3110 *J. Phys. Chem. A* **1999,** *103,* 3110−3114

Intramolecular Hydrogen Bonding in Fluorophenol Derivatives: 2-Fluorophenol, 2,6-Difluorophenol, and 2,3,5,6-Tetrafluorohydroquinone

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Received: November 20, 1998; In Final Form: February 10, 1999

Intramolecular F···H hydrogen bonding in 2-fluorophenol, 2,6-difluorophenol, and 2,3,5,6-tetrafluorohydroquinone has been studied by ab initio molecular orbital calculations. Geometry optimizations at the MP2/6-31G** level resulted in two planar local minima on the potential energy surface, characterized by different orientations of the hydroxy hydrogen. In the conformers where the hydroxy hydrogen points toward a fluorine, the computations suggest weak intramolecular F···H hydrogen bonding interactions. Characteristic changes in the geometrical parameters upon hydrogen bonding are manifested in the lengthening of the C−F bond involved in the interaction by 0.01 Å, in the lengthening of the O−H bond by 0.003 Å, in the decrease of the C−O−H bond angle by 1°, and in a tilt of the C−F and C−O bonds toward each other, as compared with the geometries of the parent molecules. The hydrogen bonds shorten in the order 2-fluorophenol > 2,6-difluorophenol > 2,3,5,6-tetrafluorohydroquinone (C_{2h}) > 2,3,5,6-tetrafluorohydroquinone (C_{2v}), implying strengthening of hydrogen bonds in the opposite direction. The strength of hydrogen bonding and its overall consequences in the rest of the molecule are less pronounced in systems where the hydrogen bond occurs in five-membered rings than when it is part of a six-membered system.

Introduction

Hydrogen bonding (HB) appears in a great variety of situations, being responsible, among others, for conformational properties, for molecular packing in crystal structures, as well as for biological activity in many physiologically important systems.[1] HB systems containing oxygen and nitrogen acceptors have been extensively studied, while somewhat less attention has been paid to interactions with halogens. Based on the observed characteristics of different crystalline halides, the fluoride and chloride ions are known to be strong hydrogen-bond acceptors.[1,2] In contrast, studies of organic compounds containing C−F···H−X (X = O, N) moieties indicate that the F···H intramolecular HB is generally weak,[3−12] even when the analogous situations with oxygen acceptor show strong HB interactions.[13,14]

We have been interested in probing into the structural peculiarities of HB in the F···H interaction and its geometrical consequences in the rest of the molecule.[15−17] Quantum chemical calculation is the technique of choice for these studies. The levels of theory applying MP2 or DFT with moderate basis sets have proved to provide reliable information on the structural changes in a series of molecules that are consistent with those observed in experimental studies of a more limited scope. The computational probe makes it possible to collect consistent information for extended sets of molecules for which the error of determination can be considered systematic and thus hardly influencing the structural *changes* on which our discussions are based.[18]

Recently, we reported computational results on intramolecular HB involving the trifluoromethyl group in 2-(trifluoromethyl)-vinyl alcohol,[15] 2-(trifluoromethyl)phenol,[16] and its derivatives.[17] The potential energy surfaces (*PES*) of the molecules display two minima, the global minimum being characterized by a −C−C−F···H−O−C− hydrogen-bonded six-ring moiety. In the phenol derivatives both the OH and the CF_3 groups are out of the plane of the benzene ring. Other geometrical characteristics include a considerable lengthening of the C−F bond involved in HB, a shortening of the C−O bond as well as alterations in the carbon skeleton geometry, as compared to the parent molecules containing either the donor or the acceptor groups only. These changes are in agreement with the notion of resonance-assisted hydrogen bonding.[19,20] The most peculiar feature of these F···H intramolecular hydrogen bonds, distinguishing them from analogous O···H−O and N···H−O interactions, occurs in the OH group. While in the analogous interactions with oxygen and nitrogen the O−H bond lengthens considerably upon HB,[2] it remains unaffected in the trifluoromethyl derivatives. This constancy of the O−H bond length is in agreement with the negligible change of the OH stretching frequency in syn 2-(trifluoromethyl)phenol as compared to its non-hydrogen-bonded anti conformer, according to both experiments and calculations.[15,21]

