Resonance-assisted hydrogen bonding in terms of substituent effect

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A B S T R A C T

A quantitative description of resonance-assisted H-bond in terms of σ-scale of substituent effect for proton-donating and proton-accepting groups is presented. Application of the proposed approach to malonaldehyde and *ortho*-hydroxybenzaldehyde shows that formation of H-bonding significantly changes the electronic properties of interacting groups expressed by σ-values, which furthermore explains the increase of π-electron delocalization in such RAHB systems. The presented analyses are based on quantum-chemical modelling at B3LYP/6-311+G** level.

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1. Introduction

H-bonding belongs to the most important interactions since it is responsible for many chemical, physical and biological properties of various molecules and chemical systems.[1] It also plays an important role in the development of new materials.[1] The general scheme of H-bonded system(s) is as below:

$$R—A—H\cdots B—R' \qquad (1)$$

where A and B are the electronegative atoms,[2] A–H is a proton-donor whereas B a proton-acceptor. If R and R′ are bonded covalently to each other, forming one molecule, the H-bond is intramolecular. In the case when the proton-donating and proton-accepting groups are linked via π-conjugated bonds, an interplay between the H-bonding and π-electron delocalization in the linking chain is observed. For such cases, Gilli and co-workers[3] introduced a concept of resonance-assisted hydrogen bonding (RAHB). Based on much experimental material, they assumed that there is a cooperative effect between H-bond strengthening and π-electron delocalization of conjugated bonds linking the proton-donating and proton-accepting groups. This phenomenon was noticed for the first time in the sixties,[4] and was later also

supported by Scheiner[5] and may be found in the NBO-type approaches.[6] Although the idea of RAHB has been recently criticized,[7] it serves as a useful qualitative concept and is widely studied.[8]

The electronic properties of A–H and B groups involved in intramolecular H-bonding changes in comparison with their states before interaction.[9] For instance, the consequences of H-bond formation may be observed in energy changes between the H-bonded system and its 'open' conformation[10] (see Scheme 1). It should be however emphasized that such difference in energy consists of at least three contributions: H-bond formation and changes in π-electron delocalization, which stabilizes the system in question, and deformation energy, which destabilizes it.[11,12]
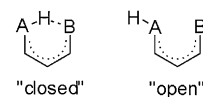
Scheme 1.

Since the interacting groups, A–H and B, may be considered as substituents, their electronic properties may be described by the Hammett substituent constants σ,[13–17] which express the degree of electron-donating or electron-accepting (depending on the nature of substituent in general) power of the substituent, and in general, the higher is the absolute value, the stronger the donating/attracting properties are. In the origins of the substituent constant concept, the electronic properties of substituents were determined

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by changes in rate or equilibrium constants of specially designed reactions when the main reagent became substituted.[18] Since the nature of the interaction between the substituent and the reaction site depends among other things on the reaction type, a variety of substituent constants are in use.[16,19] For instance, σ^+ constants are designed for π-donors interacting with an electron-accepting reaction site, whereas σ^- for π-acceptors interacting with an electron-donating reaction site.

In general, in the RAHB systems, the π-proton-donating group A–H is an electron donor when considered as a substituent and is characterized by negative σ values. Analogously, the proton-accepting group B is a π-electron-accepting substituent with positive σ values. In consequence, in the H–A–R″–B system, which may form an intramolecular H-bond, two terminal groups (substituents) A–H and B may interact via a covalent chain of bonds since they have opposite electronic properties. As the result of engagement in H-bonding, the A–H bond length should elongate and consequently its electron-donating properties as substituent should become stronger. Simultaneously, the proton approaches B, leading to the formation of B···H$^{\delta+}$ and as a consequence, the electron-attracting power of B in B···H$^{\delta+}$ should increase in comparison with B itself. Thus the magnitude of the substituent effect should consequently increase.[20]

The aim of our study is to show the changes in electronic properties of A–H and B groups in RAHB systems, caused by engagement in H-bonding interaction A$^{\delta-}$–H$^{\delta+}$···B, in a quantitative way, i.e., by the use of Hammett substituent constants.

