Acc. Chem. Res. **2002,** *35,* 887−894

Structural Characteristics of Intramolecular Hydrogen Bonding in Benzene Derivatives

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Received January 2, 2002

ABSTRACT
In this Account, the intramolecular hydrogen bonding (HB) properties of various proton acceptor groups (BX_n: C═N, NO_2, C═O, P═O, F, CF_3) with OH and NH_2 (AH) in benzene derivatives are assessed on the basis of gas electron diffraction, spectroscopic, and quantum chemical results. The most important properties are the HB energy, the characteristic geometrical changes in the interacting groups (lengthening of the A−H and B−X, shortening of the C−A and C−B bonds) and in the benzene ring, and the vibrational properties of the AH groups. These properties are characteristic of the particular HB interaction (in particular of the AH and BX_n pair in single and multiple hydrogen-bonded systems); however, they cannot be related directly to the computed HB energies.

Introduction

The concept of hydrogen bonding (HB) has been around in chemistry for close to a hundred years. This interaction is intimately involved in the structure and properties of water in its various phases and of molecules in aqueous solution. There is the well-known role of the hydrogen bond as a structural element in large molecules such as proteins, including enzymes, and nucleic acids. There are then indications that hydrogen bonds play an important role also in biological electron transfer across long distances. The principles of HB have been utilized in the design of new materials capable of self-assembly into well-ordered crystal structures, for molecular recognition of organic molecules, and for self-assembly of spherical, helical, and cylindrical structures. There have been numerous monographs about hydrogen bonding,[1,2] focusing on various properties of HB with an emphasis on intermolecular interactions.

Intramolecular HB, although less common and often weaker than its intermolecular counterpart, may also exert a considerable impact on molecular properties. It includes the relative stability of structural isomers (conformers), the charge distribution within the molecules, and reactivity.

Accurate structural data on benzene derivatives containing intramolecular HB have been collected from gas-phase electron diffraction and high-level theoretical studies. They have uncovered subtle details of molecular structure that had previously not been available. Our probing into the geometry and energetics of ortho-substituted benzene derivatives[3−20] has shown marked structural changes in both the interacting groups and the rest of the molecule as a consequence of intramolecular HB.

In the present paper we review the structural, energetic, and vibrational properties of phenol and aniline derivatives showing intramolecular HB. The selected acceptor (BX_n) groups, C═N, N═O, C═O, P═O, F, and CF_3, cover a broad range from *strong* to *weak* HB interactions. We present an analysis of the following:

(i) the HB energy (estimated from the relative energies of the hydrogen-bonded and non-hydrogen-bonded conformers);

(ii) the geometrical characteristics of the donor (AH) and acceptor (BX_n) groups in the hydrogen-bonded systems, as compared with those of the respective parent molecules;

(iii) the impacts of HB on the benzene ring;

(iv) the vibrational characteristics of these intramolecular hydrogen bonds.

The experimental data (r_g parameters) included in this Account stem from our gas-phase electron diffraction investigations. The advantage of the electron diffraction method is that it targets isolated molecules and the information it yields is free from the influence of intermolecular interactions. Although the technique is less suited for molecules of lower symmetry, the introduction

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10.1021/ar020003b CCC: $22.00

Table 1. Hydrogen Bonding Energies (kJ/mol) and Selected Geometrical Characteristics (Å)