To extend our investigations on F···H−O hydrogen bonding, we selected three fluorophenol derivatives for the present

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10.1021/jp984493u CCC: $18.00

TABLE 1: Computed Energies[a] of the Conformers of 2-Fluorophenol (1) and 2,3,5,6-Tetrafluorohydroquinone (3)

molecule	symmetry	E^b (au)	ΔE (kJ/mol)
1A	C_s	−405.489 79	0.0
1B	C_s	−405.485 16	12.2
3A	C_{2h}	−777.575 90	0.0
3B	C_{2v}	−777.575 47	1.1

[a] Computed at the MP2/6-31+G**//MP2/6-31G** level including zero-point-vibrational energy correction (ZPVE). ZPVEs were obtained from harmonic vibrational frequencies calculated at the HF/6-31G** level (0.103874 au for **1A**, 0.103 594 au for **1B**, 0.082 707 au for **3A**, and 0.082 750 au for **3B**) and scaled by a factor of 0.89 in accord with known overestimates at this level.[32] [b] Absolute energies. 1 au = 2625.5 kJ/mol.

study: 2-fluorophenol (**1**), 2,6-difluorophenol (**2**), and 2,3,5,6-tetrafluorohydroquinone (**3**). Structural information on the title compounds is available from gas-phase electron diffraction (ED),[10,11] vibrational spectroscopy,[22−26] and low-level quantum chemical calculations.[27−30] All these studies indicated weak F···H−O intramolecular hydrogen bonds in the molecules in which the F···H interaction is part of five-membered rings formed by HB. The F···H(O) distances obtained by electron diffraction suggested a decreasing HB strength of **3** > **2** > **1**.

The main goal of the present study was the determination of the characteristics of the intramolecular HB in the title compounds and their comparison with the six-membered systems of HB studied previously.[15−17] For consistency with our results on trifluoromethyl derivatives,[15−17] the calculations were performed at the MP2/6-31G** level. The effects of HB on the molecular geometry were determined by comparison of characteristic geometrical parameters with those of the parent fluorobenzene (**4**), phenol, 1,3-difluorobenzene (**5**), hydroquinone, and 1,2,4,5-tetrafluorobenzene (**6**) computed at the same level of theory. The title compounds offered also an opportunity to investigate the effect of increasing fluorination on the characteristics of HB.

Computational Details

Ab initio molecular orbital calculations were performed at the second-order Møller−Plesset (MP2)[31] level of theory with only the valence orbitals active, using a 6-31G** double-split-valence plus polarization basis set. The geometries were fully optimized by gradient optimization routines. The minimum character of the optimized geometries was confirmed by vibrational analysis at the HF/6-31G** level based on optimized geometries at the same level. Zero-point vibrational energy (ZPVE) corrections were derived from the HF/6-31G** results, scaling the computed values by a factor of 0.89 to account for known overestimates at this level.[32]

To assess the relative stability of the conformers of **1** and **3**, MP2/6-31+G** energies were computed for the MP2/6-31G** geometries, in view of the experience that diffuse functions on heavy atoms may be important for reliable hydrogen binding energetics.[33] All the calculations were carried out using the GAUSSIAN 94 package.[34]

The computed energies of the conformers of **1** and **3** are compared in Table 1, and the geometrical parameters of **1**−**6** are shown in Tables 2 and 3. For convenient comparison the numbering of atoms in the parents corresponds to that in the respective title molecules (Figure 1).

