

Hydroxyl group as a substituent with varying electronic properties: Effect of strength of H-bonding on charge density changes in Ph–OH...F⁻ complexes

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Abstract Due to gradual and controlled changes of interatomic distances between heavy atoms in OH...F⁻ of C₆H₅OH...F⁻ systems it was possible to study the electronic structure evolution. Computation at B3LYP/6-311+G(d,p) level of theory was performed for this purpose. Changes in charges at atoms and characteristics at bond critical points (BCPs) of the H-bond region and also in distant parts of the systems were investigated by means of natural bond orbitals (NBO) and atoms in molecules (AIM) analyses. It is shown that at the border line between partially covalent and non-covalent H-bonding (Espinosa et al. in J Chem Phys 117:5529, 2002; Grabowski et al. in J Phys Chem B 110:6444, 2006) with the H...F interatomic distance ~1.8 Å the hydrogen atom has the most positive charge. In addition, the change in the atomic charge values in the interacting region affects the

phenyl ring properties. The decrease of the sum of atomic charges as well as of the aromaticity was noticed when the OH...F distance is shortened.

Keywords AIM · Electronic properties · Intermolecular hydrogen bond · NBO

Introduction

Electronic properties of substituents are described most frequently by means of the Hammett constants, σ_p , or their modifications (for a general idea see recent reviews, e.g.: Krygowski and Stepień [1] and Exner and Bohm [2]). For current compilations of numerical data see Hansch et al. [3] and Shorter [4, 5]. It is well known that if $\sigma(X) > 0$ then the substituent X is electron attracting, whereas $\sigma(X) < 0$ characterizes electron donating X. However, it is also well known that substituent effects depend on the environment [3, 6–8] and the kind of reaction [1, 2], in which they are investigated. Hence there appear plenty of scales of numerical characteristics of substituent effects.

It was shown very recently that the components of H-bond, the proton donating and proton accepting groups, A–H and B, respectively, may be considered as substituents which, as a result of H-bond formation, change their group electronegativities, as it was presented for H-bonded complexes of F⁻/HF with phenol/phenolate [9] and anilinium/aniline/anilide systems [10].

On the other hand, there is a large number of descriptors describing H-bonding based on its strength, structural parameters and electronic characteristics. It is claimed in the frame of resonance assisted hydrogen bonding (RAHB) [11] and similar concepts [12, 13] that as a result of H-bond formation, there is a transfer of electron charge from one to

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another component of the H-bond. There is a long literature debate discussing such issues [14–18]. Recently, the charge transfer from the proton donating, (AH), and proton accepting, (B), groups in the intramolecular H-bonding was considered in terms of their electronic properties quantified by means of the Hammett substituent constants [19].

Following the above-discussed H-bonding properties a new question arises, namely how the OH group changes its electronic properties as a result of interaction between hydroxyl group in phenol and the approaching fluoride. The procedure of approaching F^- to the proton donating groups, turned out to be very successful in investigation of the dependence of long-distance changes in the structure and aromaticity of the ring on the strength of H-bonding [20–23]. The main aim of the present study is a detailed analysis of the effect of strength of H-bonding on charge density changes in the $Ph-OH...F^-$ complexes. The combination of electronic structure analyses methods, such as atoms in molecules (AIM) [24] and natural bond orbitals (NBO) [25], was applied to give the answer to the question.

