Theoret. Chim. Acta (Berl.) 45, 157–165 (1977)

THEORETICA CHIMICA ACTA

A Study of the Hydrogen Bond by Means of Comparative Calculations

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The nature of the hydrogen bond is investigated by means of a comparative analysis of some hydrogen bonded and hydrogen-like bonded systems. It is concluded that the hydrogen bond is determined by electrostatic interaction between the proton and the region of high electron density in the neighbour molecule.

Key words: Nature of the hydrogen bond – Hydrogen bond

1. Introduction

In recent years the best method for theoretical studies of the hydrogen bond has been believed to be non-empirical SCF MO calculation of the $B \cdots H–A$ complex considered as a whole system, where B and HA could be rather large molecules. The majority of the authors suppose that in hydrogen bond formation, beside the electrostatic interaction and short range repulsion, an important role is played by the effects connected with redistribution of electronic density both inside the subsystems and between them. However, the relative weights of all of these contributions are still disputed. A more or less up-to-date review of the theory of the hydrogen bond is presented in [1].

We are going to study the nature of the hydrogen bond by performing SCF calculations in the restricted basis sets of Gaussian functions. Such an approach to the problem demands some explanations. The point is this – the results of calculation of such a weak intermolecular interaction as the hydrogen bond depend on the concretely chosen restricted basis set. Most strongly basis set dependent are the results concerning the division of total interaction energy into components having some physical meaning. Therefore in this work we would not undertake such an attempt. Instead, we shall use a comparative study method.

Having selected suitable restricted basis sets for the chosen collection of molecular systems and exchanging partners taking part in the formation of the hydrogen bond, we shall follow those changes in the binding characteristics which are determined by the replacement that has been done. Naturally, conclusions obtained by such a method cannot be quantitative, they are heuristic in their character and they allow us to come to definite qualitative conclusions about the nature of the hydrogen bond.

2. Standpoint and Method

The binding energies and delocalization effects between two subsystems are often exaggerated in absolute value when calculation is made with restricted basis sets. This is connected with the additional possibility of improving the description of each subsystem at the expense of the basis set of another one. This problem was discussed in detail in the literature during the last years (see [2], and Refs. therein). To give an example of this exaggeration of hydrogen bond energy, it is appropriate to refer to the first non-empirical calculation of the water dimer [3]. In this work the value of 12.6 kcal/mole for the hydrogen bond energy was obtained, while the experimental and the Hartree-Fock values are equal approximately to 5 kcal/mole [4]. Such a great over-estimation of binding energy is due to the fact that the authors of Ref. [3] used a non-contracted $5s3p$ (O) + $3s$ (H) Gaussian basis set for the description of a single water molecule and therefore there were many free basis functions of one water molecule that served for the better description of another water molecule. It is clear that for reducing an undesirable effect of exaggeration of the binding energy it is important to contract reasonably the initial restricted basis set. It would be possible to give many literature references in which calculations using such contracted restricted basis sets lead to correct values of both the binding energy and electronic density distribution. We shall show this below with our example of dimer calculation.

However, though the total energy of the hydrogen bond can be correctly calculated with restricted basis sets, attempts in the frame of the SCF MO LCAO method to

Table 1. Decomposition of the hydrogen bond energy (kcal/mole) for $H_2O \cdots H_2O$ complex. Literature data[a]

Authors	Basis	Electrostatic attraction + exchange repulsion	Delocalization contributions (polarization + charge transfer)	Total energy of H-bond (without dispersion energy)
Kollman, Allen [5]	restricted	−4.5	−3.0	−7.5
Morokuma [7]	restricted	+1.9	−8.4	−6.5
Diercksen, Kraemer, Roos [8]	extended	−4.7	−0.1	−4.8

[a] Geometry of the complex and the method of decomposition are the same in the works of all authors.

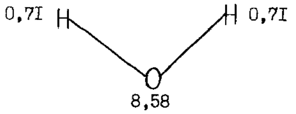
divide this energy into physically meaningful components [5–7] lead to results strongly dependent on concretely chosen restricted basis sets. In Table 1 we collect literature data that are taken from different works [5, 7, 8] concerning the decomposition of the hydrogen bond energy for the water dimer. The method of decomposition of the total energy into components was just the same in all the works cited, but the results obtained were quite different. Data in [8] were obtained with an extended-basis-set near-Hartree-Fock calculation; data in [5] and [7] with restricted basis set calculations.

