JOC Article

Molecular Geometry as a Source of Chemical Information. 3. How H-Bonding Affects Aromaticity of the Ring in the Case of Phenol and *p*-Nitrophenol Complexes: A B3LYP/6-311+G** Study[†]

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Molecular geometries of phenol and *p*-nitrophenol (ArOH) interacting with fluoride were optimized at the B3LYP/6-311+G** level of theory taking as constraints the planarity of the systems and the linearity of the $O\cdots H\cdots F$ moiety. For *p*-nitrophenol complexes, the substituent effect stabilization energy (SESE) was computed, and for all systems aromaticity indices, HOMA, and out-of-plane components of NICS(1) and $NICS(1)_{zz}$ were calculated. SESE values depend strongly on the $O\cdots F$ distance, the same as both aromaticity indices. Variation in HOMA values for the studied $ArOH\cdots F^-$ complexes is within the range of 0.55 to ~ 1.0 and for $NICS(1)_{zz}$ between -12 and -26 ppm. It was also found that a decrease in aromaticity is well correlated with the variations of C−O bond length.

Introduction

Despite the lack of a unique and precise definition[1−4] the concept of aromaticity belongs to the most frequently used in organic chemistry and related fields. According to ISI,[5] in the period of 1996−2003, about 20 papers were published every day in which the terms aromatic or aromaticity appeared as a key word, either in the title or in the abstract.

The terms *aromaticity* and/or *aromatic* are associated with a cyclic π-electron delocalization and then, as a consequence, are associated with a set of particular properties. The following properties are the most important and often accepted as the criteria of aromaticity:[1,2,6,7](a) an increase of stability measured by resonance energy[8] (actually defined in a more refined way and named as aromatic stabilization energy);[2,9,10] (b) intermediate bond lengths between the values typical of single and double bonds—associated with small bond length alternation;[11−14] (c) π-electron ring current formation when the molecule is exposed to and external magnetic field[15,16] (this is associated with an anisotropy of magnetic susceptibility, an increase of exaltation of magnetic susceptibility, and typical ^{1}H NMR chemical shifts;[16−18] magnetism-based index NICS[19] (nucleus independent chemical shift) and particularly the *z*-component of the shielding tensor $NICS(1)_{zz}$ shows well this property[20,21]); and (d) typical reactivity in which the π-electron delocalization is retained, an important criterion often applied by organic chemists.[22] The substitution is more preferred than the addition for typical aromatics.[23]

The most rigorous definition of aromaticity requires the fulfillment of all the above-mentioned criteria,[6] and

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[†] In memory of our friend Professor Piotr K. Wrona (1949−2004).

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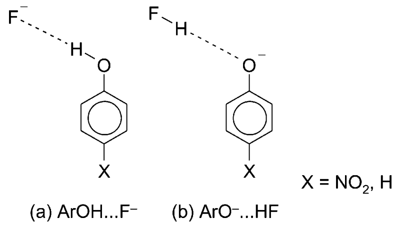
any systems which do not follow all of them are defined as only partially aromatic.

Aromaticity is associated with geometry in two ways: not only may it be described by geometry-based indices[7] but also a given π-electron fragment in some greater π-electron system may be affected dramatically by its molecular (structural) environment.[4,24−26] The most spectacular finding is associated with the realization of the Clar sextet concept.[27] In polycyclic benzenoid hydrocarbons, the "empty" rings or those possessing a double bond exhibit really very low values of aromaticity indices such as NICS[19] (nucleus independent chemical shift) or HOMA[14,25] (harmonic oscillator model of aromaticity).

