Chemical Physics 456 (2015) 34–40

Contents lists available at ScienceDirect

Chemical Physics

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

Long-range behavior of noncovalent bonds. Neutral and charged H-bonds, pnicogen, chalcogen, and halogen bonds

Binod Nepal, Steve Scheiner *

Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0300, United States

ARTICLE INFO

Article history:
Received 30 January 2015
In final form 15 April 2015
Available online 21 April 2015

Keywords:
Ab initio
MP2
SAPT
Electrostatic energy

ABSTRACT

Ab initio calculations show the drop in interaction energy with bond stretch ΔR can be fit to a common power n, in the functional form ΔR^{-n}. This exponent is smaller for charged H-bonds, as compared to neutral systems, where n varies in the order pnicogen < chalcogen < halogen bond. The decay is slowest for the electrostatic term, followed by induction and then by dispersion. The halogen bond has the greatest sensitivity to bond stretching in terms of all three components. The values of the exponent n are smaller for electrostatic energy than would be expected if it arose purely as a result of classical multipole interactions, such as dipole–dipole for the neutral systems. The exponents are larger when the fitting is done with respect to intermolecular distance R, rather than to its stretch relative to equilibrium length, although still not precisely matching what might be expected on classical grounds.

1. Introduction

Over the years, a great deal of information has accumulated regarding molecular interactions. Perhaps the most widely studied of these noncovalent forces is the hydrogen bond (HB), which embodies nearly a century of research [1–15] over the years. The HB was followed in ensuing years by examination of other related noncovalent bonds. The halogen bond, in which the bridging H is replaced by a halogen atom, was the next [16–29] in this chronology. While an attraction between a halogen and another electronegative atom seemed counterintuitive at first, it was realized that the partial negative charge around a halogen atom is quite anisotropic and contains positive as well as negative sub-regions. The electrostatic attraction is supplemented by a transfer of charge from the acceptor atom to the R–X σ^* antibonding orbital, where R represents any atom covalently attached to halogen X. The catalogue of noncovalent bonds was soon enlarged by the finding that the halogen can be replaced by other electronegative atoms, most particularly those of the chalcogen [30–40] and pnicogen [41–51] families.

The vast majority of information that has arisen about these various noncovalent bonds has been concerned with equilibrium geometries, those structures in which the donor and acceptor groups are situated fairly close to one another, where component attractive and repulsive forces balance one another. However, these interactions do not disappear when the two species begin to separate; they are merely weakened. The rate at which this weakening occurs has important implications. For example, if the noncovalent bond strength were to undergo only gradual decline, its effects would be important even if the two relevant groups were removed by fairly long separations. There is presumably a cutoff distance for each interaction, beyond which any lingering attractive forces are small enough to be comfortably ignored. But what is the cutoff for each sort of noncovalent bond, and how rapidly does the interaction energy approach this threshold? In a related question, what is the functional dependence of interaction energy on the separation distance R? The answers to these questions are especially important to the formulation of empirical functions designed to incorporate the effects of various noncovalent bonds into force fields that are used to simulate the dynamics of various systems.

In terms of explicit consideration of noncovalent bonds that are stretched well beyond their equilibrium separation, the H-bond has motivated a certain amount of limited study. In most cases, the interaction energy has been traced out, point by point, over a range of intermolecular distance. However, few of these studies extended this range of separation beyond 2 or 3 Å. Moreover, there have been scarce attempts to fit these points to a particular function, particularly at long range. There has been even less work in this direction addressing charged HBs, either cation-neutral or anion-neutral. And other noncovalent bonds, most notably the aforementioned halogen, chalcogen, and pnicogen bonds have been largely ignored [52] in terms of their long-range energetics.

* Corresponding author.
E-mail address: steve.scheiner@usu.edu (S. Scheiner).

http://dx.doi.org/10.1016/j.chemphys.2015.04.008
0301-0104/

The present work represents an attempt to fill in the existing gaps in our knowledge of the long-range behavior of the various sorts of noncovalent bonds. The neutral HB is compared to its ionic analogues, and these systems are then placed in the context of the halogen, chalcogen, and pnicogen bonds. The focus lies on the long range interaction, going out to as far as 11 Å stretched beyond the equilibrium separation. Attempts are made to ascertain which sort of function fits the computed binding energies at these long separations, and the results compared to what might be expected on simple physical grounds.

2. Theoretical methods

Calculations were carried out at the MP2/aug-cc-pVDZ level of theory, as implemented in the Gaussian-09 [53] software package. Each dimer was first fully optimized with no geometrical restraints. In order to examine the sensitivity to intermolecular separation, the optimized distance was stretched in fixed increments: 0.1 Å for the first 6 Å, and then 0.2 Å beyond that point. For each intermolecular distance, the remainder of the geometry was fully optimized. The binding energy at each point was computed as the difference between the energy of the heterodimer and the sum of energies of the isolated monomers, again fully optimized. This binding energy was corrected for basis set superposition error via the counterpoise procedure [54]. The interaction energy differs from the binding energy in that it is defined relative to the sum of the energies of the monomers when fixed in the geometry they adopt within the complex. The total interaction energy was dissected into various components by SAPT analysis using the MOLPRO [55] program. Kitaura-Morokuma energy decomposition was carried out using GAMESS [56]. Best fits of the energies to the intermolecular separation were analyzed via KaleidaGraph software.

