bonded structures to elucidate the potential role of cooperativity. Another crystallographic study by Bilewicz et al. [51] demonstrated cooperativity in certain XB structures, as well as the anisotropy in the electron density around the halogen atom involved in the XB, which may be important in its linearity.

The current work examines a number of extended halogen bonded systems possessing up to five XBs. The systems examined were based on the perfluorocarbon-hydrocarbon self-assembling systems characterized by Metrangolo et al. [19]. For these systems, two specific questions will be examined: (i) What is the role of cooperative effects on the linear XB strength? and (ii) How does the linear XB strength compare with that of the interchain stacking interaction? Most of the current work examines complexes between 1,2-diiodoperfluoroethane and cyanogen, malonodinitrile, and succinonitrile: $(C_2F_4I_2)_x$—$(NCCN)_y$, $(C_2F_4I_2)_x$—$(NCCH_2CN)_y$, and $(C_2F_4I_2)_x$—$(NCCH_2CH_2CN)_y$, where x,y = 1–3. This allows for a systematic analysis of the change in BE and halogen bond lengths as a function of system size. A unique aspect of this present investigation is the examination of the inter-chain stacking energies for the NCCN and $NC(CH_2)_2CN$ systems, which provides a comparison with the BEs of linear XBs. Although the NCCN complexes are model systems, the $NC(CH_2)_2CN$ complexes examined correspond to the smallest of those experimentally studied by Metrangolo et al. [19].

2. Computational methods

All reported calculations were performed with *Gaussian 09* [52] for Windows, while some preliminary investigations used *Spartan 16* [53] for Windows and Apple OS. Unlike our previous XB investigation [54], which used the MP2 method to calculate the BEs, recent benchmarks of various quantum mechanical methodologies [30] and the sizes of the systems led us to examine more computationally efficient methods. The final methods chosen were consistent with previous reports of those most accurate for the description of XB systems [30] and included both M06-2X [55] and ωB97-XD [56] hybrid functionals. Various polarized basis sets were examined and it was determined that a combination of a $6\text{-}31+G^*$ quality basis set on light atoms, $6\text{-}311G^{**}$ basis set on H atoms, and a modified LANL DZ basis set with a relativistic core potential on the I atom gave results almost identical to a number of larger basis sets tested. The iodine basis set is the LANL 41 contraction of the sp Gaussian functions supplemented with a set of uncontracted diffuse sp functions with exponent 0.031 (even-tempered) to yield an overall TZ quality valence basis set. The diffuse nature of the sp set on all "heavy" atoms helps describe the polarizability of these atoms in the systems studied and should be sufficient to describe the dispersion interactions in these complexes. Standard polarization functions were added to all atoms with α_d 0.80 for C, N, and F, along with α_p 1.10 for H. The exponent for the d-function for the I atom was 0.292 as used in our previous work [54].

It has been reported that certain small basis sets can give accurate results for XB BEs if balanced with the appropriate functionals [33]. This was in fact seen in this work, where the previously defined basis set yielded BEs very close to those of much larger sets. For example, calculations on 1:1 complexes of $C_2F_4I_2$ with NCCN and $NCCH_2CN$ gave corrected BEs within 3% of those with the following basis sets: (i) aug-cc-pVDZ (C, H, N, F) plus the aforementioned I basis set plus two d-type functions (α_d 0.4729 and 0.1932), and (ii) aug-cc-pVDZ (C, H, N, F) with the Stuttgart-Dresden core potential on I and the (4s5d2d) → (2s3p2d) valence basis set. The use of a relativistic correction has been reported to be necessary in order to treat the XB in systems containing heavier halogen atoms [30,39]. Although the basis sets used do not meet the "gold standard" for describing the XB, it is believed that sufficient evidence has been accumulated to give confidence that the basis sets in conjunction with the DFT methods used are sufficient to describe the basic nature of the XB in these extended systems.

Due to the shallowness of the potential for the intermolecular interactions, all geometry optimizations were done using a *tight* criteria for convergence of the forces and displacements and an *ultra fine grid* for the numerical integrations. In a number of cases the maximum and/or RMS displacements were not fully converged, however, the force and energy change criteria were met. Zero point energy (ZPE) evaluations and verification of all stationary points as minima were done by analytically calculating the vibrational frequencies. Due to the low energies of some of the vibrational modes, it was not uncommon to have one or two very low magnitude imaginary frequencies in the final optimized structure.

Assessment of the extent of basis set superposition error (BSSE) on the BEs was estimated with the counterpoise correction (CPC) method of Boys and Bernardi [57]. Due to the large number of molecular components all CPC corrections were done using two fragments. For linear systems, the two fragments were defined as: (i) all 1,2-diiodoperfluoroethane monomers and (ii) all dicyano monomers. In these cases, the distances of the nearest neighbor monomers in the same fragment were on the order of > 6 Å. Test calculations to assess the extent of BSSE for monomers in the same fragment revealed that these were very small, e.g. ~0.02 kJ/mol per interaction at ~6 Å. For interchain BSSE estimates, calculations were performed by defining the fragments as the individual linear chains. Such a division does not correct for intrachain BSSE, but does provide a separate estimate for the desired interchain effect. Here the BSSE was larger than for the linear chains and amounted to ~2.5 kJ/mol per stacked pair.

Given that the Boys and Bernardi correction overestimates the true BSSE [58], since it does not project out the occupied space of the superimposed orbitals, the corrections as implemented are sufficient to examine the trends sought in this work. It should be noted that although the BEs were corrected for BSSE, optimizations were not performed with the CPC. However, given the flatness of the potential energy surfaces with respect to the XB coordinates, changes in the predicted halogen bond lengths should have an insignificant effect on the calculated BEs.

The energy for formation of the linear XB complexes was calculated as $\Delta E = E(\text{XB complex}) - x{\cdot}E(\text{monomer 1}) - y{\cdot}E(\text{monomer 2})$ and then corrected for BSSE and ZPE. Since all complexes are more stable than the monomers, the BEs are reported in the tables as $BE = -\Delta E$ to avoid the repetitive use of the negative sign.