A much weaker effect on aromaticity is caused by intermolecular interactions. Katritzky has shown[28] that aromaticity of most heterocycles and some carbocycles (e.g., azulene) increases with an increase of polarity of the medium. Another clear illustration of the dependence of aromaticity on the intermolecular interactions is related to the changes of HOMA values for *p*-nitrosophenolate anion in crystalline state of hexahydrated salt of magnesium (HOMA = 0.63) and trihydrated salt of sodium (HOMA = 0.46).[14] The difference is a result of a quite different net of H-bonding of these two salts. In the case of the hexahydrated salt, both functional groups, $-NO$ and $-O^-$, are almost equally hydrated, with almost the same number of close contacts with the H atom of water molecules: the oxygen atom in the $-NO$ group has two close contacts with the H atoms of water molecules, whereas the $-O^-$ group has three such contacts. The picture for the trihydrated salt is different—mostly the nitroso group is hydrated and its oxygen atom has three close contacts with the H atoms whereas the $-O^-$ group has only one such contact. As a result, in the first case the less quinoid-like structure is induced than in the case of sodium salt, when the intramolecular charge transfer from the $-O^-$ group toward the $-NO$ group is enhanced by the presence of more H-bonds to the $-NO$ group. This results in lower aromaticity of the ring in the case of sodium salt. Interestingly, in the case of the Crick−Watson pairs of bases in DNA and RNA it was observed that aromaticity of pyrimidine bases increases in the pair bound by intermolecular H-bond in comparison with the isolated bases.[29]

The above examples encouraged us to undertake a systematic study in order to analyze the title problem. As model systems we have chosen phenol and *p*-nitrophenol molecules complexed via H-bond with bases. The substantial intramolecular charge transfer between the nitro and hydroxyl groups results from electronic properties of these substituents. The appropriate substituent constants for the $-NO_2$ group are $\sigma_p = 0.78$[30] and $\sigma_p^- = 1.27$; assuming strong positive charge on the nitrogen of the $-NO_2$ group in *para* position, for $-OH$ $\sigma_p^+ = -0.92$, for $-O^-$ $\sigma_p^+ = -2.3$.[31] In the case of phenol, no such effect appears, and therefore, it is taken for comparisons. In the process of H-bond formation the electron-donating ability of the hydroxyl group increases, since the process of the proton removal from the oxygen atom and its approaching the base is associated with an increase of a negative charge at the oxygen atom. To study this effect, we have applied ab initio modeling for a system in which a fluoride is approaching along the line of the O−H bond of phenol and *p*-nitrophenol, leading to spectacular changes in molecular geometries and for which the C−O bond length was assumed to be a convenient approximate measure of H-bond strength.[32]

SCHEME 1. Structural Scheme of the Computational Model: (a) Fluoride Approaches the Oxygen Atom in the Hydroxyl Group and (b) Hydrofluoric Acid Approaches the Oxygen Atom in the Phenolate Anion



Methodology

Ab initio modeling was applied to the phenol- and *p*-nitrophenol−fluoride complexes: the fluoride is approaching the molecule of *p*-nitrophenol/phenol along the line of a prolongation of O−H bond direction, as shown in Scheme 1.

Becke-style three-parameter density functional theory using the Lee−Yang−Parr correlation functional[33] and 6-311+G** basis set (B3LYP/6-311+G**) were used to optimize the molecules' and complexes' geometries.

Partial geometry optimization (since O···F distance is controlled and linearity of O···H···F is assumed) was

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performed in all cases of complexes: ArOH with F^- and $ArO^- \cdots HF$. Full optimization at the same level of theory for *p*-nitrophenol, *p*-nitrophenolate anion, phenol, and phenolate anion resulted in planar structures so during optimizations of complexes all the dihedral angles were frozen. All calculations were performed using the Gaussian98 series of programs.[34]

Geometry parameters of the ring (CC bond lengths) are used to estimate aromaticity index HOMA,[12,14] which reads

$$\mathrm{HOMA} = 1 - \frac{\alpha}{n}\sum(R_{\mathrm{opt}} - R_{\mathrm{i}})^2 \qquad (1)$$

where n is the number of bonds taken into the summation; α is a normalization constant (for CC bonds $\alpha = 257.7$) fixed to give HOMA = 0 for a model nonaromatic system, e.g., Kekulé structure of benzene[11] and HOMA = 1 for the system with all bonds equal to the optimal value R_{opt} assumed to be realized for full aromatic systems (for CC bonds R_{opt} is equal to 1.388 Å); R_{i} stands for a running bond length.