Results and Discussion

TABLE 2: Selected Geometrical Parameters[a] of 2-Fluorophenol (1), 2,6-Difluorophenol (2), Fluorobenzene (4) and *m*-Difluorobenzene (5)

parameter	experimental[b]		calculated				
	1A	**2**	**1A**	**1B**	**2**	**4**	**5**
C_1-C_2			1.397	1.400	1.395	1.389	1.390
C_2-C_3			1.384	1.386	1.386	1.389	1.390
C_3-C_4			1.398	1.398	1.396	1.396	1.396
C_4-C_5			1.397	1.394	1.397	1.397	1.396
C_5-C_6			1.396	1.398	1.389	1.397	1.390
C_6-C_1			1.394	1.396	1.397	1.396	1.390
$(C-C)_{mean}$	1.395(4)	1.394(4)	1.394	1.395	1.393	1.394	1.392
$O-H$	0.954(13)	0.939(16)	0.968	0.966	0.968		
$C-O$	1.378(10)	1.362(36)	1.366	1.368	1.362		
C_2-F_8	1.353(12)	1.358(56)	1.368	1.353	1.366	1.358	1.355
C_6-F_{12}		1.346(48)			1.351		1.355
$\angle C_6-C_1-C_2$	119.8(20)	117.9(35)	118.5	118.4	116.9	118.4	117.0
$\angle C_1-C_2-C_3$	121.5(21)	122.4(25)	122.7	121.7	123.2	122.5	122.7
$\angle C_2-C_3-C_4$	119.8(25)	119.1(20)	118.4	119.4	118.2	118.4	118.2
$\angle C_3-C_4-C_5$	118.2(24)	119.0(24)	120.0	119.8	120.5	120.4	121.0
$\angle C_4-C_5-C_6$	122.6(17)	119.1(20)	120.8	120.3	119.5	119.9	118.3
$\angle C_5-C_6-C_1$	118.2(20)	122.4(25)	119.8	120.4	121.8	120.4	122.7
$\angle C-O-H$	101.9(39)	96.7(42)	107.1	108.1	106.8		
$\angle C_2-C_1-O$	120.8(40)	121.0(23)	121.3	117.0	122.9		
$\angle C_3-C_2-F_8$	120.3(48)	120.1(23)	120.8	120.0	120.9	118.8	119.0
$\angle C_5-C_6-F_{12}$		118.5(38)			120.3		119.0
$F_8\cdots H_{13}$	2.125(55)	2.054(79)	2.180		2.203		
$O_7\cdots F_8$	2.735(22)	2.715(67)	2.718	2.663	2.732		
$\angle O_7-H_{13}\cdots F_8$	120.8(45)	127.1(51)	113.7		113.0		
$\angle O_2-F_8\cdots H_{13}$	79.0(17)	77.7(33)	81.3		81.4		

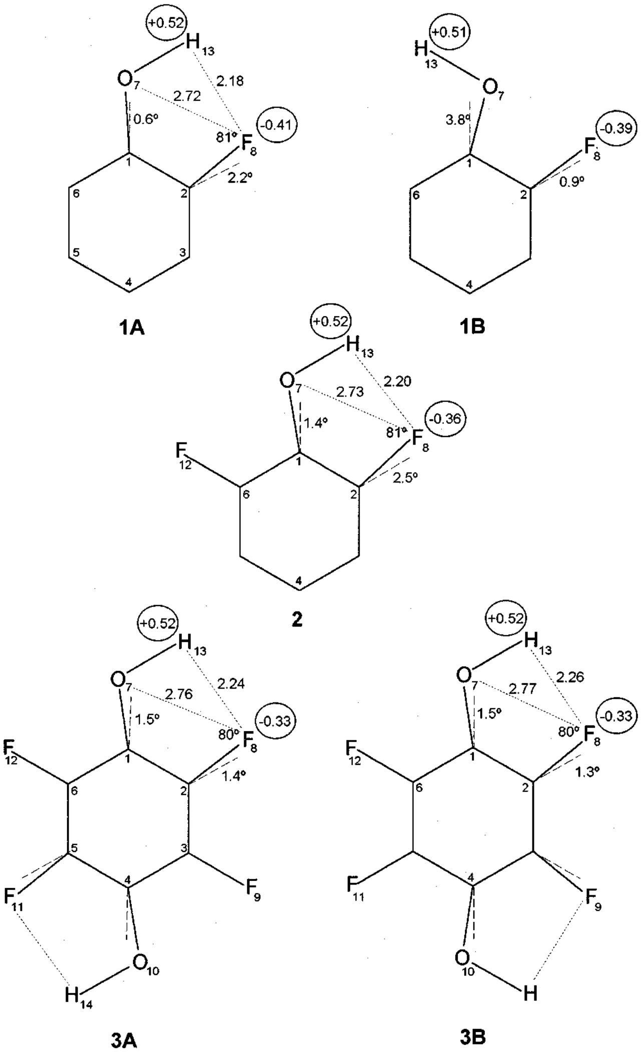
[a] Bond lengths are given in angstroms; angles, in degrees. Calculated geometrical data were obtained at the MP2/6-31G** level. [b] From gas electron diffraction;[11] the bond lengths are r_g parameters.