It is seen that restricted basis set calculations, except for their mutual discrepancy, lead to a great exaggeration of delocalizational contributions. Data [8] show that all these contributions are rather small and that the hydrogen bond is mainly electrostatic in its nature (certainly, taking into account exchange repulsion between charge clouds of two molecules). Forestalling events, we may say that our conclusions coincide with this point of view.

The systems H_2O, LiOH, OH^-, F^-, Li^+ were chosen for our calculation. All computations were done by the FUGA program [9] which realizes the SCF MO LCAO method for the closed shell systems in the basis of lobe Gaussian functions. The initial Gaussian basis $7s3p$ (O, F atoms) was contracted to $3s1p$, $7s$ (Li atom)–to $3s$, $3s$ (H atom)–to $1s$. Basis sets and contraction coefficients were taken from [10] for O, F, H atoms and from [11] for Li atom. As an example we give some characteristics of the H_2O molecule obtained in our calculation: $E_{\text{total}} = -75.7543$ a.u., $R_{OH} = 0.96$ Å, $\angle$ HOH $= 106°$. Below we shall discuss some complexes of the above mentioned systems that were connected (or not connected) by hydrogen- or hydrogen-bond-like bonds. In this discussion we shall focus our attention on the changes in bond energies and Mulliken's atomic charge distribution only. So, in order not to overload the paper by odd figures, the figures that have nothing to do with the discussion are not given below. In all cases the geometry of a molecule forming the hydrogen bond, is preserved as such as it is obtained by energy minimization in isolated calculation (it is known that this is a rather reliable approach in hydrogen bond calculations, see e.g. [4]). The intersystem distances referred to are equilibrium distances, unless otherwise stated. Geometrical structure of the complexes is always illustrated by schematic drawings where electronic charges on atoms are pointed out.

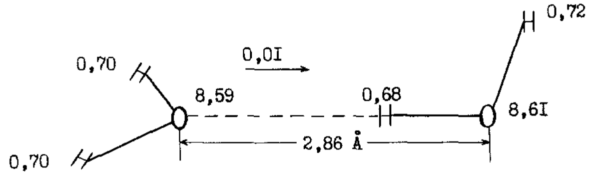
3. Results and Discussions

Let us first discuss the water dimer molecule. The electron charge distribution obtained for the isolated water molecule is



(I)

In the water dimer formed by the linear hydrogen bond (the planes of the two water molecules perpendicular to each other), charge distribution changes in the following



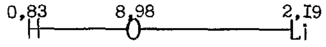
(II)

way. The calculated value of energy of the hydrogen bond in the water dimer (II) is equal to 5.6 kcal/mole. The arrow marks the charge transfer from the proton acceptor molecule to the proton donor molecule.

First of all, let us note that, in comparison with (I), the changes in the charge distribution in dimeric water (II) obtained by a restricted basis set calculation coincide exactly with the redistribution obtained in extended basis set calculations (see, e.g., [12]). The energy of the hydrogen bond obtained by us is also in good agreement with Hartree-Fock and experimental results [4, 8].

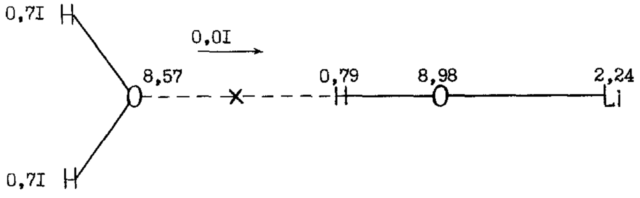
Charge redistribution touches upon all atoms in (II), but what is most essential in passing from (I) to (II) from the point of view of hydrogen-bond formation? Certainly the most important factor is the decrease of electronic density by 0.03 e on the hydrogen atom which takes part in the formation of the hydrogen bond, and the displacement of this density to the electronegative atom A. The corresponding density difference contour maps [4, 6] show that the electronic density decreases in the region of the hydrogen bond itself. Decrease of electronic density near the hydrogen atom in the hydrogen bond must be regarded as the most peculiar characteristic of this bond which distinguishes it from any chemical bond and gives electrostatic character to it: the partly bared proton interacts with the region of high electron density in the partner molecule. So one can suppose that this decrease of electronic density on the H atom which in its turn is due to exchange repulsion between the B and HA molecules, is the reason for the hydrogen bond formation.

