STUDY OF HYDROGEN BONDING IN SOLUTIONS

A Thesis
Submitted to
The University College For Girls
Ain Shams University
Cairo

by

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B. Sc. (special)

In partial fulfillment of the requirements
for the degree of
MASTER OF SCIENCE

April 1970

NOTE

The candidate has attended postgraduate courses for two years in Physical and Inorganic Chemistry covering the following topics:

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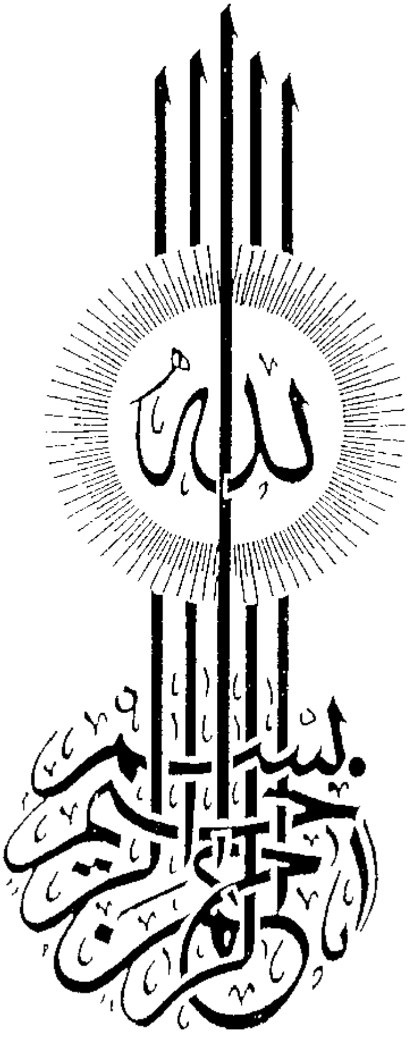
فرع الكيمياء


بسم الله الرحمن الرحيم

ACKNOWLEDGEMENT

The author wishes to express her most sincere appreciation to Dr. Ahmed A. Taha. Dr. Taha's help, advice, encouragement and suggestions, which were so willingly given during the course of this research, will never be forgotten.

Special acknowledgement is given to Dr. Saleh A. Awad for his guidance and assistance during the course of this investigation.

The author will remember with gratitude the co-operation of all the members of the Department of Chemistry.

The computer time donated by the University of Oklahoma, U.S.A., which was highly valued, is also appreciated.

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STUDY OF HYDROGEN BONDING IN SOLUTIONS.
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CHAPTER I

INTRODUCTION

Many years ago, scientists recognized that special theories were necessary to explain the behavior of associated compounds.[1] Emperically, they found that association was more likely among molecules containing certain functional groups than among others. For example, alcohols and phenols formed associated complexes readily, whereas hydrocarbons did not. A particularly tenacious interaction was recognized in molecules with hydrogen-containing functional groups.[2,3] Investigations have established that when covalently linked with an atom of a highly electronegative element (especially fluorine and oxygen), the hydrogen atom is capable of combining with one more atom of the same element giving rise to the so called "hydrogen bond".[4]

This peculiarity of the hydrogen atom is due to the fact that when it loses its only electron to form a bond with a strongly electronegative element, a nucleus of very small size remains, almost devoid of any electron shell. It is, therefore, not repelled, but attracted by the electron shell of any third atom and may interact with it.

An outstanding example of the hydrogen bond formation is the self-association of hydrogen fluoride, water and ammonia. In such cases, the hydrogen atom acts as a link between two electronegative atoms giving rise to the formation of relatively complex molecular species by the union of two or more simple molecules. The presence of the hydrogen bonds in such compounds accounts for many of their abnormal properties, as for example, their high melting and boiling points, and high heats of vaporization.

The phenomenon of hydrogen bond formation is very important because of its widespread occurrence in inorganic, organic and biological materials. The most fruitful applications of the hydrogen bridge theory will be to a better understanding of the nature and behavior of complicated organic substances such as gels, proteins, starch, cellulose, sugars, haemoglobin and related substances. Entire industries have been founded on the connecting and disconnecting of hydrogen bonds, for example, the industry of synthetic fibers and papers. Among the rapidly opening fields of applications of hydrogen bonding are catalysis, enzymes activity, dyeing, kinetics and adsorption. The rate of passage of a compound through a chromatographic column is partly determined by interactions, involving hydrogen bonding, between the compound and the adsorbent.