TABLE 3: Selected Geometrical Parameters[a] of 2,3,5,6-Tetrafluorohydroquinone (3) and 2,3,5,6-Tetrafluorobenzene (6)

parameters	experimental[b]		calculated		
	3A	**3B**	**3A**	**3B**	**6**
C_1-C_2			1.396	1.394	1.389
C_2-C_3			1.390	1.388	1.393
C_3-C_4			1.396	1.394	1.389
C_4-C_5			1.396	1.397	1.389
C_5-C_6			1.390	1.392	1.393
C_6-C_1			1.396	1.397	1.389
$(C-C)_{mean}$	1.392(3)	1.394(3)	1.394	1.394	1.390
$H-O$	0.955(10)	0.952(10)	0.968	0.968	
$C-O$	1.352(10)	1.353(9)	1.362	1.363	
C_2-F_8	1.352(13)	1.350(12)	1.358	1.358	1.348
C_6-F_{12}	1.345(17)	1.343(13)	1.345	1.345	1.348
$\angle C_6-C_1-C_2$	117.1(6)	117.0(5)	117.8	117.8	118.8
$\angle C_1-C_2-C_3$	121.5(3)	121.5(2)	122.4	121.2	120.6
$\angle C_2-C_3-C_4$			119.8	121.2	120.6
$\angle C_3-C_4-C_5$			117.8	117.8	118.8
$\angle C_4-C_5-C_6$			122.4	121.0	120.6
$\angle C_5-C_6-C_1$	121.5(3)	121.5(2)	119.8	121.0	120.6
$\angle C-O-H$	98.6(25)	98.2(24)	107.1	107.3	
$\angle C_2-C_1-O_7$	119.5(13)	119.4(12)	122.6	122.7	
$\angle C_5-C_4-O_{10}$			122.6	119.5	
$\angle C_3-C_2-F_8$	121.7(16)	122.1(17)	120.2	120.7	119.2
$\angle C_5-C_6-F_{12}$	119.2(16)	119.6(9)	120.0	119.5	119.2
$F_8\cdots H_{13}$	2.03(7)	2.02(7)	2.235	2.257	
$O_7\cdots F_8$	2.67(5)	2.66(5)	2.756	2.772	
$\angle O_7-H_{13}\cdots F_8$	123.3(28)	123.8(29)	112.6	112.2	
$\angle C_2-F_8\cdots H_{13}$	79.8(16)	80.2(16)	80.3	79.7	

[a] Calculated at the MP2/6-31G** level. Bond lengths are given in angstroms; angles, in degrees. [b] From gas electron diffraction;[10] the bond lengths are r_g parameters. The data refer to separate refinements assuming the presence of either C_{2v} or C_{2h} model only.