Computational details

The geometry of the studied complexes was minimized on the basis of potential energy surface (PES) obtained from density functional theory (DFT) [26, 27]. The hybrid functional of Becke [28, 29] with Lee, Yang and Parr gradient correction [30] B3LYP, was applied. The triple-zeta split-valence basis set, denoted as 6-311+G(d,p) according to Pople's nomenclature [31] was used to provide expansion of the Kohn-Sham orbitals and describe the geometric and electronic structure parameters. A series of complexes were prepared assuming a linearity of the hydrogen bond. The studied structures were calculated as a result of the energy minimization for the fixed distances between heavy atoms involved in the intermolecular H-bonding and the geometry optimization of the remaining internal degrees of freedom. The maximum distance between O and F atoms involved in H-bond formation (see Scheme 1) was set initially to 4.0 Å and it was shortened, using 0.2 Å, 0.1 Å, 0.05 Å and 0.005 Å decrements, to the distance before which the proton transfers from phenol to F^- occurred. This shortest distance between the heavy atoms of the H-bond, in the $Ph-OH...F^-$ complexes, was found to be 2.504 Å. Harmonic frequencies were calculated to confirm that the structures of the studied complexes correspond to the minima on the PES. Only one negative frequency was found for the obtained complexes, indicating the proper route of the proton on the path realized by H-bonding of the system under consideration. Interaction energy, according to the supermolecular approach with

consideration of the basis set superposition error [32] (BSSE), was calculated as follows:

$$E_{\text{int}} = E_{A...B}(\text{basis}_{A...B}; \text{opt}_{A...B}) - E_A(\text{basis}_{A...B}; \text{opt}_{A...B}) - E_B(\text{basis}_{A...B}; \text{opt}_{A...B}), \quad (1)$$

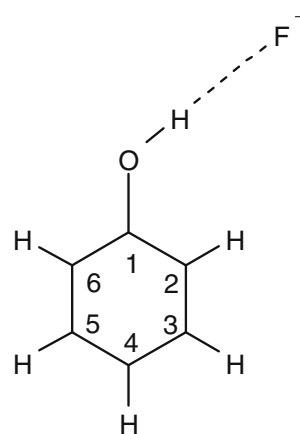
where $E_A(\text{basis}_{A...B}; \text{opt}_{A...B})$ means that the energy of molecule A, E_A , is calculated using internal coordinates of the A and B molecules, $\text{basis}_{A...B}$ (i.e., a ghost basis set at the B molecule is included), and for their geometry obtained during the optimization procedure of the A...B complex, $\text{opt}_{A...B}$. The other terms in Eq. 1 should be understood in the same way.

Subsequently, the natural bond orbitals method [25], NBO 5.G [33], was applied to calculate atomic charges and to evaluate natural bond order, and its ionic and covalent contributions, for the O–H bond involved in intermolecular interaction. According to the NBO analysis, hydrogen bonding corresponds to an intermolecular donor-acceptor interaction between a lone pair (LP) of the Lewis base (the H-bond acceptor, in our case F^-) and the proximate antibonding orbital (σ^*) of the Lewis acid (the H-bond donor, in our case O–H). The strength of this interaction, E_{NBO} , may be estimated as:

$$E_{\text{NBO}} = E_{\text{LP} \rightarrow \sigma^*}^{(2)} + E_{\text{steric}}, \quad (2)$$

where $E_{\text{LP} \rightarrow \sigma^*}^{(2)}$ means the second-order stabilization energy $\text{LP}_F \rightarrow \sigma_{\text{O-H}}^*$ interaction and E_{steric} denotes the steric repulsion of LP_F and $\sigma_{\text{O-H}}$ energy.

Subsequently, the wavefunction necessary for further atoms in molecules (AIM) analysis [24, 34] was generated for each of the studied 17 structures. This part of simulations was performed using the Gaussian03 [35] suite of programs. Atoms in molecules (AIM) theory was used to



Scheme 1 Schematic presentation of the studied 17 complexes. The strength and electronic properties of the $-OH...F^-$ intermolecular H-bond are modulated by the F^- anion position

calculate atomic charges as well as the properties of selected critical points. It should be mentioned here that the AIM formalism ought to be applied at the equilibrium geometry so that the standard nomenclature related to bond and ring critical points (BCPs and RCPs) can be used. In our case, we discuss non-equilibrated structures and therefore the electronic and topological properties of the studied complexes cannot be fully related to the terminology of the classical AIM theory. However, to facilitate the discussion, we will label the located critical points as BCPs and RCPs following the convention frequently found in numerous AIM studies of non-equilibrium structures [36–40]. The properties of found BCPs were analyzed on the basis of the electron charge density, ρ , and its Laplacian, $\nabla^2\rho$, as well as kinetic (G_{CP}), potential (V_{CP}) and total energies (H_{CP}) – parameters determining bonding properties [24, 41, 42]. The obtained data provided us with additional information about the nature of chemical bonding present in the investigated complexes. Special attention was devoted to the evolution of properties in the intermolecular hydrogen bond. The properties of the hydrogen bond were examined by application of Popelier's criteria [41, 43]. The AIM analysis was carried out using the AIMPAC package [44].