2. Results and discussion

2.1. The concept

First of all, it is necessary to find a way to model a relationship between the strength of H-bond associated with the position of proton in the A–H···B bridge and the electron-donating power of A$^{\delta-}$–H$^{\delta+}$ and electron-accepting power of –B···H$^{\delta+}$ expressed by the use of the σ^+ and σ^- constants, respectively. In order to describe the variable H-bonding, we apply a computational model of varying H-bond strength, already presented in the literature.[11,21] This approach is based on A–H···F$^-$ and B···H–F interactions for which the A···F and B···F distances are controlled and varied in order to simulate the changes of H-bonding strength. For determination of substituent constant values of A$^{\delta-}$–H$^{\delta+}$ and –B···H$^{\delta+}$, the method for estimation of σ from exocyclically substituted derivatives of fulvene and heptafulvene, respectively, may be employed.[22] This approach allows for determination of σ values from π-electron delocalization in the fulvene/heptafulvene rings, which in fact is sensitive to substitution at the exocyclic carbon atom (Scheme 2). π-Electron-donating substituents increase π-electron delocalization in the fulvene ring and π-electron-accepting substituents in the heptafulvene ring. Such effects are associated with the general tendency to posses 6 π-electrons in the ring. The appropriate empirical equations where π-electron delocalization is expressed by HOMA[23] index (Harmonic Oscillator Model of Aromaticity, for definition see Methodology) are presented below:[22]
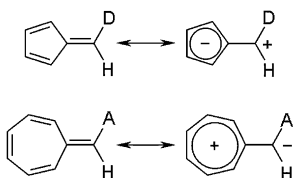
$$\sigma_p^+ = -2.401 \cdot \text{HOMA(fulvene)} - 0.736 \quad (2)$$

$$\sigma_p^- = 4.208 \cdot \text{HOMA(heptafulvene)} - 0.655 \quad (3)$$

In both cases the substituent constants, σ^+ and σ^-, are used for the *para*-position, since for this position the description of substituent interactions is most similar to that observed in cases of push–pull interactions discussed in this paper. Incorporation of both above-mentioned models allows for the estimation of σ values for A–H and B groups involved in H-bonding of different strength.

2.2. Calculation of σ^+ for proton-donating substituent

Let us now consider the most common proton-donating group, which is the hydroxyl group –OH. Application of the two above-mentioned approaches may be schematically presented as in Scheme 3.

The experimental value of the substituent constant for the –OH group, $\sigma^+=-0.92$, refers to the case of infinite distance $d(\text{O}\cdots\text{F})$. If, after the proton transfer, the HF molecule is infinitely far, the other limiting value of substituent constant is σ^+ for the –O$^-$ group, and it is equal to –2.30.[16] Undoubtedly the values of σ^+ for intermediate situations, when the proton is between O···F, have to be between these two above-mentioned limiting σ^+ values. For all fixed interatomic O···F distances, optimization leads to an optimal position of proton in the O–H···F$^-$ region. Thus the length of O–H and C–O bonds as well as C–C bonds in the ring are known and allow one to calculate the HOMA value for the ring, which in turn serves for estimation of σ^+ value from Eq. 2. Then one can correlate the C–O bond length known as a numerical measure of H-bond strength in phenols[11,24] and the σ^+ value as presented in Figure 1, and approximate the relation by linear regression (Eq. 4).

$$\sigma^+(\text{OH}) = 15.50 \cdot d_{\text{C–O}} - 21.88 \quad cc = 0.99 \quad (4)$$

As a result, the obtained relation (Eq. 4) may be used to estimate the σ^+ value of any –OH group involved in H-bonding by considering the neighbouring C–O bond length.
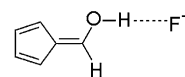
2.3. Calculation of σ^- for proton-accepting substituent

The case where the proton in the H-bond is approaching the proton-accepting group may be treated in a similar way as described above. In order to present a general idea the proton-accepting group –CHO is chosen and thus we consider 8-formyl-heptafulvene interacting with HF (Scheme 4).

Again, H-bonding interaction leads to changes of π-electron delocalization in the ring, which can be measured by the HOMA index. Then from Eq. 3, assigned for electron-accepting substituents, the appropriate σ^- values for –CHO···HF substituent of fixed O···F distance may be estimated. The resultant σ^- values may be correlated with C–O bond length of the –CHO group involved in H-bonding, as presented in Figure 2.

$$\sigma^-(\text{CHO}) = 25.73 \cdot d_{\text{C–O}} - 30.54 \quad cc = 0.99 \quad (5)$$

The dependence of σ^- values on C–O bond length in the formyl group is nearly linear and may be applied to estimate the value of σ^- for any formyl group interacting via H-bond.

Scheme 2. Stabilization of fulvene by electron-donating substituent, D, and heptafulvene by electron-accepting substituent, A.

Scheme 3.