1. Individual Structures and Conformers. *Parents.* The molecular geometries of the parents have been investigated extensively by different experimental and theoretical methods: fluorobenzene (**4**),[35−38] phenol,[16,18,39−43] 1,3-difluorobenzene (**5**),[36,44] hydroquinone,[43,45−47] 1,2,4,5-tetrafluorobenzene (**6**).[48] However, MP2/6-31G** data, to be used in our comparison, were available for phenol[16] and hydroquinone[47] only. Thus, the MP2/6-31G** geometries of **4**−**6** have also been computed in the present study and are given in Tables 2 and 3, respectively.



1A **1B** **2** **3A** **3B**

Figure 1. Numbering of atoms and selected calculated characteristics of intramolecular hydrogen bonding: hydrogen bond length (Å); O···F nonbonded distance (Å); C−F···H(O) nonbonded angle; tilt of C−O and C−F bonds away from the bisectors of the respective ring C−C−C angles; natural charges of the interacting H and F (circled, in atomic units from NBO analysis) obtained from MP2/6-31+G**//MP2/6-31G** calculations.

Among the parents the conformation of hydroquinone is especially interesting, because it may be associated with the conformational properties of **3**. The molecule has two stable planar conformers, differing in the relative orientation of the hydroxy hydrogens. Computational results at various levels of theory favor slightly the C_{2h} conformer (by ca. 0.5 kJ/mol), over C_{2v}.[47]

2-Fluorophenol (1). Previous computations at the Hartree−Fock level indicated two minima on the PES of **1** (Figure 1) with the hydrogen-bonded syn conformer (**1A**) being more stable than the anti form (**1B**).[27,29] The presence of intramolecular HB in **1A**, and the predominance of this conformer in the gaseous phase was supported by IR measurements[24] and a recent gas electron diffraction analysis.[11] Our computations are in agreement with these results. The computed energy difference between **1A** and **1B** is 12.2 kJ/mol at the MP2/6-31+G**//MP2/6-31G** + ZPVE level of theory (cf. Table 1). This is twice the experimentally determined energy difference of 6.8 ± 0.3 kJ/mol based on the torsional frequencies observed in the far-IR spectrum.[24] Data from other sources include a value of ca. 2 kJ/mol from gas electron diffraction[11] and 16.7 kJ/mol from HF/6-31G calculations.[29]

In Table 2 geometrical parameters of **1** obtained from electron diffraction[11] and from the present computations are compiled. The overall patterns appear consistent, apart from the fact that the electron diffraction bond lengths are r_g average parameters while the computed results refer to r_e equilibrium distances.[49] The large experimental errors make the comparison of limited value only. The quantum chemical calculations provide a detailed picture of the endocyclic structural variations in the benzene ring including the C−C bond lengths whereas only their mean value could be extracted from the electron diffraction analysis. This mean value agrees remarkably well with the mean of the computed C−C bond lengths.

For our discussion of the intramolecular HB interaction, the geometrical parameters of the OH and CF_3 groups are especially important. The calculated O−H and C−F bond lengths are larger than the experimental values, the differences somewhat extending beyond the error limits. In view of the vibrational contribution to the electron diffraction r_g values, this is at variance with expectations.[49] Among the bond angles the computed C−O−H angle has the largest deviation from the experimental one, though the experimental error of this parameter is also large. We note that similar deviations between experimental and computed parameters of the hydroxy group were found for phenol[16] as well.

Because of the low population of **1B** in the gas phase, the ab initio computations are the only source of information on the geometrical differences between the syn and anti conformers of **1**. The main differences appear in the C−F bond length and in the $C_2−C_1−O$ and $C_1−C_2−F$ bond angles (cf. Table 2). The longer C−F bond and larger $C_1−C_2−F$ angle in **1A** are well-known effects of intramolecular hydrogen bonding interactions[13−17] while the decrease of the $C_2−C_1−O$ angle in **1B** is consistent with the OH hydrogen turning away from the fluorine and the resulting steric interaction with the adjacent CH hydrogen. We note the rather short $O_7···F_8$ distance in the non-hydrogen-bonded **1B** (Table 2) is accompanied by a 0.9° tilt of fluorine toward the oxygen. This feature is at variance with the expected electrostatic repulsion between the two negatively charged atoms. The situation may be similar to that found in *cis*-1,2-difluoroethylene.[50,51]

2,6-Difluorophenol (2). Due to the symmetric fluorine substitution around the hydroxy group, **2** has one stable conformer with a planar hydrogen-bonded moiety (cf. Figure 1). Comparing the calculated geometrical parameters with the electron diffraction data[11] (Table 2) similar comments can be made to those on 2-fluorophenol. The MP2/6-31G** results hint of a slight quinoidal character of the benzene ring in that two of the CC bonds are slightly shorter than the other four.