Results and discussion

Scheme 1 displays the approach of F^- to OH introducing substantial changes in the atomic charge distribution and geometry of the whole system. The closer F^- is to the proton of OH group, the stronger the H-bond. The evolution of selected metric parameters in the studied complexes, OH bond lengthens and the C–O bond shortens, are presented in S1. The hydrogen bond length, $d_{H...F}$, quantifies the strength of the interaction as it was recently shown [9, 45]. Moreover, as shown in Fig. 1, the energy variability of the H-bonding calculated based on the NBO analysis for complexes with a gradual change of the strength of interaction, Eq. 2, is similar to that obtained for 83 experimentally observed (Y–H...O, Y = C, N, O) hydrogen bonds [46].

Let us look at the changes of the atomic charge distribution at atoms in the H-bond region and its closest vicinity. The atomic charges were calculated according to two schemes: NBO and AIM to give a deeper insight into electronic structure changes related to the evolution of the geometric parameters. The scatter plots in Figs. 2 and S2 reflect the dependences of the atomic charges: q_H , q_F , q_O , and the sum of atomic charge at the phenyl ring, Σq_{ph} ; all of them are plotted against the hydrogen bond length changes, $d_{H...F}$. As we can see, the only non-monotonical changes are observed for the charge at the hydrogen atom q_H (Fig. 2). In this case the maximum value of the atomic

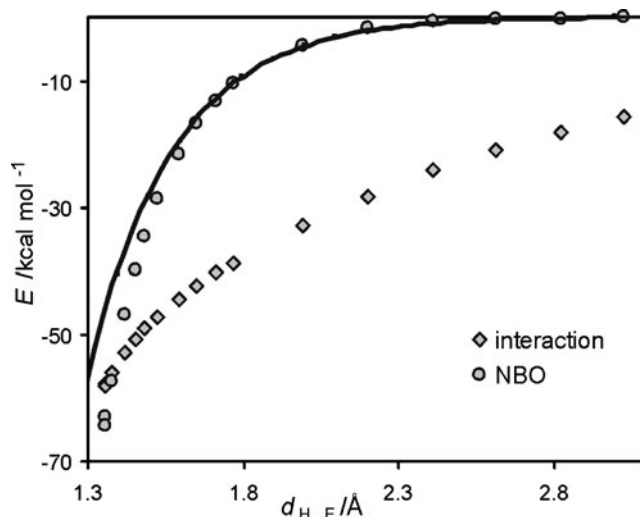


Fig. 1 Relationships between the H-bond energy and its length, $d_{H...F}$, for non-equilibrium, simulated complexes Ph–OH... F^- . Curve represents exponential fitting [46] for 83 experimentally observed (Y–H...O, Y = C, N, O) hydrogen bonds. Diamonds denote the interaction energy, Eq. 1, whereas circles mean the strength of the H-bonding according to the NBO analysis, Eq. 2

charge appears around $d_{H...F} \sim 1.8 \div 1.9$ Å. This result is common to both NBO and AIM analyses. All remainder monotonic dependences (see Fig. S2) could be explained by the influence of geometric parameters on the electronic structure. The approaching fluoride loses a part of its negative charge (Fig. S2a) coming closer to the –OH group. As a result a part of this charge is located at the oxygen atom (Fig. S2b), which with a decrease of $d_{H...F}$ becomes more negative. This withdrawing effect is associated with a substantial shortening of C–O bond (see Fig. S1). Another part of the charge is withdrawn by the phenyl ring, as shown in Fig. S2c.