		calcd								ED (r_g)		
B	molecule	ΔE^a	H···X	A···X	Δ(A−H)	Δ(C−A)	Δ(B−X)	Δ(C−B)	ref	H···X	A···X	ref
C=N	2-iminomethylphenol	35.4	1.745	2.632	0.023	−0.025	0.004	−0.016				
NO_2	2-nitrophenol	29.6	1.747	2.600	0.012	−0.014	0.013	−0.005		1.72(2)	2.58(1)	5
	2-nitroresorcinol	21.2 (42.4)^b	1.717	2.571	0.011	−0.016	0.011	−0.020		1.76(4)	2.56(1)	4
	4,6-dinitroresorcinol	32.9 (65.8)^b	1.744	2.600	0.013	−0.015	0.013	−0.005		1.72(2)	2.60(1)	6
	2,5-dinitrohydroquinone	27.6 (55.3)^b	1.765	2.609	0.010	−0.011	0.012	−0.003				
	2-nitrovinyl alcohol	43.0	1.747	2.602	0.021	−0.020	0.017		20			
	2-nitroethanol	4.0	2.134	2.819	0.004	−0.007	0.005		20			
C=O	salicylaldehyde	28.4	1.788	2.664	0.015	−0.021	0.011	−0.026		1.74(2)	2.65(1)	8
	2,5-dihydroxyterephthalaldehyde	22.6 (45.2)^b	1.799	2.669	0.014	−0.018	0.009	−0.019		1.76(1)	2.667(8)	7
	4,6-dihydroxyisophthalaldehyde	33.0 (66.0)^b	1.772	2.665	0.017	−0.024	0.012	−0.026				
P=O	2-phosphinylphenol	13.3	1.787	2.712	0.017	−0.021	0.010	−0.015	17			
F	2-fluorophenol	12.2	2.180	2.718	0.002	−0.002	0.015^c		16	2.125(55)	2.735(22)	19
	2,6-difluorophenol		2.203	2.732					16	2.054(79)	2.715(67)	19
	2,3,5,6-tetrafluorohydroquinone (C_{2h})		2.235	2.756					16	2.015(69)	2.657(54)	18
	2,3,5,6-tetrafluorohydroquinone (C_{2v})		2.257	2.772					16			
CF_3	2-trifluoromethylphenol	7.2	1.983	2.771	0.000	0.000	0.023	−0.006	12	2.05(6)	2.792(13)	14
	2-trifluoromethylresorcinol	8.1 (16.2)^b	1.841	2.654	−0.002	−0.002	0.016	−0.014	15			
	2,6-bis(trifluoromethyl)phenol		1.972	2.760					15			
	2-trifluoromethylvinyl alcohol	17.1	1.912	2.704	0.005	−0.010	0.028^c		13			
F	2-fluorobenzamine		2.315	2.717						2.464(20)	2.737(10)	11
	2,6-difluorobenzamine		2.401	2.749						2.407(13)	2.743(5)	11

[a] Computed at the MP2/6-31+G**//MP2/6-31G** level in the present study. The zero-point vibrational energy corrections were obtained from HF/6-31G** frequency analysis and scaled by 0.9135. [b] Normalized to one hydrogen bond; the total HB energy of the molecule is given in parentheses. [c] Δ(C−F) in the fluorobenzene derivatives (BX_n = F).

of constraints from ab initio computations can considerably enhance its capabilities.[5,8]

The computational methods are important tools also in themselves. In addition to modeling the isolated molecule, they are free from random errors, unlike the experimental data. However, the errors of the computed data may often be quite large, but by using an advanced theory (MP2, DFT) in conjunction with a large enough basis set, they can be considered to be systematic errors within a group of related molecules.[3] On that basis, reliable trends can be predicted from the calculations. Therefore, the quantum chemical computational techniques are well suited for investigation of large series of molecules to evaluate general trends in various properties.

Computed geometrical data of the target molecules have been obtained at various levels of theory. For correct comparison, it is desirable to have a consistent set of data. In our experience, the standard MP2/6-31G** level of theory has proved to provide reliable molecular geometries. The molecules, for which MP2/6-31G** data were not available, have been reoptimized at this level in the present study using the Gaussian 98 program package.[21] The HB energies were obtained by MP2/6-31+G** single-point calculations on the MP2/6-31G** geometries, recognizing the importance of diffuse functions on the heavy atoms for HB energetics.[22] Changes in the reference geometry upon introduction of the diffuse functions were found to be negligible.[13,17] Moreover, these marginal geometrical changes are not reflected in the computed single-point energies, as revealed by test calculations on 2-nitrophenol and 2-trifluoromethylphenol.[12]

Discussion

Energetics and Geometrical Characteristics of HB. First we assess the HB strength of various acceptors in these intramolecular interactions. Lacking experimental data on the non-hydrogen-bonded species, this assessment is based solely on the computed energetics (Table 1).[23] The HB preference of the target acceptors with phenolic OH can be ranked as follows:

$$C{=}N > NO_2 \sim C{=}O > P{=}O \sim F > CF_3$$

From Table 1, the preference of the sp^2 nitrogen and oxygen for HB is obvious. The HB energy, however, decreases when the heavier P is included in the acceptor group. We note the strong dependence of the HB energy on the degree of substitution and on the relative spatial arrangement of the substituents. The hydroquinone derivatives form hydrogen bonds, which are about 6 kJ/mol weaker, while the 4,6-disubstituted resorcinols are about 4 kJ/mol stronger than the corresponding derivatives with only one hydrogen bond. The weaker HB in 2-nitroresorcinol may be due to considerable repulsive forces in this strained system.