Now let us replace the proton donor molecule in (II) by the LiOH molecule. In the LiOH molecule, electronic charge distribution is the following:



(III)

At the same distance between the oxygen atoms as in (II) we obtain the next scheme (IV)



(IV)

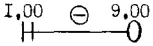
The binding is absent in (IV)! Of course, it is absent at any distance between the molecules. The repulsion energy between these molecules in (IV) at $R_{OO} = 2.86$ Å is equal to 3.1 kcal/mole. Comparing (II) and (IV) we see that the water molecule in (IV) is not polarized, but just as in (II), 0.01 e is transferred onto the LiOH molecule.

The hydrogen atom taking part in this "hydrogen bond" lost 0.04 e of its electronic density.

The main conclusion following from comparison of (II) and (IV) is the next one. The existence of the hydrogen bond is not defined by relative loss of electronic density on the H atom in the hydrogen bond but by the resulting value of this electronic density. An electronic charge of 0.79 e on the H atom appeared to be too large for forming the hydrogen bond. In (IV) binding is absent in spite of the fact that the relative decrease of electronic charge on the central H atom was even more (0.04 e) than in complex (II) (0.03 e).

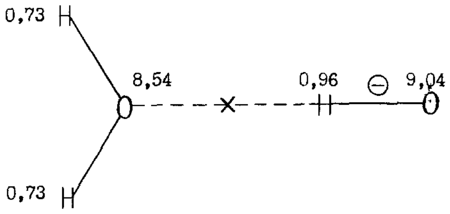
From the comparison of schemes (II) and (IV) it is possible to come to the conclusion that the charge transfer from the proton acceptor molecule to the proton donor molecule is not an evidence of hydrogen bond formation. In both cases this charge transfer of 0.01 e is too small and it takes place in spite of formation or non-formation of the hydrogen bond. Generally, it seems that in restricted basis set calculations one should not give much attention to such a small intersystem charge transfer as 0.01 e [2].

Let us consider now the extreme case in succession of schemes (II) and (IV) taking away the last right H atom in (II), i.e. consider the interaction between H_2O and OH^-. System $H_3O_2^-$ is known as an example of a "strong" hydrogen bond $(HOHOH)^-$ but in this case we have another configuration $H_2O \cdots HO^-$. The ion OH^- has the following distribution of electronic charge



(V)

Calculating the $H_2O \cdots HO^-$ complex as a whole we obtain the distribution of charges shown in scheme (VI).

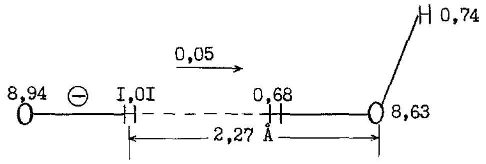


(VI)

The systems strongly repel each other in spite of the formal realization of the hydrogen bond fragment $-O \cdots H–O$. The energy of repulsion at the same fixed distance $R_{OO} = 2.86$ Å is equal to 19 kcal/mole. Intersystem charge transfer is absent, the systems are strongly polarised in opposite directions. Comparing (II), (IV) and (VI) we can see that slight polarization of the proton acceptor molecule under the electrostatic force of the partly bared proton is a characteristic feature of the hydrogen bond.

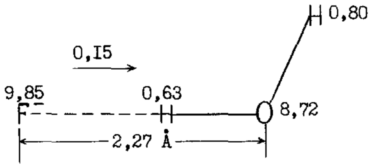
So, complex (VI) is unbound with respect to OH^- and H_2O. This fact was known long ago [13]. Beside that, the authors of Ref. [13] found that complex $H_3O^+ \cdots H–OH$ (the plane of H_3O^+ perpendicular to the $O^{\oplus} \cdots H–O$ line) was also unbound with respect to H_3O^+ and H_2O, despite involving a formal $O \cdots H\text{–}O$ "hydrogen bond". In [14] this result was commented on from the point of view of a positive electrostatic potential surrounding H_3O^+. We can put it in a very simple manner: H_3O^+ is a positively charged particle and it cannot approach H_2O on the hydrogen side.

