

## HYDROGEN BONDING BY C—H GROUPS

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# Preface

The hydrogen bond is a well documented phenomenon, having been found and characterised in a very wide variety of systems of chemical interest. The literature of hydrogen bonds can only be described as immense, as witnessed by the comprehensive 1960 monograph *The Hydrogen Bond* by Pimentel and McClellan which lists over 2000 references up to about 1956. There has been no abatement of interest in the subject since that time and the book *Hydrogen Bonding* by Vinogradov and Linnell, published in 1971, makes no attempt to collect all the relevant literature of the intervening years.

It has always been recognised that the most important classes of hydrogen bonds are those involving O–H and N–H groups. Hydrogen bonded to other atoms may also form hydrogen bonds, but these are, as a rule, weaker and less frequently observed. Consequently, Pimentel and McClellan's book [309] deals with the subject of C–H hydrogen bonds in four pages, while that of Vinogradov and Linnell [389] devotes a few scattered sentences to the subject. Hence, in view of the continuing interest in C–H hydrogen bonding, which has already resulted in more than 300 papers dealing with them, it was felt that there was a need to have the knowledge of the subject collected together so as to facilitate the evaluation of our present knowledge and the formulation of fruitful approaches to further study of the phenomenon.

Chapters 3, 4 and 5, which form the bulk of this book, contain collections of the available information concerning the hydrogen bonding properties of  $sp^3$ ,  $sp^2$  and  $sp$  C–H bonds respectively. Wherever possible, the data have been collected in tabular form and reduced to a common basis. For example, NMR chemical shift differences between solvents are all listed in parts per million (ppm) and the two appropriate solvents are given.

No attempt has been made to provide a complete discussion of the various methods of detection and characterisation of hydrogen bonds; such a discussion is to be found in Pimentel and McClellan's excellent book [309]. However, a short review of those methods which have been of greatest use in examining C–H hydrogen bonds comprises Chapter 2.

The bibliography is as complete as it could reasonably be made, through 1972. Some papers whose mention of C–H hydrogen bonds is peripheral and add nothing to our understanding of them, have been omitted. If there be any further omissions, these were not intended.

The nomenclature of chemical compounds is throughout as nearly systematic

in line with IUPAC recommendations as possible (see *Nomenclature of Organic Chemistry*, Butterworth, London, 1969). In a few cases, non-systematic names have been used in an attempt to make a point clearer: e.g. triethoxyphosphine oxide, rather than triethyl phosphate for  $(\text{C}_2\text{H}_5\text{O})_3\text{PO}$ . Data have been converted into SI units wherever they are given in the literature in other units.

Thanks are due to the University of Malaya for its support, particularly for my extensive use of the library facilities and for some assistance with the typing. Especially appreciated was the co-operation and assistance of Mrs Agnes How who sought out and obtained scores of articles from various obscure sources.

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R. D. GREEN

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# List of Symbols

$A-B$	a 'normal' covalent type chemical bond
$A\cdots B$	a weaker bond (e.g. a hydrogen bond)
$K_\phi = \frac{\{AB\}}{\{A\}\{B\}}$	equilibrium constant for formation of a complex, where $\{X\}$ is the activity of species X
$\Delta_\phi H, \Delta_\phi S, \Delta_\phi G$	enthalpy (entropy, Gibbs free energy) change upon complex formation
$\Delta_m H$	enthalpy change of mixing
$\Delta_1^v H$	enthalpy change of vaporisation
$B$	second virial coefficient
$\nu$	wavenumber (in $\text{cm}^{-1}$ ) of a vibrational mode
$w_{1/2}$	full width at half height of a vibrational band in the infrared or Raman spectrum
$A$	intensity of infrared absorption band
$\Delta_c$	chemical shift difference between associated and non-associated molecules
$\Delta_s$	chemical shift difference in two solvents