Nucleus independent chemical shifts estimated in the center of the ring—NICS[19] and 1 Å above—NICS(1)[35] as well as NICS$(1)_{zz}$[21] were calculated at the B3LYP/6-311+G** level of theory using the GIAO method.

The factor analyses of the data were done using SYSTAT 10 for Windows.[36]

Results and Discussion

Two systems of H-bond complexes are considered: $[PhO \cdots H \cdots F]^-$ and $[p\text{-}NO_2PhO \cdots H \cdots F]^-$, each in two situations. One of them deals with a stronger interaction (Scheme 1a) and the other with a weaker one (Scheme 1b).

The difference between these two cases is associated with a different behavior of proton while decreasing the O···F distance. In the case presented in Scheme 1a, at a particular distance the proton transfers from oxygen to fluoride. This means that there are two potential wells. It is not observed in the case shown in Scheme 1b as there is only one minimum for proton position. It may be concluded from this observation that when the HF molecule is approaching the ArO^- the proton transfer is not observed. It was found that the O···F distance for proton transfer for the *p*-nitrophenol complex is longer than for phenol, with values equal to 2.601 and 2.503 Å, respectively. The difference is due to a substantial difference in the interactions in *p*-nitrophenol and phenol complexes with fluoride. In the first case, a strong through-resonance effect between the $-NO_2$ and $-OH$ groups appears. Approaching the fluoride causes a weaker O−H bond, which in turn assists a stronger charge transfer from oxygen to the nitro group. In consequence, a less negative charge at oxygen in the −OH group allows one to transfer proton at a longer O···F distance. There are no such interactions in the case of the $PhOH \cdots F^-$ complex; hence, the O···F distance should be shorter to induce proton transfer from hydroxyl group to fluoride accompanied with HF formation.

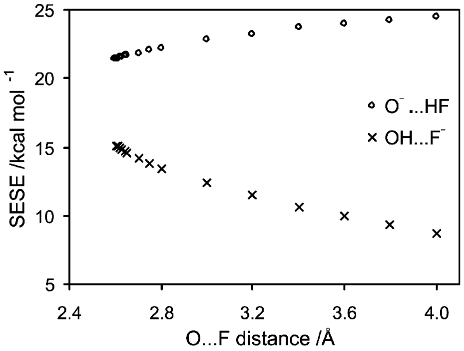
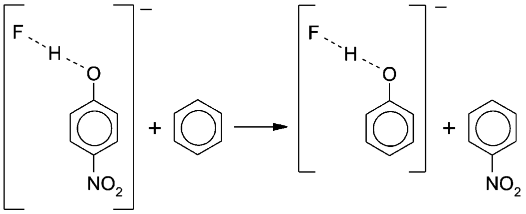
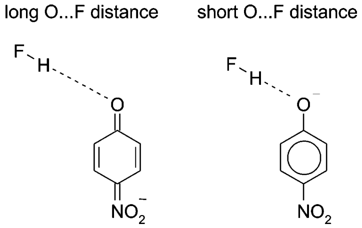


FIGURE 1. Scatter plots of SESE values for two kinds of H-bonds (Scheme 1) against the O···F distance.

SCHEME 2. Schematic Reaction Used for Calculation of SESE for the *p*-NO_2 Substituent



SCHEME 3. Scheme of Canonical Structures Associated with the Geometry Changes in the Ring Due to H-bond Formation (Scheme 1b) for Extremal Values of O...F Distances.



The substituent effect is well described by a substituent effect stabilization energy (hereafter abbreviated as SESE),[37] which is defined as a difference in energy between the products and the substrates in the appropriate homodesmotic[38] reaction. SESE for nitro complexes were calculated according to the reaction in Scheme 2.

