Do Identical Polar Diatomic Molecules Form Stacked or Linear Dimers?

Hydrogen Bonding is Not Just Dipole–Dipole Interactions

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The interaction of two identical polar neutral molecules is modeled by two equal but oppositely charged point particles at a fixed distance of separation. The total Coulomb potential energy of this system is calculated as a function of this distance, x, and the distance, y, between their centers of mass. We find that when the y/x ratio is less than about 3.1619, the linear configuration has the lower energy, whereas when this ratio exceeds 3.1619, a stacked structure is more stable. Interestingly, when two real polar molecules, such as HF interact, neither of these structures are formed. It is 'hydrogen bonded'. The NaF dimer on the other hand, has a global minimum as stacked structure at a y/x ratio of about 1, significantly smaller than 3.1619!

Introduction

The overwhelming dominant force between atoms in a molecule is electrostatic in nature. Thus, it might seem that the topic of chemical bonding simply reduces to the application of Coulomb's law, namely, like charges repel, unlike charges attract, and the force varies as the square of the distance of separation between the charges. The equilibrium configuration of a molecule as well as two or more molecules in proximity must then be the spatial configuration of electrons and nuclei in which all the attractive and repulsive Coulomb interactions balance and cancel. Of course, a chemical system may possess more than one equilibrium configuration. We refer to such stable structures as isomers, but it would be expected

that one isomer would be the most stable. This deceptively simple notion of determining structure from electrostatics however, encounters a huge problem, when account is taken of the wave nature of matter, in particular, that electrons cannot be represented as point charges but rather as a distributed charge cloud. Pauling summarized all efforts to understand bonding within a molecule in the first half of the 20th century in his classic book, *The Nature of Chemical Bond* [1].

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Understanding about intermolecular interactions or bonding between molecules has been evolving from the time of van der Waals equation and one of us has previously written a few articles in *Resonance* on this topic [2-4]. Of particular interest in the present article is how to understand the present and predict the structure of molecular complexes. For a long time chemists have introduced simplified models to deal with the complex problem of intermolecular bonding. One of the most useful has been the concept of hydrogen bonding initially proposed to explain, for example, the high boiling point of H_2O compared to H_2S. Pauling considered hydrogen bonding as simple electrostatic interactions. He concluded that hydrogen atom with one electron can have only one bond and so the attraction between H in one H_2O molecule having a partial positive charge and the O in a neighboring H_2O molecule having a partial negative charge is purely electrostatic. In the last few decades, it has become clear that even for intermolecular bonding, at longer distances than that of typical covalent bonds, it is important to consider the electrons as a distributed charge cloud. This led to serious debates about the nature of the hydrogen bond which has been summarized in a recent technical report published by the International Union of Pure and Applied Chemistry (IUPAC) [5]. A novel definition of hydrogen bond has also been proposed by IUPAC in 2011 [6].

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More recently it has been found useful to consider related phenomena involving other atoms, and halogen bonding (group 17), chalcogen bonding (group 16) and pnicogen bonding (group 15) were proposed [7,8]. Such an interaction involving the most important element for life, carbon (group 14), i.e., carbon bonding, has been proposed based on studies on gas phase complexes [9] and observed in crystal structure as well [10]. In a presentation on this topic by E Arunan to the Chemistry Department of Stanford University, a question arose concerning what the most stable configuration of two identical polar molecules is when they form a dimer. If these polar molecules are approximated as two charges of opposite polarity separated by a distance x, would the most stable configuration of dimers of polar molecules be found to be linear in a head-tail-head-tail configuration or would the most stable configuration be that of a stacked configuration in which the head-tail of one polar molecule lies below the tail-head configuration of its partner? The reader is encouraged to make a guess before reading further as to what is the most stable configuration. A study of this topic was initiated by Cedric Williams who was a visiting summer intern in the laboratory of Richard Zare as part of the Howard Hughes Medical Institute EXROP program. What follows next is what we have found.