2,3,5,6-Tetrafluorohydroquinone (3). Similarly to the parent hydroquinone, **3** has also two stable conformers with C_{2h} (3A) and C_{2v} (3B) symmetry (cf. Figure 1). Both structures are characterized by two equivalent F···H−O hydrogen bonds. The only previous study of the molecular geometry of **3**, an electron diffraction investigation, suggested a mixture of two conformers in the gaseous phase but was inconclusive regarding their relative abundance.[10] Our calculations resulted in **3A** being favored by 1.1 kJ/mol at the MP2/6-31+G**//MP2/6-31G** + ZPVE level (cf. Table 1). Hence, in the gaseous phase at room temperature the two conformers appear with similar populations.

The computed and experimental geometrical parameters of **3** are compared in Table 3. We note, that the electron diffraction data refer to separate refinements assuming the presence of either a C_{2v} or C_{2h} model only.[10] In agreement with the experimental results the calculated geometrical parameters of the two conformers are very similar. The differences in the bond lengths of the two forms are 0.001−0.002 Å. Among the bond angles, the tilt of the C−O bond away from the bisector of the C_6−C_1−C_2 angle as well as that of the C−F_8 and C−F_{12} bonds away from the bisectors of the respective endocyclic angles are essentially the same in the two conformers (cf. Figure 1 and Table 3). Larger differences can be observed only in the deformation of the benzene ring from D_{6h} symmetry, which is an expected consequence of the different relative orientations of the hydroxy hydrogens in the C_{2h} and C_{2v} structures. All these characteristics suggest similar HB strength in the two conformers. A slight difference is indicated by the somewhat smaller F_8···H_{13} distance in **3A** accompanied by the smaller C_1−C_2−F_8 angle as compared to that in **3B** (Table 3).

2. Hydrogen Bonding. The computed geometrical characteristics of the title molecules are consistent with weak intramolecular HB in **1A**, **2**, **3A**, and **3B**. The most important structural features are as follows:

(i) The F_8···H_{13} distances, 2.18, 2.20, 2.24, and 2.26 Å in **1A**, **2**, **3A**, and **3B**, respectively (cf. Figure 1), are shorter than the sum of the van der Waals radii of fluorine and hydrogen, 2.55 Å.[52] Compared with the hydrogen bond length of 1.87(5) Å in hydrogen fluoride dimer,[53] the present results point to rather weak intramolecular HB in the title compounds.

(ii) The O_7···F_8 distances, 2.72, 2.73, 2.76, and 2.77 Å in **1A**, **2**, **3A**, and **3B**, respectively (cf. Figure 1), correspond to the sum of the van der Waals radii of oxygen and fluorine, 2.75 Å.[52]

(iii) The C−O−H bond angles, 107.1°, 106.8°, 107.1°, and 107.3° in **1A**, **2**, **3A**, and **3B**, respectively (cf. Tables 2 and 3), are smaller than those in the respective parents calculated at the same level of theory (108.4° in phenol,[16] 108.3° and 108.4° in **7A** and **7B**[47]). In **1B**, lacking HB interaction, this angle is 108.1° (cf. Table 2).

(iv) The tilt of the C_2−F_8 bonds away from the bisector of the C_1−C_2−C_3 angle toward the OH group was calculated to be 2.2°, 2.5°, 1.4°, and 1.3° for **1A**, **2**, **3A**, and **3B**, respectively (cf. Figure 1).