We observe that the range of variation of SESE values for *p*-nitrophenol···F^- complexes (~6 kcal/mol) is greater than for *p*-nitrophenolate···HF complexes (~3 kcal/mol) as shown in Tables S1 and S2 (Supporting Information). Figure 1 shows how SESE for these two systems (Scheme 1) varies with changes in the O···F distance.

In the case of $p\text{-}NO_2PhOH \cdots F^-$ interactions (Scheme 1a), the shortening of the O···F distance is associated with an increase of the negative charge at oxygen atom leading to a stronger weight of the quinoid-like structure. Opposite to this, when HF is approaching the oxygen atom (Scheme 1b), the weight of the quinoidic structure decreases, as shown in a simplified Scheme 3.

In all of the above-mentioned cases, the structural consequences on the ring and consequently the changes

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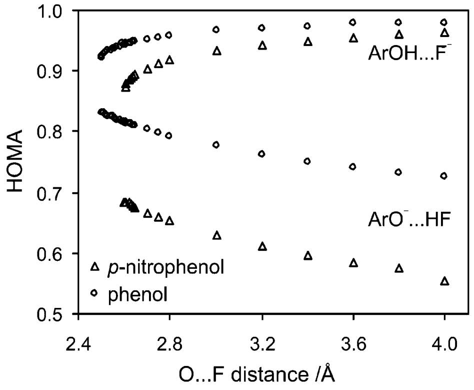

FIGURE 2. Variation of HOMA values for ArOH···F⁻ and ArO⁻···HF interactions for *p*-nitrophenol and phenol complexes.

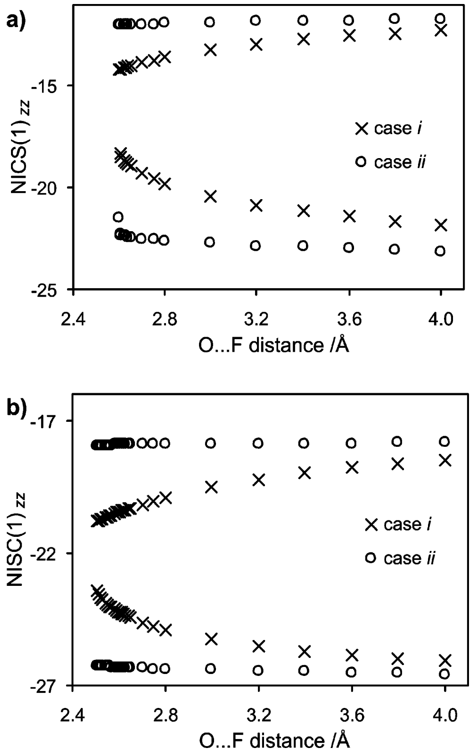

FIGURE 3. Variation of $\mathrm{NICS}(1)_{zz}$ values (calculated with F⁻/HF, case *i*, and without, case *ii*) for ArOH···F⁻ and ArO⁻···HF interactions for (a) *p*-nitrophenol and (b) phenol complexes.

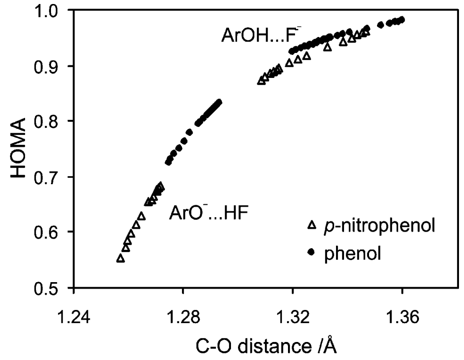

FIGURE 4. Relationships of HOMA values plotted against C−O bond length for *p*-nitrophenol and phenol complexes with fluoride. Two kinds of interactions are taken into account (Scheme 1).