Mathematical Methods

We begin by formalizing the problem with the structures, stacked and linear, defined in *Figure* 1. Here, x denotes the bond length of the polar molecule, whereas y denotes the axial distance between them in the dimer. Q denotes the magnitude of the charge held by each molecule ($|+Q| = |-Q|$).

In order to compare the stabilities of the two orientations, we calculate their Coulomb potential energies [11].

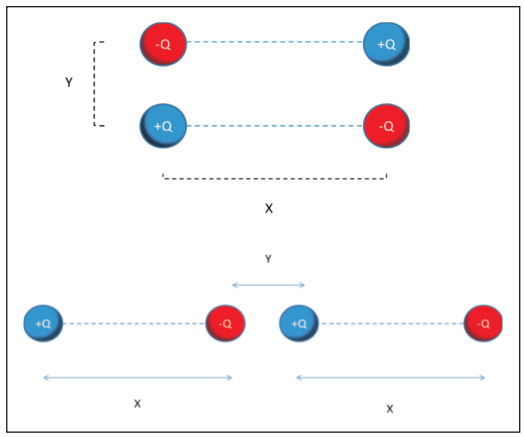


Figure 1. Stacked (top) and linear (bottom) arrangements of two polar diatomic molecules having opposite charges +/– *Q*.

For the stacked orientation, we have:

$$U_{\mathrm{s}}(x,y) = \frac{2kQ^2[xy-(x+y)\sqrt{x^2+y^2}]}{(xy)\sqrt{x^2+y^2}}\,. \qquad (1)$$

As for the linear orientation, we have:

$$U_{\mathrm{l}}(x,y) = \frac{2kQ^2[-(x^3+2x^2y+3xy^2+y^3)]}{[(xy)(x+y)(2x+y)]}\,. \qquad (2)$$

Here, k denotes Coulomb's constant, and Q, x, and y retain their previously defined roles. By setting the potential energies of these two orientations (equations (1) and (2)) equal to each other and asserting that the solution curve $y = f(x)$ will look like a linear multiple of x, i.e., $y = \lambda x$ for some real positive number λ, we can find a set of points where the potentials of the two orientations are equivalent. To find this ratio λ, we further manipulate our potential energy equation using λx in place of y. This yields the quartic equation:

$$\lambda^4 - 8\lambda^2 - 6\lambda - 1 = 0\,. \qquad (3)$$

There are four analytical solutions to this equation, all of which are extremely messy, as often is the case for quartic functions. However, satisfactory approximations of the roots may be made by taking the infinite limit of

Newton's Method, using various x_0. That is,

$$f(x) = x^4 - 8x^2 - 6x - 1\,; f'(x) = 4x^3 - 16x - 6\,;$$
$$x_0 = 3;$$
$$\lambda_1 = \lim_{n\to\infty}[x_{n+1}] = \lim_{n\to\infty}\left[x_n - \frac{f(x_n)}{f'(x_n)}\right] \approx 3.161900787\,.$$

Similarly, for $x_0 = 2$, $\lambda_2 \approx -2.3777$, for $x_0 = 0$, $\lambda_3 \approx -0.2481$, and for $x_0 = -1$, $\lambda_4 \approx -0.5361$. The last two solutions, $\lambda_3$andλ_4 are negative and unphysical as they lead to intermolecular separation smaller than intramolecular separation. In principle, λ_2 cannot be disregarded as unphysical since positive and negative just imply different directions. In any case, we consider only λ_1 henceforth and the arguments are valid for λ_2 as well, *vide infra*.

This solution yields our 'equivalency curve' $y = \lambda x \approx 3.1619x$, i.e., when $y = 3.1619x$, the potential energies for both linear and stacked orientation are the same for all values of x. When y is smaller than $3.1619x$, the linear orientation has lower potential energy compared to the stacked one and it is the preferred orientation. When y is greater than $3.1619x$, stacked orientation is the preferred one. *Figure* 2 shows the graphical representation of the potential energies as a function of x and λ. Of course, we are referring to nonzero values of x; if we considered only Coulomb interactions all neutral atoms, such as the H atom, would collapse to a point. This behavior is a hint that our treatment will prove to be incomplete. This fact will become more apparent in what follows.