3. Results

The fully optimized geometries of the heterodimers are illustrated in Figs. 1–4. Neutral H-bond pairs with OH, FH, and CH proton donors were considered. The bold numbers in Fig. 1 indicate the counterpoise-corrected binding energies which span a range from 1.8 kcal/mol for $F_3CH\cdots NH_3$ to 11.6 kcal/mol for $FH\cdots NH_3$. The HBs are considerably stronger, with binding energies as large as 41.2 kcal/mol, when an anion is used for proton acceptor, for systems pictured in Fig. 2. Very strong HBs are also associated with a cationic proton donor, as in the cases depicted in Fig. 3, considering both NH^+ and CH^+ donor groups. Recent work has focused attention on variants of HBs, where the bridging atom

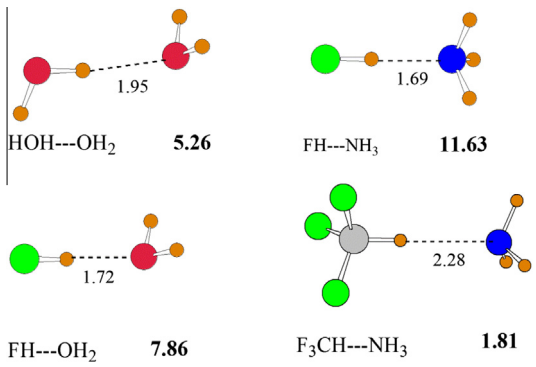

Fig. 1. Optimized geometries of neutral–neutral H-bonded complexes. The bold number indicates counterpoise-corrected binding energy in kcal/mol, distances in Å.

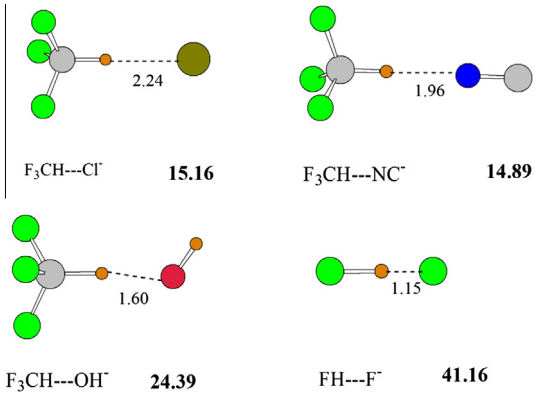

Fig. 2. Optimized geometries of anion-neutral H-bonded complexes. The bold number indicates counterpoise-corrected binding energy in kcal/mol, distances in Å.

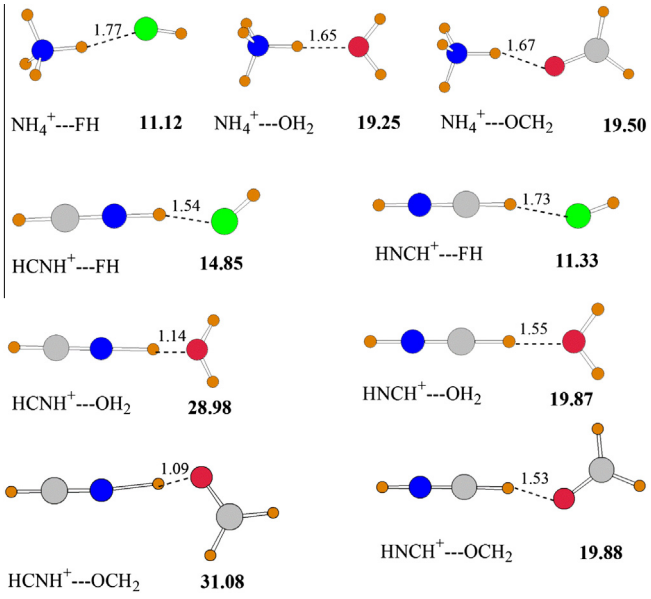

Fig. 3. Optimized geometries of cation-neutral H-bonded complexes. The bold number indicates counterpoise-corrected binding energy in kcal/mol, distances in Å.

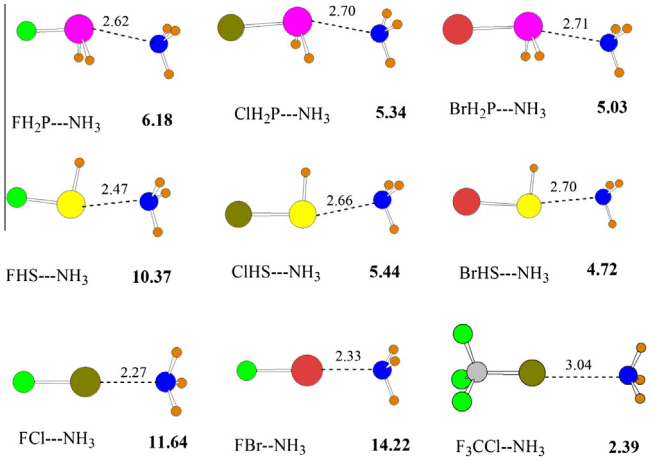

Fig. 4. Optimized geometries of pnicogen, chlacogen and halogen bonded complexes. The bold number indicates counterpoise-corrected binding energy in kcal/mol, distances in Å.