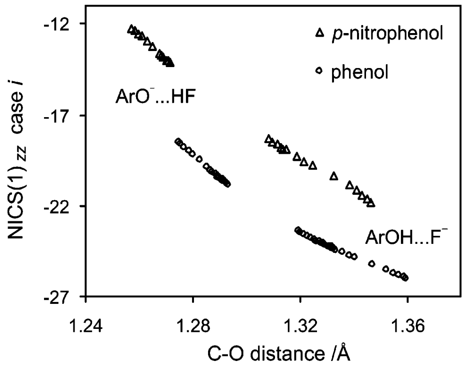

FIGURE 5. Relationships of $\mathrm{NICS}(1)_{zz}$ (case *i*) values plotted against C−O bond length for *p*-nitrophenol and phenol complexes with fluoride. Two kinds of interactions are taken into account (Scheme 1).

in the π-electron delocalization should be found. To study these changes, the geometry-based index HOMA[14] and magnetism-based aromaticity indices $\mathrm{NICS}(1)_{zz}$[21] were used (Tables S1−S4, Supporting Information). Figures 2 and 3 show how these indices vary with the changes in the O···F distance.

Figure 2 shows the variation of HOMA values for both kinds of interactions (Scheme 1). The most remarkable difference in the variation of HOMA values between substituted and unsubstituted phenol complexes appears in the ArO⁻···HF interactions. Aromaticity of the ring in the *p*-nitro derivative is significantly lower than for unsubstituted phenol. This is due to the quinoid-like form induced by a through resonance effect in the *p*-nitro derivative (Scheme 3). This is not observed in the case of stronger H-bonds ArOH···F⁻, since there is not as much negative charge located on oxygen, and consequently, there is a weaker through-resonance effect between the hydroxyl and nitro group, particularly for a longer O···F distance.

Analyses of relationships of $\mathrm{NICS}(1)_{zz}$ on the O···F distance differ in results depending on whether the F⁻/HF is included (case *i*) or not (case *ii*) into the computation of $\mathrm{NICS}(1)_{zz}$ for the same geometry of the aromatic moiety. Figure 3 shows the variation of $\mathrm{NICS}(1)_{zz}$ dependent on O···F distance for *p*-nitrophenol complex (3a) and for phenol complex (3b). The most important finding is that if the computations of $\mathrm{NICS}(1)_{zz}$ are carried out taking into account counterion F⁻ (Scheme 1a) and HF (Scheme 1b), then the variation in $\mathrm{NICS}(1)_{zz}$ values is substantial. If the $\mathrm{NICS}(1)_{zz}$ values are computed for the same geometry of the ring, but for ArOH and ArO⁻ only, then the variation of $\mathrm{NICS}(1)_{zz}$ values is negligible. The picture for NICS(1) and NICS is qualitatively the same as for $\mathrm{NICS}(1)_{zz}$; thus, it is not discussed here.

Very recently, it has been shown[32] that the C−O bond length in phenols may be used as a reliable measure of the strength of H-bond in complexes with bases. Figures 4 and 5 show that aromaticity indices HOMA and $\mathrm{NICS}(1)_{zz}$ (case *i*) correlate nicely in a monotonic way with C−O bond length in both phenol and *p*-nitrophenol complexes with fluoride. It should be noted here that both