Having determined the preferred orientation of two polar molecules using this simple model, we examine some real examples. Let us consider dimers of HF and NaF as typical polar molecules from a recent study [12]. Their structures are shown in *Figure* 3. The HF dimer has a structure which is neither linear nor stacked. It is a typical example for a 'hydrogen-bonded' complex. It has

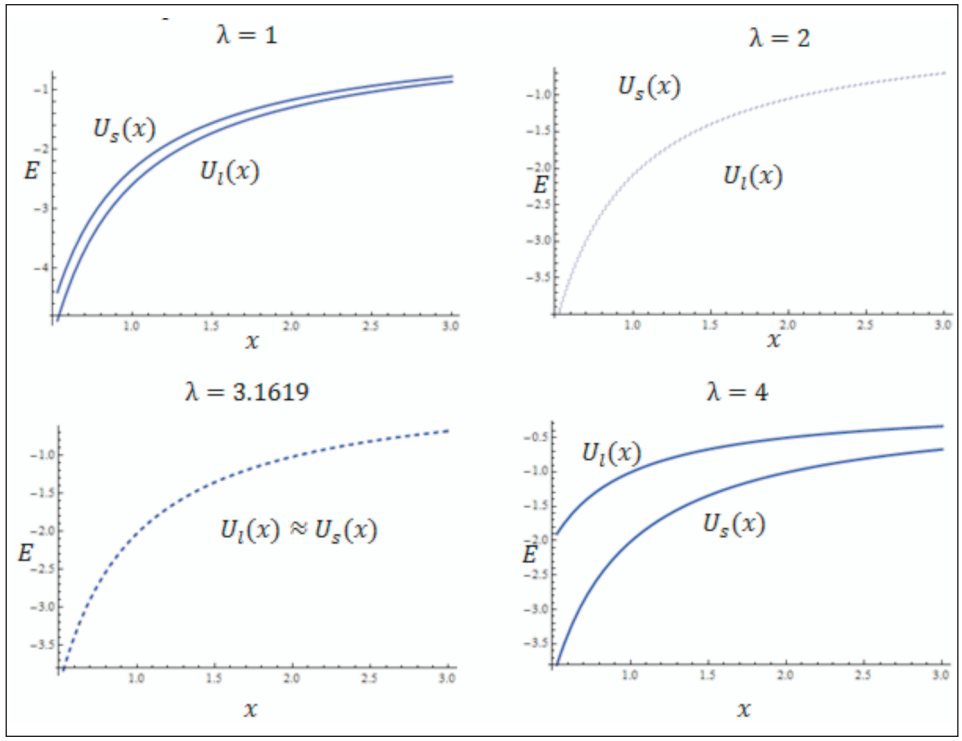
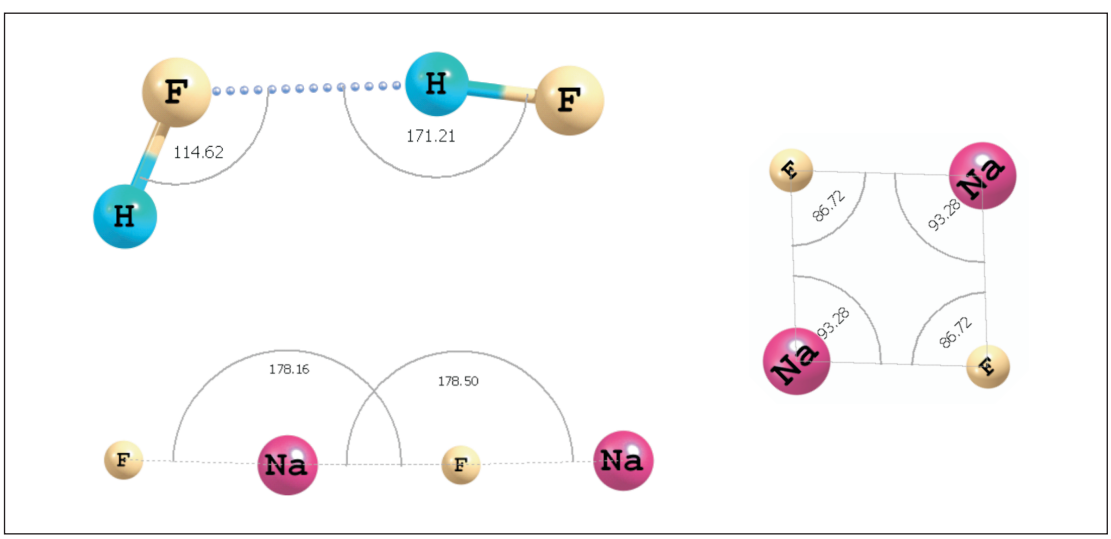