The changes displayed in Figs. 2, S1 and S2 are associated with more distant consequences observed in the phenyl ring, which as a result of approaching F^- becomes less positively charged. Finally, the decreased positive charge in the ring is associated with a decrease of aromaticity (quantified by HOMA index [47, 48]) of the ring as shown in Fig. 3.

Since hydrogen atoms in the aromatic ring are positively charged, an obvious consequence of the decrease of the positive charge in the ring is associated with the presence of the negative charge at *ortho*, *meta* and *para* carbon atoms, as displayed in Fig. 4. Only in the case of the C1 carbon atom, substituted by the hydroxyl group involved in interaction, an increase of the positive charge (from 0.327 up to 0.358) with an increasing strength of H-bonding is observed. It is shown in Fig. 4 that the approaching fluoride to –OH causes a substantial increase of the negative charge in both *ortho* positions and it is still stronger in *para* position. The observation is in line with the directing rule of the electrophilic substitution [49].

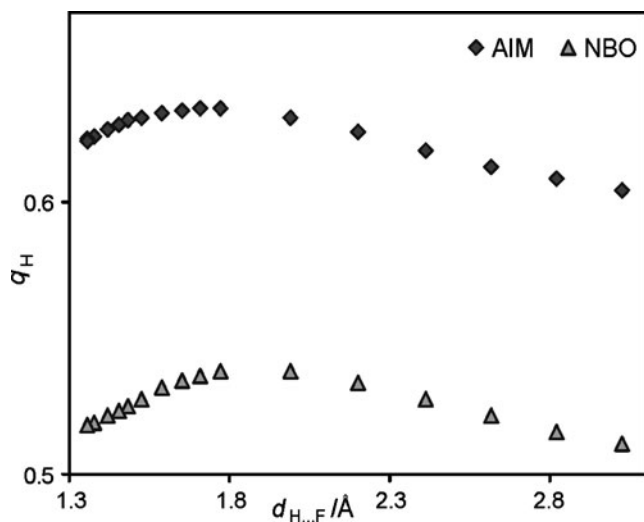


Fig. 2 Dependences of atomic charges at the hydrogen atom involved in the interaction, q_H as a function of the hydrogen bond length, $d_{H...F}$, for Ph–OH...F[−] complexes. Diamonds and triangles denote AIM and NBO results, respectively

All already presented relationships are in line with our knowledge and expectations, but we still have an open question concerning the dependence of q_H in Fig. 2. It is shown that the dependence is not monotonic. In order to answer this question let us look at the OH...F[−] interaction using atoms in molecule theory, (AIM) [24].

The fact that the O–H bond is elongated whereas the C–O and H...F bonds become shorter shows adequate changes in electron density at BCPs of the bonds as a consequence of the interaction strength evolution, see Fig. S3.

The electron density and its Laplacian calculated at BCPs are local properties characterizing the covalent and

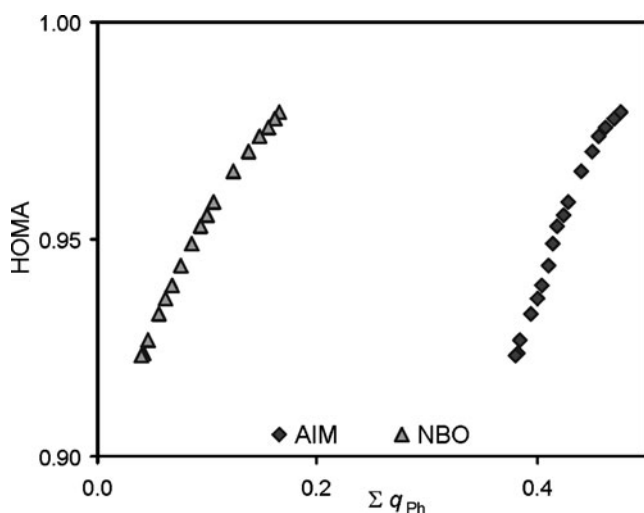


Fig. 3 Dependence of HOMA on the sum of atomic charge at the phenyl ring, Σq_{Ph} , for phenol interacting by H-bond with F[−]. Diamonds and triangles denote AIM and NBO results, respectively