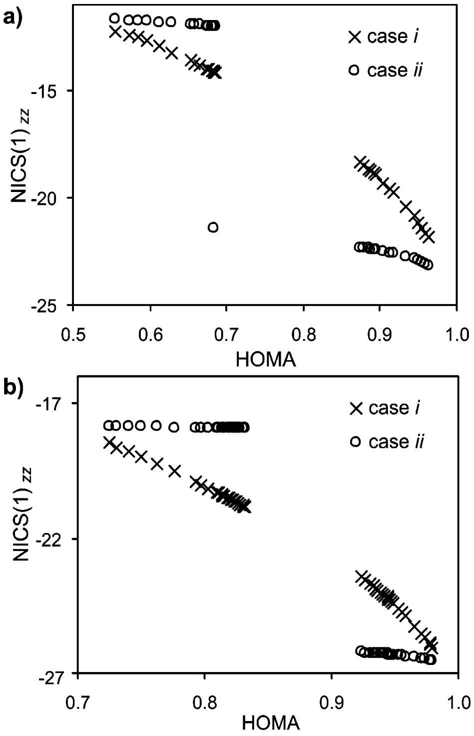

FIGURE 6. Relationships between NICS(1)$_{zz}$ and HOMA for (a) *p*-nitrophenol and (b) phenol complexes. Two kinds of interactions (Scheme 1) were considered.

cases of Scheme 1 for H-bonding are taken into account in Figures 4 and 5.

In both cases, the increase of H-bond strength is accompanied with a substantial change of aromaticity. The shortening of C−O bond causes a decrease of π-electron delocalization. It is in line with an earlier observation[39] that if the group attached to the ring is linked by a bond with an increasing order, aromaticity of the ring decreases. For ArOH···F$^-$ interactions, when $-$C$_{Ar}$OH is a proton-donating group, the shorter is C−O bond length, the stronger is H-bonding. Opposite that, for ArO$^-$···HF interactions, when $-$C$_{Ar}$O$^-$ is a proton-accepting system, the shorter the C−O bond, the weaker the H-bond.

Comparison of the changes for all descriptors allows us to discuss the problem of a statistical dimensionality of aromaticity—the point of a vivid dispute in the past decades.[9,25,40] Figures 6−8 present mutual relationships between SESE, HOMA, and NICS(1)$_{zz}$.

The NICS(1)$_{zz}$ values for the case *i* exhibit a relatively strong variation for both phenol and *p*-nitrophenol complexes. The observed trends are in line with those found for HOMA values as shown in Figure 6.

Again, as observed for the dependence of NICS(1)$_{zz}$ on the O···F distance, the presence of F$^-$/HF in computation of NICS(1)$_{zz}$ (case *i*) leads to dramatically greater changes than when they are absent. HOMA does not depend on this aspect. This finding rises up a problem how strongly NICS(1)$_{zz}$, which is to describe the π-electron delocalization in the ring, may depend on side effect as, e.g., the substituent. It seems that applying NICS(1)$_{zz}$ instead of NICS and NICS(1) allow us to avoid a bias due to the substituent effect.[41] However, it is worth mentioning that only the NICS(1)$_{zz}$ values computed with inclusion of the F$^-$/HF give the picture alike that for HOMA. Contrary to this, the changes for case *ii* are negligible.

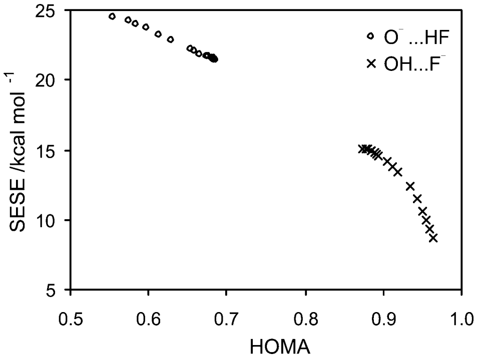

FIGURE 7. Relationships between SESE and HOMA for *p*-nitrophenol. Two kinds of interactions (Scheme 1) were taken into account.

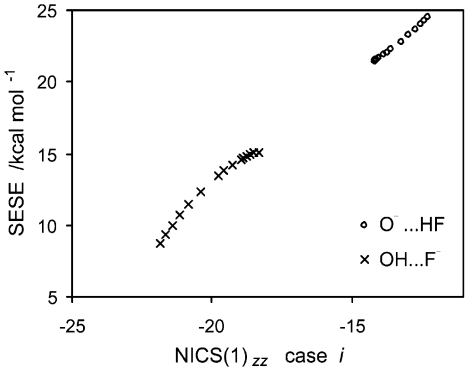

FIGURE 8. Relationships between SESE and NICS (case *i*) for *p*-nitrophenol. Two kinds of interactions (Scheme 1) were taken into account.