From these examples it is seen that the total charge of the proton donor or proton acceptor system is a critical point for the very existence of the hydrogen bond. If, for example, the proton donor system is negatively charged, then the hydrogen bond cannot be formed. In the case of scheme (VI) the H_2O molecule "feels" that OH^- is a negatively charged particle, and on the side of the oxygen this ion does not approach H_2O, even if its hydrogen is ahead. On the contrary, the OH^- ion approaches, hydrogen ahead, the H_2O molecule on the side of the hydrogen atoms, thus creating the unusual hydrogen bond $^{\ominus}H \ldots H\text{–}O$! This is illustrated by the following scheme:



(VII)

Here OH^- is the proton acceptor, H_2O is the proton donor molecule. The binding energy in (VII) at the distance of 2.27 Å between the hydrogen atom in OH^- and the oxygen atom in H_2O is equal to 12.5 kcal/mole. Such a distance is the calculated equilibrium distance in the complex $F^- \cdots H_2O$:

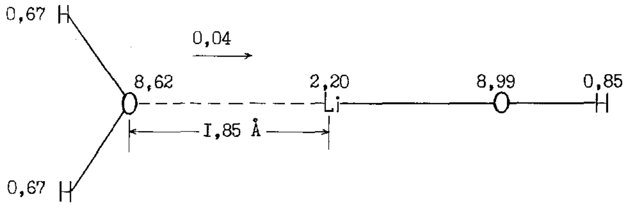


(VIII)

for which our calculation gives a binding energy value of 49 kcal/mole. The Hartree-Fock value of this energy amounts to only 24 kcal/mole [8]. The reason for the overestimation of the binding energy in this case is clear. Negative ions are described in restricted basis set calculations much worse than neutral systems [2]. For example, in the calculations used in this work the total energies of H_2O, OH^-, and F^- differ from the known Hartree-Fock values of these energies by -0.31, -0.47, and -0.51 a.u., respectively. In schemes (VII) and (VIII) we observe strong charge transfer from the ions to the water molecule; this charge transfer is especially large from the F^- ion, which is described worse than OH^-. It may be assumed that the major part of these charge transfers characterizes the degree of additional total energy lowering, i.e. the exaggeration of binding energy [2]. Certainly, therefore, the value of 12.5 kcal/mole for the binding energy in (VII) is too large. Nevertheless, we can surely say that complex (VII) is stable with a bond energy of several kcal/mole (qualitatively speaking, we may say that even if we suppose that a charge transfer of 0.15 e fully corresponds to a lowering of energy by 25 kcal/mole, then a charge transfer of 0.05 e corresponds to a lowering of energy by 8 kcal/mole, and that is why we can foresee the binding energy in (VII) to be about 4–5 kcal/mole).

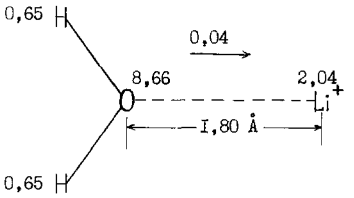
The existence of the stable complex (VII) shows that for formation of the hydrogen bond $-B\cdots H-A-$ it is not obligatory for atom B to be an electronegative atom. It is important only that there should be an extra concentration of electronic density in the place of B, for example at the expense of negative charge of the whole molecule –B, just as in case (VII).

To study the question of the uniqueness of the hydrogen bond, let us turn over the LiOH molecule in scheme (IV). Thus we come to scheme (IX).



(IX)

The binding energy in (IX) is 25 kcal/mole at the equilibrium distance $R_{OLi} = 1.85$ Å. This distance is nearly equal to equilibrium distance in the ion-molecular complex $Li^+\cdots OH_2$:



(X)

with which we should compare (IX). In (X) the binding energy is equal to 43 kcal/mole. Comparison of (IX) and (X) proves once more the ionic character of the LiOH molecule, which may be considered to some extent as a complex $Li^+(OH)^-$. As in (X), the electronic charge on the Li atom is not decreasing but increasing when complex (IX) is formed. This fact is in striking contrast to the decrease of electronic density on the H atom in the hydrogen bond. When interaction of the positive ion with the molecule is considered, it is obviously impossible to neglect the donor-acceptor character of interaction between molecular lone pair and vacant acceptor orbital of an ion. Thus, the hydrogen bond is really unique because only the hydrogen atom, participating in a chemical bond by its single electron, can form by its proton a purely electrostatic bond with the region of high electron density in the neighbour molecule, without being at the same time the acceptor of electronic density.