Astle[5] reviewed the role of hydrogen bonds in polarographic analysis. Intramolecular hydrogen bonding generally makes the reduction of a reactive group easier, consequently the internal bond will influence polarograms. Hydrogen bonding also plays an important role in fixing reaction mechanisms.

When hydrogen bonding groups are present in a reacting system, the reaction may be affected by the formation of chelated configurations or by the intermolecular packing of hydrogen bonded aggregates of reactants or resultants and solvents.

As mentioned before, hydrogen bonding involves two functional groups in the same, or in different molecules. One of these groups must serve as a proton donor (an acidic group) and the other as an electron donor (a basic group). Most commonly, the proton is donated by a carboxyl, hydroxyl, amine or amide group. Also, the proton attached to a halogen can be active in hydrogen bonding. The usual electron contributing parts of the molecule are oxygens in carbonyls, ethers and hydroxyls: nitrogens in amines and in N-heterocyclic compounds; and halogen atoms in particular molecular environments.

To give a more specific definition, Pimentel and McClellan,[6] have presented the following operational definition for the hydrogen bond:

"A hydrogen bond exists between a functional group A-H and an atom or group of atoms B in the same or a different molecule when:

a) there is evidence of bond formation (association or chelation).

b) there is evidence that this new bond linking A-H and B, specifically involves the hydrogen atom already bonded to A."

In order to subclassify hydrogen bonds, Hunter and Marriot[7] defined two kinds of the hydrogen bond A-H...B:

"homogeneous" hydrogen bonds where A and B are identical functional groups, and "heterogeneous" hydrogen bonds where A and B are different.

Oshida, et al.[8] distinguished three types of hydrogen bonds: i) the type occurring in alcohols in which the hydrogen atom moves from one oxygen atom towards another: ii) a type involving resonance, and occurring, for example, among amides: iii) another type involving a symmetrical hydrogen bond.

Sobczyk[9] has a similar classification into four types: 1) the van der Waals' type, where the proton remains strongly attached to A; 2) the shortened bond type, in which the quantum mechanical forces enhance the van der Waals' forces; 3) the symmetrical bond type: and 4) the polar bond type, in which the proton becomes strongly attached to B.

Cannon[10] proposed the following criteria for hydrogen bond formation:

1. asymmetry of the nonbonding orbital of the proton acceptor.
2. partial ionic character of the A-H bond of the donor.
3. "proton transfer can occur and a broad absorption band results."

Unfortunately, the first two of these criteria are accessible only through indirect, and sometimes heavily intuitive, interpretation of observational results. Nevertheless, Cannon[11] was led to the conclusion that the tendency of the N-H (of amides) to form a hydrogen bond will be very small. He, however, recognized the association of amides and attributed it to dipole-dipole interaction.

It is a well known fact that the formation of a hydrogen bond in a solution or a compound modifies a great many physical and a few chemical properties. The most commonly observed physical property modifications are frequency shifts of IR and Raman bands, proton magnetic resonance shifts, altered freezing and boiling points, solubility differences as a result of hydrogen bonding between solvent and solute, deviation from ideal gas and solution's laws and changed dielectric properties and electrical conductivity. Deviation from ideal gas and solution laws are caused principally by the increased molecular weight resulting when one complex unit is formed from more than one molecule. Electrical properties are unusual for hydrogen bonded substances because the dipoles are affected by the positions of the hydrogen atoms.

These abnormal properties are very helpful in detecting the existence and extent of hydrogen bonding. Hydrogen bonds were first detected through the solubility studies,[1] and were quickly found by many other classical methods available in the first quarter of the twentieth century.

Beginning in the mid-thirties, the IR and Raman spectroscopic techniques achieved major importance in the detection of the hydrogen bonding.[12-16] Still later, neutron diffraction and high resolution proton magnetic resonance measurements became available to describe the positions of hydrogen