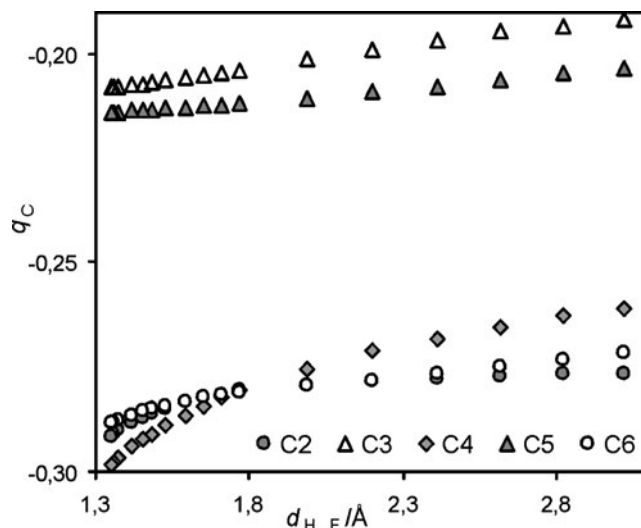


Fig. 4 NBO atomic charges at carbon atoms in the aromatic ring as a function of the H-bond length, $d_{H...F}$, for PhOH...F[−] complexes. Numbering of the carbon atoms according to Scheme 1

hydrogen bonds present in the investigated complexes. A set of criteria for H-bonding was proposed by Koch and Popelier [43] and our further discussion concerning this kind of bonding will be based on them. In order to confirm that the H-bonding exists in the examined complexes it was necessary to find atomic interaction paths at respective BCPs (the first criterion). In the case of the investigated complexes such paths were found in the whole range of the studied distances between atoms involved in the intermolecular H-bonding formation. Subsequently, the Koch and Popelier's criteria [41, 43] were applied to critical points describing the H-bonding presence. The proposed criteria require from the studied systems that the critical points found there fulfill the following conditions: the electron density at the bond critical point (BCP) at the hydrogen bridge should be in the range of 0.002–0.034 a.u. (this is the second Popelier's criterion) while its Laplacian should be between 0.024–0.139 a.u. (this is the third Popelier's criterion). The lower limit of the second criterion is not violated by any of the investigated complexes. The third criterion is fulfilled only for the systems where the separation between heavy atoms of the H-bond is equal to or shorter than 3.4 Å ($d_{H...F} \leq 2.41$ Å). The positive value of the electron density Laplacian indicates that the bonding found between H...F[−] does not have a covalent character. The negative value of the electron density Laplacian indicates a covalent character of the interaction between atoms for C–O and O–H bonds (see Fig. S3b).

Following the classification of covalent and non-covalent H-bonds [50] around H-bond proton–acceptor distance (in our case $d_{H...F}$) equal to 1.8 Å there is a border between partially covalent and non-covalent H-bond. The maximum

