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Intramolecular resonance-assisted hydrogen bonds: A theoretical description by means of atomic charges and charge fluxes



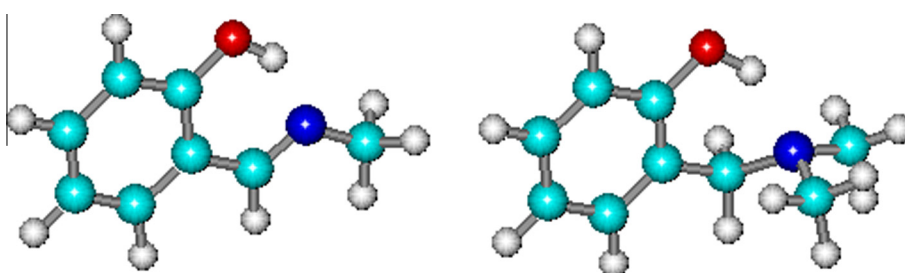
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HIGHLIGHTS

- Quadratic correlation charge fluxes ϕ_H vs. molecular IR absorption coefficients E is shown.
- The transition “free” \rightarrow intramolecular \rightarrow intermolecular H-bond is gradual.
- The hydrogen charge flux provides a quantitative and simple parameterization of H-bond strength.

GRAPHICAL ABSTRACT



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ABSTRACT

The characterization of intramolecular H-bonds in terms of atomic charges and charge fluxes (at the B3LYP/cc-pVTZ level of theory) has been extended to the case of the so called resonance-assisted (RA) H-bonds. A quadratic correlation between the charge fluxes ϕ_H and the molecular IR absorption coefficients E that includes the entire family of the studied systems (31 of them) containing both intra- and intermolecular hydrogen bonds (O–H \cdots O/N) confirmed the critical importance of the charge fluxes on the IR intensity enhancements. Since they reflect changing of the atomic charge distribution during the normal modes of vibrations, the dynamic nature of hydrogen bonding properties has been re-emphasized. The changes of the charge flux of the hydroxyl hydrogen in an RA intramolecular H-bond are between those for “free” OH bonds and the values calculated for intermolecular H-bonds. The transition “free” \rightarrow intramolecular \rightarrow intermolecular is gradual and therefore the hydrogen charge flux can be considered as practically sufficient to give quantitative measure to the intuitively obvious statement that “intramolecular H-bonding is somehow in between no H-bonding situation and intermolecular H-bonding” and thus provide a quantitative and yet simple parameterization of H-bond strength. In strictly planar molecules, the difference of the sums of charges of atoms participating in the 6-membered H-bond ring $\Delta\Sigma$ can serve as a measure of the charge delocalization after the H-bond is formed. The electronic charge is withdrawn from the group of six atoms when the H-bond is formed in nitrophenol ($\Delta\Sigma = -0.07$), while the opposite is true ($\Delta\Sigma = +0.03$) for 2-hydroxy benzylidene amine. The corresponding values of the geometrical resonance parameter Δ are 0.39 and 0.37, respectively, similar to those found for 2-hydroxy acetophenone and 2-hydroxy benzaldehyde. The extent of the π -electron delocalization as measured by the resonance parameter Δ does not follow the strength of H-bond as measured by the charge flux ϕ_H .

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Introduction

Strong intramolecular hydrogen (H) bonds (as a part of six-membered intramolecular rings), also known as resonance assisted

(RA) H-bonds [1] will be studied here. The observed characteristics of the H-bonds in enol forms of β -diketones [2] were supposed to occur due to the charge redistribution resulting in resonance stabilization. In addition, it is generally considered acceptable to relate the properties of RA H-bonds with π -electron delocalization although only in a qualitative way and indirectly [2,3] (the π -electron charge density is not calculated). Thus, one of the main

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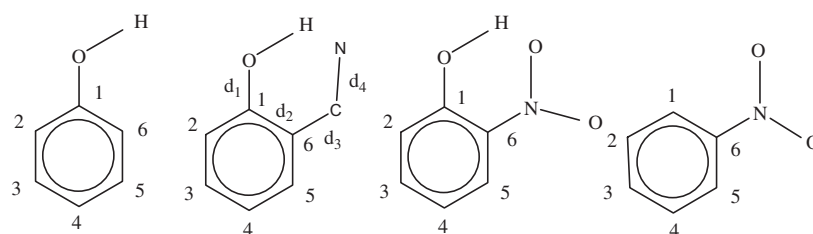
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characteristics of RA H-bonds is the existence of conjugated single and double bonds [1,2]. However, in a number of recent studies it has been shown [4,5] that the RA H-bond effect is not the primary reason behind the strength of the corresponding intramolecular H-bonds, rather it is simply a consequence of the structure of the σ skeleton of the system that puts constraints on the intramolecular ring containing the H-bond. As systems within which RA H-bond O—H \cdots N' exists, a Schiff base 2-hydroxy-benzylidene methyl amine (**sbm**) [6], has been chosen and contrasted with a Mannich base 2-hydroxy-dimethyl benzyl amine (**mbm**) having O—H \cdots N' H-bond [7] (single primed and double primed atom symbols refer to the nitrogen hybridization state). The integrated intensities of the OH bands in Mannich and Schiff bases are generally lower than in the related intermolecular H-bonded complexes because the intramolecular bonds are all bent. In Mannich bases, the tendency of the OH-group to align itself tetrahedrally with respect to the other three bonds of nitrogen atom means actually that the six-membered ring cannot be planar (the angle $\angle(C1,C6,C,N)$ (Scheme 1) in **mbm** is 44°). In Schiff bases the same angle is 0° , i.e. the six-membered ring is strictly planar. In order to make more useful comparisons and put more weight on the possible conclusions concerning the properties of RA H-bonds in **sbm**