Figure 2. Potential energy for the stacked (U_s) and linear (U_l) configurations as a function of x for various values of $\lambda = y/x$, where y, the distance between the two molecules and x, the distance between the two oppositely charged atoms in one molecule are as defined in *Figure* 1.

Figure 3. Only stable structure of HF dimer (top left) and two stable structures of NaF dimer. For the NaF dimer, the stacked orientation is the global minimum though λ is close to 1 and significantly below 3.1619.



H from one HF molecule pointing towards F from the next HF molecule and the ∠FHF is about 171°, nearly linear as expected for hydrogen bonds [5]. Moreover, the ∠HFH is 114° and one can visualize the H interacting with F towards one of its lone pairs of electrons, forming the 'hydrogen bond'. The stacked orientation in HF dimer is unstable owing to the strong repulsion between the electrons in the sigma bond in between the two atoms. On the other hand NaF dimer has two stable structures having both orientations predicted by the simple model presented above. However, the stacked orientation is more stable than the linear orientation, although λ is about 1, much less than 3.1619 [12]. For argument sake, if one were to take λ_2 and consider y to be negative, we note that the observed intermolecular distance is still less than half of this value. The NaF has a dominantly ionic bond and there is not much repulsion arising from electron density in between the two 'ions'. Consequently, the stacked configuration turns out to be more stable than the linear one.

These examples illustrate that a simple electrostatic model will be inadequate for predicting structures of molecular complexes. One needs to look at the electron density distribution in the molecule as a whole. A complete quantum description of these interactions, which takes into account the wave nature of particles, does predict the observed geometries in both cases [12]. It includes the static part of the electrostatic interaction, induction, as well as the dynamic part arising from fluctuations in the location of the electrons, which is called the dispersion interaction. The latter gives rise, for example, to the condensation of the rare gases as liquids and solids at low temperatures, as well as rare gas dimers. These should be rightfully called London molecules rather than the commonly used term 'van der Waals molecules', as pointed out by one of us recently [3]. In fact London was the first to derive an expression

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for potential energy for dispersion interactions. In his classic paper published in 1937 [13], London had already pointed out the inadequacy of static electric structures to predict the actual structures of molecules in gas phase and condensed phase. Buckhingham and Fowler had earlier shown that consideration of electrostatic multipoles, i.e., beyond dipoles, could explain the structures of some molecular complexes [14]. However, it turned out to be only a step towards the realization of the importance of including the wave nature of electrons as pointed out by Buckhingham *et al* [15] recently.

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Unlike the electrostatic forces, dispersion forces are attractive at all orientations but they are not isotropic as often assumed. Hence, they cannot be ignored in determining the global minimum. Thus, the structural shape of a molecular dimer originates from the static part of the electrostatic interaction but the probability distribution of all electron locations must be taken into account to obtain the correct shape of a molecular complex.

Conclusion

Simple model calculations based on electrostatic dipole–dipole interaction has been used to compare the potential energy of linear and stacked dimers of polar diatomic molecules. The results show that the linear configuration has a lower potential energy when the ratio of the distance between dimers to their bond lengths is less than 3.1619, beyond which the stacked configuration is the preferred geometry. These predictions are compared with known structures of HF dimer and NaF dimer. This comparison highlights the importance of looking at the total electron density distribution in a molecule when predicting the structures of molecular complexes.

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