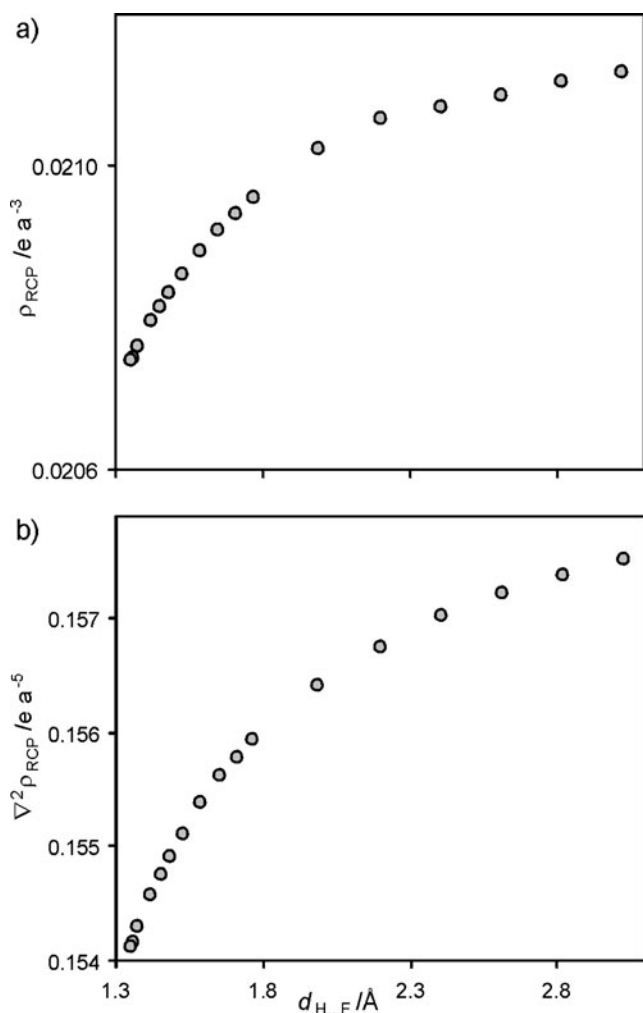


Fig. 5 Changes of (a) the electron density, ρ_{RCP} , and (b) its Laplacian, $\nabla^2\rho_{\text{RCP}}$, at the ring critical point (RCP) of the phenyl ring as a function of the H-bond length, $d_{\text{H}\dots\text{F}}$, for complexes of phenol with F^-

in dependence of q_{H} on $d_{\text{H}\dots\text{F}}$ in Fig. 2 appears just close to this border. Thus the increase of the positive charge at hydrogen atom, q_{H} , for $d_{\text{H}\dots\text{F}}$ between 3.1 Å to ~1.8 Å is associated with an increase of the strength of H...F interaction, that is a shortening of H-bond, which could be characterized as a non-covalent [50] or closed-shell [38] interaction. Discussing other properties related to BCPs, *e.g.*, kinetic electron energy density (G_{CP}), potential electron energy density (V_{CP}) and total electron energy density (H_{CP}), we are able to investigate more deeply the character of H-bonding [38] present in the studied structures. Most of the substantial changes of the above mentioned AIM energetic parameters at BCPs were observed in the case of complexes with H-bond interaction distance shorter than *ca.* 1.9 Å (Fig. S4). The G_{CP} energy is always positive (Fig. S4a) while the V_{CP} (Fig. S4b) is always negative [50]. The G_{CP} energy value at the C–O BCP increases when the F^- anion is coming closer to the bridged hydrogen. The G_{CP} at the O–H

BCP does not change in a clearly monotonic way for complexes with H-bond distance longer than *ca.* 2.0 Å (Fig. S4a). For the H...F BCP we observed that the energy is increased when the distance between atoms involved in the interaction is shorter. Discussing the V_{CP} electron energy density we observe that the energy value is decreased at the C–O and H...F BCPs when the distance between the phenol molecule and F^- is shortened. The reverse variability takes place for the O–H BCP (Fig. S4b). According to some authors, *e.g.*, Cremer et al. [51], when the electron density Laplacian has a positive value and H_{CP} is negative then the present H-bond has a partially covalent character. We encounter a similar situation when discussing our complexes. The total electron energy density (H_{CP}) is positive when the O...F distance ranges between 4.0÷3.2 Å, that is H-bond interatomic distance longer than *ca.* 1.9 Å. While the F^- is coming closer to the bridged hydrogen the H_{CP} energy becomes negative, therefore we can claim [38] that in this region the intermolecular H-bonding has partially covalent character. This may explain why there appears a maximal value of the charge at the hydrogen atom participating in the interaction for $d_{\text{H}\dots\text{F}} \sim 1.8 \div 1.9$ Å (Fig. 2), and the decrease of its positive charge for complexes with the shorter proton-acceptor distance.