In contrast to the high electronegativity and the consequently large negative excess charge of fluorine, the HB of organic fluorine acceptors is rather weak. This is apparent from both the calculated HB energies and the structural and spectroscopic characteristics (cf. Table 1, vide infra). Similarly weak intermolecular H···F hydrogen bonds have been found in the crystal.[24] The poor HB properties of organic fluorine derivatives have been explained by the low proton affinity and hardness of fluorine (low basicity, tightness of the electron shell), and by the difficulty of modifying this by intramolecular electron delocalization or intermolecular cooperative effects.[25]

In the case of BX_n = NO_2 and CF_3, the smaller ethylene analogues have also been investigated to elucidate the role of the aromatic benzene ring in the interaction. In general, in the ethylene analogues the intramolecular hydrogen

Table 2. Comparison of Selected Experimental and Computed Geometrical Characteristics of the Intramolecular Hydrogen Bonds (Å)

		ED (r_g)					calcd[a]				
B	molecule	Δ(A−H)	Δ(C−A)	Δ(B−X)	Δ(C−B)	ref	Δ(A−H)	Δ(C−A)	Δ(B−X)	Δ(C−B)	ref
NO_2	2-nitrophenol	0.011(12)	−0.022(10)	0.018(9)	−0.022(6)	5	0.013	−0.025	0.013	−0.017	
	2-nitroresorcinol	0.080(15)	−0.027(6)	0.016(4)	−0.037(8)	4	0.012	−0.025	0.011	−0.035	
	4,6-dinitroresorcinol	0.044(10)	−0.040(6)	0.018(8)	−0.025(6)	6	0.015	−0.032	0.013	−0.018	
C=O	salicylaldehyde	0.027(15)	−0.019(11)	0.013(5)	−0.017(12)	8	0.016	−0.022	0.013	−0.024	
	2,5-dihydroxyterephthalaldehyde	0.025(10)	−0.010(7)	0.019(4)	−0.010(6)	7	0.015	−0.021	0.012	−0.017	
F	2-fluorophenol	−0.004(13)	−0.003(11)	−0.003(13)		19	0.003	−0.008	0.010		16
	2,6-difluorophenol	−0.019(16)	−0.019(36)	0.002(56)		19	0.003	−0.012	0.008		16
	2,3,5,6-tetrafluorohydroquinone (C_{2h})	−0.003(11)	−0.028(10)	−0.006(13)		18	0.003	−0.012	0.000		16
	2,3,5,6-tetrafluorohydroquinone (C_{2v})						0.003	−0.011	0.000		16
CF_3	2-trifluoromethylphenol	−0.018(20)	−0.019(12)	mean	−0.006(6)	14	0.001	−0.007		−0.004	12
F	2-fluorobenzamine	0.026(20)	0.005(8)	0.009(9)		11	0.000	−0.007	0.008		
	2,6-difluorobenzamine	0.017(8)	0.005(8)	0.000(6)		11	0.000	−0.012	0.005		

[a] Computed at the MP2/6-31G** level.

bonds are stronger than in the benzene derivatives, which may be attributed to steric and electronic factors:

(i) The generally shorter C=C bond in ethylene as compared with those in benzene facilitates the approach of the donor and acceptor groups.

(ii) The unfavorable steric interaction between BX_n and the ortho-positioned aromatic hydrogen is considerably reduced in the ethylene derivatives.

(iii) The conjugation with the vinyl C=C bonds is enhanced as compared with that in the aromatic π-systems, witnessed by the shorter C−O and C−B bonds in the ethylene derivatives.[13] This may result in a stronger electronic interaction of the OH and BX_n groups through the vinyl C=C, which, according to the resonance-assisted HB theory,[26] further strengthens the hydrogen bond.