(v) Due to the repulsion between the hydroxy hydrogen and the adjacent CH hydrogen, the tilt of the C−O bond away from the bisector of the C_6−C_1−C_2 bond angle toward the other side of the ring is a well-known feature of hydroxybenzene derivatives.[40] At the MP2/6-31G** level this tilt is 2.9° in phenol[16] and 3.1° in both conformers of hydroquinone.[47] The reduced tilt of the C−O bonds in the title molecules can be ascribed to attractive HB interactions (cf. Figure 1).

(vi) The C−F bonds with fluorine involved in HB are lengthened by 0.01 Å in the title molecules as compared with the respective parents (cf. Tables 2 and 3). At the same time the C−F bonds with fluorine not involved in HB are slightly shortened (by 0.003−0.005 Å).

(vii) In agreement with our previous observations on trifluoromethyl derivatives,[15−17] there is very slight lengthening of the O−H bond upon HB with fluorine in all the title molecules.

The present investigation dealt with systems in which the HB is part of a five-membered ring. Comparing the present results with those on HB in a six-membered arrangement,[15−17] the main differences appear in the length of the hydrogen bond and in the nonbonded C−F···H(O) angle. The computed F···H(O) distance was 1.98 Å in 2-(trifluoromethyl)phenol,[16] 1.85 Å in 2-(trifluoromethyl)resorcin, and 1.97 Å in 2,6-bis(trifluoromethyl)phenol.[17] The hydrogen bonds in the title molecules are by 0.2−0.4 Å longer (cf. Figure 1) than in the (trifluoromethyl)phenol molecules, implying a weaker interaction in the fluorophenol derivatives. This is also reflected in the variation of the nonbonded C−F···H(O) angles calculated to be about 80° in **1A**, **2**, **3A**, and **3B**. The respective angle in 2-(trifluoromethyl)phenol and 2,6-bis(trifluoromethyl)phenol was calculated to be 93°,[16,17] while that in 2-(trifluoromethyl)resorcin was 100°.[17] There is a greater strain in the five-member hydrogen-bonded rings than in the six-member ones. The most relaxed arrangement of the hydrogen bond is expected when it is close to the direction of one of the three fluorine lone pairs.[54] The analogous angle H−F···H is 110° in the hydrogen fluoride dimer.[53]

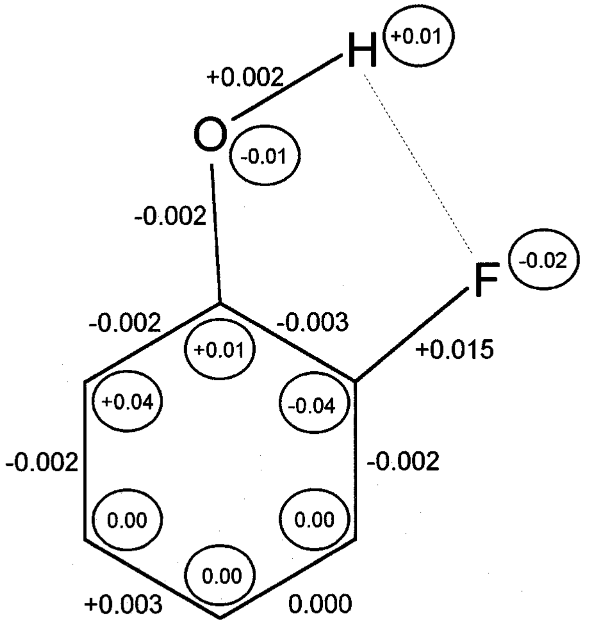


Figure 2. Changes in natural charges (circled, in atomic units from NBO analysis) and bond lengths (in angstroms) in **1A** with respect to **1B**, as obtained from MP2/6-31+G**//MP2/6-31G** calculations.