4. Conclusion

In this work we have dealt with the so-called "weak" hydrogen bond. Complexes $(FHF)^-$, $(HOHOH)^-$, $(H_2OHOH_2)^+$ with symmetrical position of the central proton are examples of the "strong" hydrogen bond. Such a "hydrogen bond" has quite a different nature from the "weak" hydrogen bond. The above complexes are the results of chemical interactions followed by essential reorganization of electronic shells, and each of them represents more the charged molecule than the ion-molecular complex. That is why their formation must be studied regarding the correlation effects. For example, in [15] it was shown that the complex $(\mathrm{H{-}O{-}H}\cdots\mathrm{OH})^-$ has a non-symmetrical structure in the SCF calculation but becomes symmetrical when CI calculation is included. In the $(\mathrm{FHF})^-$ ion two symmetrical H–F bonds have obviously a covalent nature. Thus, from out point of view, the "strong" hydrogen bond can be called a "hydrogen bond" only for historical reasons.

As far as the hydrogen bond itself, i.e. the "weak" hydrogen bond, is concerned, we come to the following conclusions about its nature.

1) The cause of the hydrogen bond, odd as it may sound, is the short range repulsion between the closed shell systems which leads to polarization of the A–H bond in the proton donor molecule and thus to formation of suitable conditions for electrostatic interaction of the partly bared proton with the high electron density region in the neighbour molecule, this region being rather distinctly localized in the space (e.g., lone pair).

2) The energy of the hydrogen bond is defined as the difference of two quantities – the energy of exchange repulsion and the energy of electrostatic attraction; this was proved by exact Hartree-Fock calculations [8]. The existence of the hydrogen bond is not defined by a relative decrease of electronic density on the H atom, but by the resulting value of this density. Thus, there exists a limiting value of the electronic charge density on the hydrogen atom which still leads to formation of the hydrogen bond, but further increase of this charge density destroys the bond completely.

3) Electronic charge transfer from proton acceptor molecule to proton donor molecule is not a characteristic feature of hydrogen bond formation. It is quite possible that such a charge transfer is absent altogether. So, the hydrogen bond is evidently neither a charge-transfer nor a donor-acceptor bond.

4) The total charge of the proton-donor or proton-acceptor system is the critical point for hydrogen bond formation. If the proton-donor system is negatively charged or if the proton-acceptor system is positively charged then the hydrogen bond cannot be formed. On the other hand, for example, if the negatively charged system is the proton-acceptor system, then a strong hydrogen bond can exist. This bond may appear even in such an unusual structure as $^{\ominus}\mathrm{H}\cdots\mathrm{H{-}A}$.

5) Replacement of the H atom by the Li atom in the hydrogen bond leads to the fundamental change in the bond character: the electronic density on the Li atom is not decreased, while such a decrease is an obligatory feature of the hydrogen bond. The hydrogen atom has no inner electrons, so the partner molecule can approach it closely, without being strongly repulsed. This uniqueness of the H atom for hydrogen bond formation is well known [16]. Here we can add that

only the H atom can form an electrostatic bond with the proton acceptor molecule, without being the acceptor of electronic density.

6) As was said, calculations in restricted basis sets lead to exaggerated estimation of those energetic contributions which are due to electron delocalization. Misunderstanding of this fact may lead to wrong conclusions. Thus, the opinion that the hydrogen bond is a sort of donor-acceptor interaction [17] is an example of such a wrong conclusion. The distinguished authors of [16] long ago emphasized that the hydrogen bond is essentially electrostatic in its nature. The work [8] gave some quantitative proof for that. In the present work we have made an attempt to show that with a critical attitude to the restricted basis set calculations, it is possible with their help to obtain certain qualitative information about the nature of the hydrogen bond, not being afraid to come into conflict with the extended basis set calculations.

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Received October 1, 1976/December 21, 1976