The importance of an sp^2 skeleton for the title interactions is demonstrated in 2-nitroethanol, where the (sp^3) C−C bond is too long to provide favorable steric conditions for HB. Consequently, the interaction energy is very small, about 4.0 kJ/mol. Even this marginally attractive interaction results in discernible structural effects.[20]

HB, however weak, gives rise to a rearrangement of the electron density distribution, resulting in characteristic changes in the spectroscopic properties and especially in the geometry of the molecule. The direct geometrical changes occur in the H···X and A···X distances, while the most important indirect ones occur in the parameters of the AH and BX_n groups. The latter effects include the lengthening of the A−H and the terminal bonds of BX_n, participating in the interactions, as well as the shortening of the C−A and C−B bonds. More subtle effects appear in the neighboring molecular moieties. All these geometrical changes are sensitive to the strength of HB.

Table 1 lists the most important geometrical characteristics of the systems investigated. For the H···X and A···X distances, both experimental and geometrical data are included. They provide a good basis for comparison of the two sources. The computed changes in the donor and acceptor geometries were evaluated with respect to those of the non-hydrogen-bonded conformers. The advantage of using the non-hydrogen-bonded reference geometry is that it takes into account the electronic interactions between the AH and BX_n groups through the molecular skeleton present in both conformers. Despite the repulsive steric interaction between A and BX_n,[27] this reference geometry has this advantage over using the monosubstituted parent molecules for evaluating the geometrical changes as a consequence of HB. On the other hand, consideration of the parent molecules is the only choice in evaluating the experimental data. In Table 2, we provide the geometrical changes upon HB as compared with the parents.[28]

The data in Tables 1 and 2 demonstrate the ability of gas-phase electron diffraction to detect the intramolecular hydrogen bond, to estimate its length as well as to discern its geometrical consequences. However, the experimental uncertainties are rather large, especially those of the distances involving hydrogen due to its relatively weak electron scattering. Therefore, the available experimental data are not always well suited to draw general conclusions, especially involving subtle changes in the geometry.

The experimental errors were considerably reduced in the H···X and A···X distances of nitrophenol and salicylaldehyde in their electron diffraction studies, as compared with those of the fluorophenol derivatives (cf. Table 1). The relative magnitudes of these distances are in good agreement with the trends predicted by the calculations. (The experimental H···O distance in 2-nitroresorcinol can be excluded due to its large uncertainty.) On the other hand, computations and experiment are at variance for the fluorophenols. However, the experimental uncertainties are so large as to render them useless for establishing any trends.[16] The same conclusion could be drawn from the analysis of the other geometrical characteristics listed in Table 2. A reanalysis of the fluorophenol derivatives by a concerted approach involving experimental and computational information would be desirable.

When looking for a relationship between the computed HB energies and the structural properties of intramolecular HB, one must take into account the geometrical constraints in these systems in contrast to the more relaxed structures of the intermolecular interactions. In a HB situation, the H···X distance is determined, in addition to the strength of the interaction, by the size and relative positions of the interacting groups. The limited freedom of the groups may result in either a shorter or a longer H···X distance with respect to the optimal one. In this way, a compressed hydrogen bond gives a smaller HB energy due to the emerging repulsive forces.

For the title structures, there is consistency between the computed HB energies and the H···X and A···X distances (cf. Table 1). The effects of a compressed hydrogen bond are best seen in 2-nitroresorcinol and 2-phosphinylphenol, while the rather long H···F distances in the fluorophenols stem partly from the angular strains of the five-membered hydrogen-bonded rings.

The HB energy could not be calculated for the polysubstituted fluorophenol derivatives in the absence of the non-hydrogen-bonded reference structures. The relative strength of these hydrogen bonds was estimated from the variations of the H···F and O···F distances within the series, giving the following sequence:[16]

$$\text{2-fluorophenol} > \text{2,6-difluorophenol} > \text{2,3,5,6-tetrafluorohydroquinone } (C_{2h}) > \text{2,3,5,6-tetrafluorohydroquinone } (C_{2v})$$

This observation is supported by the negative charge on the interacting fluorines decreasing in the same direction.[16] This is in agreement with gradually weakening electrostatic interactions between the hydrogen-bonded atoms.

The variation of the geometrical parameters of the AH and BX_n groups yields important information on the character of bonding with different acceptors. The elongation of the A−H and B−X bonds, as well as the shortening of the C−A and the C−B bonds (the latter only in six-ring HBs), reflects the electron density redistribution upon HB, and it is related to the role played by the individual groups in the interaction.