Subsequently, the changes of electron density and its Laplacian at ring critical points were calculated for all studied complexes. The data presented in Fig. 5 show a rather small variability, but are very consequent in nature. The decrease of electron density and its Laplacian is observed at the RCPs when F^- is coming closer to the –OH group. Note that the same is observed for the sum of atomic charges in a phenylic ring (Fig. S2c) and HOMA index (Fig. 3). The results are in line with the BCP characteristics (ρ_{CP} and $\nabla^2\rho_{\text{CP}}$) obtained

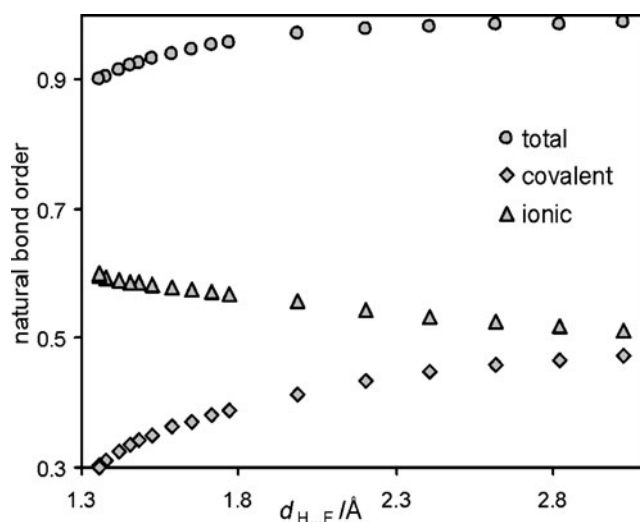


Fig. 6 Dependence of the total natural bond order and its covalent and ionic contributions for O–H bond on the length of H-bond, $d_{\text{H}\dots\text{F}}$, for complexes of phenol with F^-

for the studied complexes, showing that their changes in the –OH region modulate the properties of the aromatic ring. Moreover, the scatter plots in Fig. 5 present similar dependences of the AIM parameters on aromaticity indices (HOMA [47, 48] and NICS [52]) to those observed in six-membered rings of benzenoid hydrocarbons and their analogues [53, 54].

Undoubtedly, the reverse variability of AIM parameters at BCPs for O–H and C–O bonds in Ph–OH...F[−] complexes with increasing strength of H-bond (see Figs. S3 and S4) is in line with their lengthening and shortening, respectively (Fig. S1). Particularly large changes observed in the case of the O–H bond come from significant modification of its character, presented in Fig. 6. According to the expectations the natural bond order (total) decreases with the lengthening of O–H bond, whereas the H-bond length is shortened. Noteworthy, a simultaneous increasing of ionic and decreasing of covalent contributions to the bond order is observed.

Conclusions

Modeling of H-bonded complexes with gradually varying strength of interaction is a rich source of information [38, 40, 45, 55]. In the current study the Ph–OH...F[−] complexes were investigated with special attention paid to the modulation of the intermolecular hydrogen bond and its influence on the geometric and electronic structure properties, which were studied on the basis of NBO and AIM analyses. It is important to say that Popelier's criteria of the H-bond formation are fulfilled. It has been confirmed that electronic properties of the –OH substituent depend on the strength of the interaction of OH...F[−]. It was found that the studied interaction by hydrogen bond between the hydroxyl group, as a proton donor, and fluoride could be divided into two regions that characterize the non-covalent and partially covalent nature of the interaction. The determined borderline between them is the H-bond length, that is a proton-acceptor distance, *ca.* 1.8–1.9 Å, which is compatible with Espinosa et al. [38] and Grabowski et al. [50] classifications of H-bonds. In the case of non-covalent H-bonds, the increase of the strength of interaction causes an increase of the positive charge on the hydrogen atom of the hydroxyl group, whereas for partially covalent ones a decrease is observed. These conclusions result from the analyses of AIM parameters of selected bond critical points, since the nature of the intermolecular H-bond is dependent on the charge distribution. The changes in the H-bond strength also cause substantial structural changes in distant parts of the system: charges at all carbon atoms in the ring, its overall charge and aromaticity.

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