In our earlier studies of (trifluoromethyl)phenol derivatives, a considerable shortening of the C−C(F_3) bond was observed as compared with the parents.[15−17] This and the other geometrical characteristics of the OH group and the benzene ring could be described by a model of quinoidal resonance structures,[15−17] in agreement with the notion of resonance-assisted hydrogen bonding.[19,20] Rather than a shortening of C−C(F_3) bonds in (trifluoromethyl)phenols, there is a lengthening of C−F bonds in the fluorophenol derivatives, and the quinoidal resonance structures can hardly be applied to these systems.

The effects of HB as separable from through-bond electronic interactions of the ortho-positioned fluorine and the OH group can be investigated by comparing the two conformers of **1**. Assuming similar steric interactions between the fluorine and the OH group in **1A** and **1B**, the differences in the charges obtained by natural bond orbital (NBO) analysis[55] as well as those in the geometrical parameters may reflect the effect of HB on the electron density distribution of the molecule. In Figure 2 the changes in the natural charges and in the bond lengths of **1A** with respect to **1B** are depicted from MP2/6-31+G**//MP2/6-31G** calculations. The charge distribution of **1A** indicates weak polarization upon HB at the bonds involved in the hydrogen-bonded five-membered ring. This is in agreement with the strong electrostatic character of the F···H interaction, enhancing also the ionic character of the neighboring bonds. We note that the electron density is increased at both the carbon and fluorine of the CF group upon hydrogen bond formation. The largest decrease of electron density is observed on C_6. The charges of the other ring carbons (C_3, C_4, and C_5) are not altered by the above intramolecular interaction. Of the geometrical parameters, only the C−F bond length shows a marked increase as a result of HB. Changes of the O−H and C−O bonds are of the magnitude of those of the endocyclic bonds. It is noteworthy that the C−C bonds close to the HB region somewhat shorten while the farthest C_4-C_5 bond lengthens.

The effect of increasing fluorination on the HB interaction can be deduced from the calculated natural charges of the interacting H and F in the title molecules (Figure 1). While additional fluorine substitution had no substantial effect on the charge of the hydroxy hydrogen, a consistent electron density decrease from **1** to **3** can be observed on the fluorine in agreement with the appearance of additional highly electronegative atoms in **2** and **3**. The change in the F···H electrostatic interaction is also manifested in the marginal but consistent increase of the hydrogen bond length in the order of **1A** < **2** < **3A** < **3B**,[56] supporting an opposite order of HB strength. We note, that there is no substantial difference in the fluorine natural charge of **3A** and **3B**. Here the geometrical characteristics of the two conformers may be responsible for the difference in the hydrogen bond length.

Conclusions

1. The computations indicate weak intramolecular F···H hydrogen bonding in 2-fluorophenol, 2,6-difluorophenol, and 2,3,5,6-tetrafluorohydroquinone.

2. Characteristic changes in the rest of the molecule upon HB are manifested in the lengthening of the C−F bond involved in the interaction by 0.01 Å, in the lengthening of the O−H bond by 0.003 Å, in the decrease of the C−O−H bond angle by 1°, and in the tilt of the C−F and C−O bonds toward each other as compared with the parent molecules.

3. The F···H hydrogen bonding interaction increases the ionic character of the bonds involved in the hydrogen-bonded five-membered ring region.

4. The nonbonded F···H(O) and F···O distances (F involved in hydrogen bonding) increase in the following order: 2-fluorophenol < 2,6-difluorophenol < 2,3,5,6-tetrafluorohydroquinone (C_{2h}) < 2,3,5,6-tetrafluorohydroquinone (C_{2v}), indicating a gradual decrease of hydrogen bond strength in this order.

Acknowledgment. This research has been supported by the Hungarian Scientific Research Foundation (OTKA No. T030053).

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(56) Geometry optimizations of **1A** and **2** at the MP2/6-31+G** level of theory supported the MP2/6-31G** results for the relative order of the $F_8 \cdots H_{13}$ distances. From the MP2/6-31+G** calculations the $F_8 \cdots H_{13}$ distances are 2.225 and 2.240 Å for **1A** and **2**, respectively.