The ideal case, when both the donor and acceptor groups participate to an equal or nearly equal extent in the interaction, can be suggested for the acceptors C=O and P=O. These interactions result in a somewhat larger elongation of the O−H bond than that of the C=O/P=O bonds (Table 1), in agreement with the more rigid character of a double bond. A dominant role of the OH group in HB is observed when the acceptor is C≡N. A slightly larger contribution of the NO_2 group can be suggested in the nitrophenols. The acceptor groups have a dominant role in the fluoro and trifluoromethyl derivatives; here, the O−H bond remains unchanged upon HB. The impact of the acceptor groups on bond length changes can be ranked as follows:

$$\Delta(\text{O−H}):\ \text{C≡N} \gg \text{P=O} > \text{C=O} > \text{NO}_2 \gg \text{F} > \text{CF}_3$$

$$\Delta(\text{C−O}):\ \text{C≡N} > \text{P=O} \sim \text{C=O} > \text{NO}_2 \gg \text{F} > \text{CF}_3$$

$$\Delta(\text{B−X}):\ \text{CF}_3 \gg \text{F} > \text{NO}_2 > \text{C=O} \sim \text{P=O} \gg \text{C≡N}$$

$$\Delta(\text{C−B}):\ \text{C=O} \gg \text{C≡N} > \text{P=O} \gg \text{CF}_3 \sim \text{NO}_2$$

This nonsystematic variation of the donor and acceptor bonds excludes any simple relationship with the computed HB energies. Even very weak hydrogen bonds may be associated with considerable changes in the geometry, as shown by the 0.023-Å lengthening of the C−F bond in 2-trifluoromethylphenol. There is a good correlation, however, between the HB energies and the geometrical changes within the series of an acceptor group (cf. the mono- and polysubstituted derivatives of $BX_n = NO_2$ and C=O).

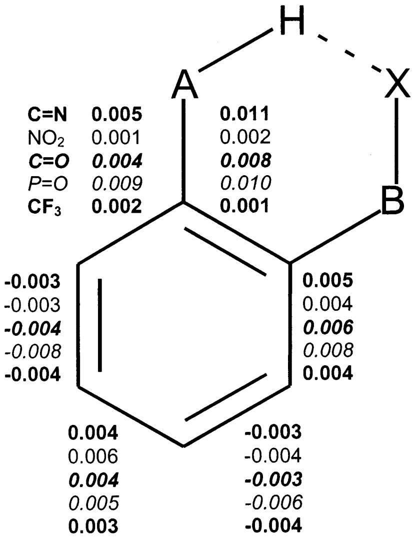


FIGURE 1. Characteristic changes in the ring C−C bond distances in the mono-hydrogen-bonded derivatives.

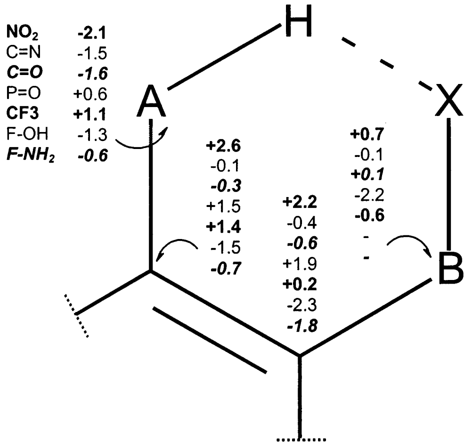


FIGURE 2. Characteristic bond angle changes upon HB derived using the parent reference geometries (mono-hydrogen-bonded derivatives).

The bond angles of the donor and acceptor groups also show characteristic alterations upon HB. The two groups could be expected to lean toward each other to facilitate their interaction in HB. There is, however, no consistency in this respect in our results (Figure 2).[29] Most of the C−A−H and C−B−X angles decrease (up to 2°), while several C−C−A and C−C−B angles increase by the same amount upon HB. Besides the attractive HB, the ligand−ligand interactions are also important in determining the optimal bond angles. In 2-fluorophenol and 2-fluorobenzamine, with marginal steric effects due to the five-membered hydrogen-bonded moiety, all the above-mentioned bond angles decrease. On the other hand, in 2-nitrophenol and 2-trifluoromethylphenol, the large steric interactions may be responsible for the tilt of the AH and BX_n groups away from each other. At the BX_n groups of these molecules, a weak attractive interaction can also be assumed between the non-hydrogen-bonded oxygen or fluorine of BX_n and the adjacent ring hydrogen.