and **mbm**, some other similar molecules having intramolecular O—H \cdots O' or O—H \cdots O' H-bonds and their isomers without H-bonds (**n** is appended to the abbreviated name of a molecule) and the corresponding intermolecular H-bonded complexes too have been added (Fig. 1, for more detailed description see below).

Although the strength of intramolecular H-bond is an ill-defined concept due to lack of a suitable reference system [8–10], it is nevertheless extensively used, most often for qualitative purposes. It is generally possible to describe a particular intramolecular H-bond XH \cdots Y as stronger than the other one by using suitable quantity such as the XY distance or the electron density at the critical point from X to Y [4,5]. In this work, the strength of an H-bond will be discussed in terms of calculated, but measurable spectroscopic quantities, the frequency shift of the OH stretching vibrations, $\Delta\bar{\nu}(OH)$, the enhancement of its absorption coefficient, ΔE and the H-bond enthalpy or free energy difference between the two conformers. The latter quantity can be considered as the most suitable one for the characterization of the H-bond strength.

Recently a characterization of intra- and intermolecular H-bonds in terms of atomic charges and charge fluxes [11] has been proposed [12]. Based on the spectroscopic criteria, the intramolecular H-bonds studied in that work (O—H \cdots O and O—H \cdots π as



Scheme 1. Atom numbering.

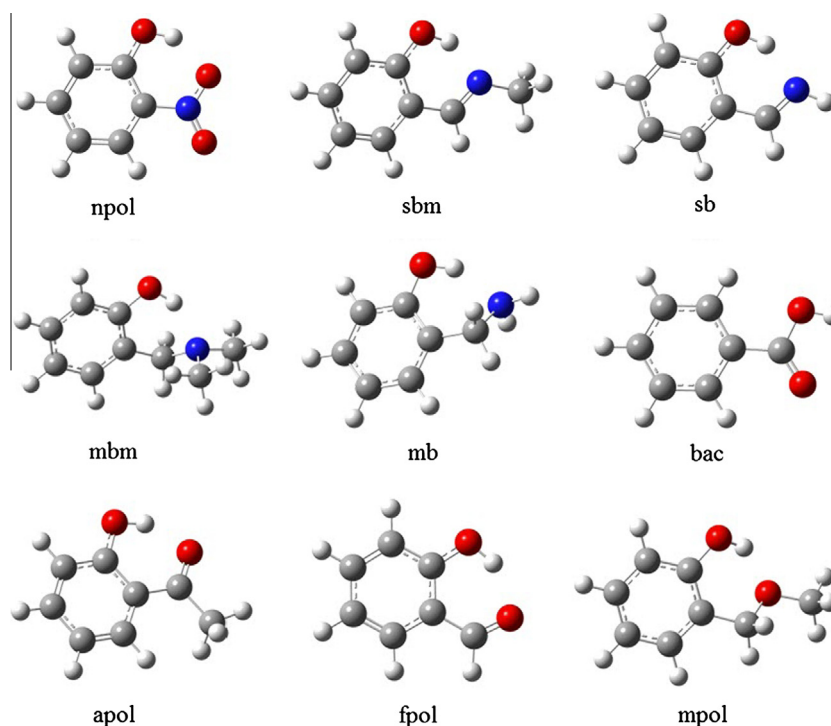


Fig. 1. Molecules with intramolecular H-bonds (except **bac**): group A – nitrophenol (**npol**); group B – 2-hydroxy benzylidene methylamine (Schiff base, **sbm**) and 2-hydroxy benzylidene amine (**sb**); group C – 2-hydroxy dimethyl benzylamine (Mannich base, **mbm**) and 2-hydroxy benzylamine (**mb**); group D – benzoic acid (**bac**); group E – 2-hydroxy acetphenone (**apol**), 2-hydroxy benzaldehyde (**fpol**); group F – 2-methoxy methyl phenol (**mpol**).

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