The dependence of HOMA on SESE for both cases (Scheme 1) for *p*-nitrophenol complexes is monotonic (Figure 7). However, for the higher values of SESE, i.e., for O$^-$···HF interactions, HOMA values are lower and practically linear with SESE. This is understandable. The $-$O$^-$ interacts strongly through the ring with the nitro group, and the quinoid-like structure is formed which is definitely less aromatic than in the case of OH···F$^-$ interactions, where oxygen is a much weaker electron donor. In the latter case, linearity is broken. The increase of HOMA is associated with a decrease of SESE. The same picture is observed for the SESE vs NICS(1)$_{zz}$ plot, as shown in Figure 8.

Geometric parameters of the ring, bond lengths R_i (i = 1, ..., 6) and bond angles α_i (i = 1, ..., 6) for [PhO···H···F]$^-$ and [p-NO$_2$PhO···H···F]$^-$ systems were the subject of factor analysis (Table 1). In cases when only R_i or only α_i was taken into account, we obtained

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TABLE 1. Factor Analysis Data for $[PhO\cdots H\cdots F]^-$ and [*p*-$NO_2PhO\cdots H\cdots F]^-$ Systems: Percentage of Total Variance Explained by Main Factors

system	$[PhO\cdots H\cdots F]^-$	$[NO_2-PhO\cdots H\cdots F]^-$	$[PhO\cdots H\cdots F]^-$	$[NO_2-PhO\cdots H\cdots F]^-$
variable	R_i	R_i	α_i	α_i
% of total variance explained	93.3	99.6	97.4	98.9

mostly one main factor. This means that the changes in geometry of the ring are concerted for a given kind of H-bond interactions. Moreover, both main factors are linearly correlated with C−O bond lengths with the correlation coefficients over 0.999.

Conclusions

The most important conclusion is that aromaticity of the ring of *p*-nitrophenol and phenol complexes with fluoride depends monotonically on the strength of the H-bond. The overall effect of changes is substantial: HOMA ranges in ∼0.45 units and $NICS(1)_{zz}$ in ∼14 ppm and both variations depend strongly on the substituent effect. The ranges for HOMA for phenol complexes is ∼0.25 whereas for *p*-nitrophenol is ∼0.4 (Figure 4). Like those for $NICS(1)_{zz}$, the ranges are ∼8 and ∼10 ppm for phenol and *p*-nitrophenol complexes, respectively (Figure 5).

Computations of $NICS(1)_{zz}$ for $ArOH\cdots F^-$ and $ArO^-\cdots HF$ complexes lead to completely different values dependent on whether the distant fluoride ion or hydrofluoride molecule is taken into account in computations or not. In both cases, the same geometry of the ring was considered. In the first case, variations of $NICS(1)_{zz}$ and HOMA are monotonically equivalent; in another case, variation in $NICS(1)_{zz}$ values is almost nil.

Factor analyses have shown that the changes in geometry due to the H-bonding are concerted, and main factors correlate excellently with H-bond strength described by C−O bond length.

Substituent effect stabilization energy SESE for phenol substituted in the para position with the $-NO_2$ group is enormous; it ranges from ∼8 kcal/mol for the $OH\cdots F^-$ interaction up to ∼25 kcal/mol for $O^-\cdots HF$. Note that homodesmotic ASE value (aromatic stabilization energy) for benzene itself is equal to 20.3[42] or 23.9 kcal/mol.[43]

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Supporting Information Available: Aromaticity indices, SESE values, computed total energies, and C−O bond length varying with O···F distance for *p*-nitrophenol and phenol complexes. Details concerning computations, schematic input files and the Cartesian coordinates of optimized complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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