All this shows the individual character of each $A-H\cdots X-B$ interaction and that the above geometrical properties depend on the particular donor−acceptor pair. The most favored arrangement of the interacting atoms, i.e., penetration of the hydrogen into the electron cloud of BX_n, can be achieved in different ways. Our results indicate that it is hard to draw a general conclusion on the geometrical consequences of HB in these systems.

Concerning the observations derived by using the parent geometries for reference, these data are affected by the neglect of through-ring intersubstituent electronic interactions in the reference structures. However, in most cases the changes in the bond lengths upon HB were found to be similar to those discussed above. Considerable deviations were found only in the $\Delta(C-A)$ and $\Delta(C-B)$ data of nitrophenols and in the $\Delta(C-A)$ differences in fluorophenols. In these molecules, the electronic interaction between the OH and acceptor (NO_2, F) groups appears to be very large in the non-hydrogen-bonded conformers.

The data in Table 2 show consistency between the electron diffraction results and the computed ones. The geometrical changes in the $BX_n = NO_2$ and C=O systems determined by experiment well reflect the trends discussed above. Only the smaller effects in the BX_n = F and CF_3 derivatives may be masked by experimental errors.

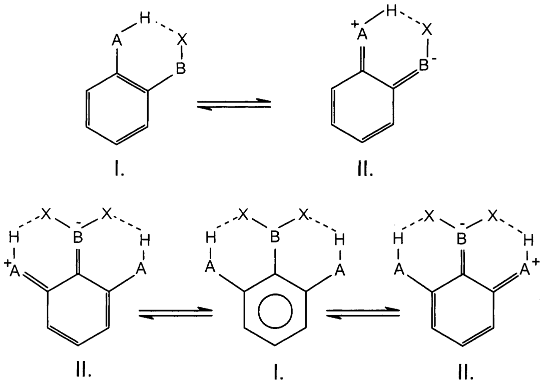
In addition to the general characteristics discussed above, we note some additional geometrical features of the intramolecular HB systems:

(i) The hydrogen-bonded six- and five-ring moieties are planar (and coplanar with the benzene ring), with the only exception of the aromatic CF_3 derivatives. In 2-trifluoromethylphenol, an asymmetric bifurcated hydrogen bond has been detected, with both the O−H and C−F bonds being turned out of the plane of the benzene ring.[12,14] In 2-fluoromethylphenol with a single $H\cdots F$ contact, an analogous nonplanar arrangement was found,[14] although the shortest $H\cdots F$ distance would correspond to the coplanar one. On the other hand, a coplanar hydrogen-bonded moiety was found in 2-trifluoromethylvinyl alcohol, presumably referring to a significant role of the aromatic ring in the benzene derivative. The major effect determining the out-of-plane position of the C−F bond in 2-trifluoromethylphenol is probably a $\pi(\text{ring}) \rightarrow \sigma^*(C-F)$ interaction favoring the orthogonal conformation of the CF_3 group.[30]

(ii) The barrier to internal rotation of the BX_n groups in the hydrogen-bonded derivatives increases considerably with respect to that of the BX_n parents.[7−9,17,31]

(iii) The simultaneous HB interactions in the resorcinol derivatives of NO_2 and CF_3 result in about twice as large changes in the common geometrical parameters (C−N and C−C bonds, O−N−O and F−C−F angles, etc.) than in the respective phenol derivatives containing a single interaction.[4,15] This implies at least approximate additivity in the geometrical consequences of these hydrogen bonds.

Scheme 1



Impacts of HB on the Benzene Ring Geometry. Substitution of hydrogen in benzene results in a perturbation of the electron density distribution followed by changes in the chemical and physical properties.[32] Substituent effects are well observed on the molecular geometry: in monosubstituted derivatives, changes up to a hundredth of an angstrom in the ring bond lengths and a few degrees in the bond angles have been demonstrated.[32] These changes can be even larger in the case of polysubstitution when the substituents interact with each other through the benzene ring. Most powerful are the π interactions between ortho- and para-positioned substituents assisted by a tendency of the benzene ring to form quinonoid-type resonance structures. A reference case is the *p*-nitroaniline molecule,[32] where strong π-donation from the amino group is coupled with π-acceptance of the nitro group.

In intramolecular HB, the ortho-positioned donor and acceptor groups have a strong electronic interaction through the benzene ring. This is reflected primarily by the shortening of the C−A and C−B bonds in the non-hydrogen-bonded conformers as compared to the bond distances in the parent molecules (vide supra), but pronounced effects can also be recognized in the more compact ring geometry. Here, we have to distinguish between the six- and five-membered HB systems. In the six-ring systems (BX_n: C=N, NO_2, C=O, P=O, CF_3), the considerable shortening of the donor C−A as well as the acceptor C_2-N, C_2-C, and C_2-P bonds upon HB refer to some double-bond character of these bonds, as indicated by the resonance forms II in Scheme 1. There is yet another characteristics of the *o*-quinonoid structure in the benzene ring: the C_3-C_4 and C_5-C_6 bonds are shortened while the other four C−C bonds are lengthened upon HB (cf. Figure 1). The largest C−C elongation was observed in the bond between the interacting AH and BX_n groups. The changes are most pronounced in 2-phosphinylphenol, while the weakest appears in 2-trifluoromethylphenol. Again, there is no direct correlation with the computed HB energies, nor with the geometrical changes of the donor and acceptor groups.

Essentially the same conclusion could be drawn from the more scarce electron diffraction data,[5,8] keeping in mind the difference in the reference structures.[33] Accordingly, the changes in the experimental C−C bond lengths were somewhat larger than the computed ones derived from the non-hydrogen-bonded conformers. This demonstrates the potential of the electron diffraction method to provide at least qualitative information even on weak intramolecular interactions.

The above structural variations can be well interpreted by means of the resonance-assisted hydrogen bonding model.[26] The resonance structures presented in Scheme 1 reflect the trends of the geometrical changes. It is in the nature of such schemes that they exaggerate the changes in bonding. The essence of these changes is that HB enhances the contribution of the quinonoid-type resonance forms to the overall structure. On the other hand, this resonance strengthens the HB itself through a feedback effect.

The resonance model can well be applied for the resorcinol and hydroquinone derivatives with two HB interactions implying an interconversion between two resonance structures (cf. Scheme 1). However, the model is not applicable to the five-ring systems present in the fluorophenol and fluoroaniline derivatives. The lack of resonance support in these structures may also contribute to the weakness of the H···F interactions in these systems.

Vibrational Characteristics. The vibrational properties most characteristic upon HB are the changes in the stretching and torsional vibrations of the A−H group. The red shift of the A−H stretching frequency (ν_{AH}), being closely related to the lengthening of the A−H bond, is the most often used spectroscopic indicator of HB. A correlation has been found between this shift and various HB properties, such as the enthalpy of hydrogen bond formation, A−H distance, A···B distance, etc.[1] The characteristic blue shift of the A−H torsional frequency (τ_{AH}) stems partly from the slightly increased double-bond character of the C−A bond (vide supra) and partly from the restricted mobility of the hydrogen-bonded A−H hydrogen.

Several species from the target systems have been investigated in the gaseous phase by IR spectroscopy, viz., 2-nitrophenol,[34] 2-nitroresorcinol,[35] salicylaldehyde,[36] 2-fluorophenol,[36] 2,6-difluorophenol,[37] 2,3,5,6-tetrafluorohydroquinone,[36] and 2-trifluoromethylphenol.[36] For other compounds, solution-phase (cyclohexane, $CHCl_3$, or CCl_4) IR data are available (4,6-dinitroresorcinol,[38] 4,6-dihydroxyisophthalaldehyde[36]). However, these frequencies may be somewhat influenced by solvent effects. Because the non-hydrogen-bonded species could not be observed in the spectra, except for 2-fluorophenol,[39] the shifts of the ν_{OH} and τ_{OH} frequencies upon HB (Figure 3) were evaluated with respect to the parent compounds.

Similarly to the geometric properties, there is poor correlation between the calculated HB energies and the vibrational characteristics. On the other hand, both the red shifts of the ν_{OH} and the blue shifts of the τ_{OH} frequencies correlate markedly with the computed lengthening of the O−H bond upon HB. Even the very small geometrical differences within the nitrophenol derivatives are reflected in the vibrational data (cf. Table 1 and Figure 3). We note the marginal effects in the spectral properties of 2-fluorophenol and 2-trifluoromethylphenol, pointing again to the weak nature of these intramolecular hydrogen bonds. No shifts can be observed in the ν_{OH} and τ_{OH} frequencies of 2-trifluoromethylphenol, in agreement with the unchanged O−H bond length upon HB.

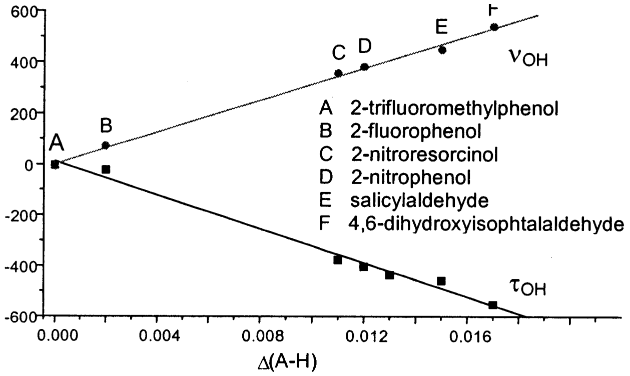


FIGURE 3. Characteristic red shifts of the OH stretching and blue shifts of the OH torsional vibrations with respect to the frequency of the respective parents (phenol and resorcinol) in the function of the O−H bond lengthening upon HB.

For a few compounds, complete vibrational assignments are available, such as 2,6-difluorophenol,[37] 2-nitrophenol,[34] and 2-nitrorezorcinol.[35] They are based on joint experimental and theoretical analyses using the scaled quantum mechanical (SQM) method. The normal coordinate analysis of these molecules showed that the OH stretching as well as the OH and BX_n torsional vibrations are pure; even a mixing of the torsional modes with other out-of-plane vibrations can be ignored. Therefore, these frequency values are characteristic of the HB interaction. On the other hand, the COH in-plane bend and other vibrations of the hydrogen-bonded moieties are strongly mixed with vibrations of the benzene ring; thus, their information content is limited in this respect.

Concluding Remarks

The structural characteristics of intramolecular HB in benzene derivatives are determined by three important interactions:

1. The electronic intersubstituent interactions through the benzene ring. The consequences of these interactions are manifested also in the geometrical parameters of the non-hydrogen-bonded conformers. The shortening of the C−A and C−B bonds as well the rearrangement of the electron density distribution in the benzene ring can be characterized by a contribution of the quinonoid resonance form to the overall structure.

2. The through-space intramolecular HB interaction. Hydrogen bonding strengthens the quinonoid resonance character of the aromatic system, in agreement with the resonance-assisted hydrogen bonding model.[26]

3. Repulsive steric interactions between the substituents and with the neighboring ring hydrogens. This effect may be responsible for a lower than expected total interaction energy of the short H···X contacts.

The most important conclusions of our overview are the following:

(i) A ranking is established for the acceptor strength, based on the computed interaction energies:

$$C{=}N > NO_2 \sim C{=}O > P{=}O \sim F > CF_3$$

(ii) The changes in geometrical properties appear to be a sensitive measure of the nature of HB of a particular acceptor. As the most significant effects, the A−H and B−X bonds may lengthen by about 0.025 Å, while the C−A and C−B bonds may shorten by about 0.025 Å. In addition, there are changes, up to 0.01 Å, in the benzene C−C bonds.

(iii) No direct correlation emerges between the HB energies and the geometrical changes. This shows the individual character of each A−H···X−B interaction, and the individual alteration of the electron density distribution, as manifested in different geometrical characteristics.

Of the available methods for structural studies, the quantum chemical calculations are the best suited for the investigation of such weak interactions. The two important disadvantages of experimental methods are the experimental error (having a magnitude often comparable to the investigated effects) and the lack of ideal reference. However, our results have demonstrated the potentials of gas-phase electron diffraction to provide at least qualitative information on such weak intramolecular interactions. Its performance can be further improved by joint application of experiment and computation, especially when using state-of-the-art levels of theory in a concerted analysis.

This research was supported by the Hungarian Scientific Research Foundation (OTKA No. T030053) and by the Ministry of Education of Hungary (FKFP 0364/1999). A.K. gratefully thanks the Bolyai Foundation for financial support. Dr. V. Izvekov is thanked for the IR data of salicylaldehyde.

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AR020003B