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# Varying Electronegativity of OH/O$^-$ Groups Depending on the Nature and Strength of H-Bonding in Phenol/Phenolate Involved in H-Bond Complexation

**Tadeusz M. Krygowski**

*Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland*

**Halina Szatyłowicz***

*Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland*

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Application of the Domenicano et al. method of estimating group electronegativity from angular geometry of the ring in monosubstituted benzene derivatives allowed us to find how the electronegativity of OH/O$^-$ groups in H-bonded complexes of phenol and phenolate depends on the nature and strength of H-bond. For complexes in which the OH group is only proton donating in the H-bond, a linear dependence of the estimated electronegativity on $O\cdots O(N)$ interatomic distance was found for experimental (CSD base retrieved) data. The following rule is observed: the weaker the H-bond is, the more electronegative the OH group is. If apart from this kind of interaction the oxygen is proton accepting, then an increase of electronegativity is observed. Modeling (B3LYP/6-311+G**) the variation of the strength of the H-bond by the fluoride anion approaching the OH leads to qualitatively the same picture as the scatter plots for experimental data.

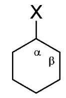
## Introduction

Electronegativity is a frequently used chemical term, describing "the power of an atom in a molecule to attract electrons to itself".[3] There have been many attempts, based on different assumptions, to define numerically the magnitude of the property that this term tentatively describes.[1,4−9] It has generally been accepted that this quantity should be described in the numerical scale introduced by Pauling.[3,10] Early on, the term was considered as an invariant property of atoms,[4,10] and then it was found that it depends on hybridization,[11] oxidation state,[12] and the number and nature of surrounding atoms in the molecule. The concept, initially defined for atoms, was extended into groups.[6,8,9a,13] Even if the basic idea for all those approaches is common, the mutual relationships between numerical values of electronegativities are far from excellent.[1]

In 1975, the existence of a correlation between ipso angle and the atom electronegativity[14] and then the group electronegativity of the substituent[6] emerged from experimental data of monosubstituted benzene derivatives.[15] Recently, Domenicano et al. repeated this kind of study employing ab initio (HF/6-31G*) optimized geometries of 75 monosubstituted benzene derivatives and obtained even more convincing results.[16] Consequently, they introduced a new way of estimating group electronegativity,[1] $\chi$, based on application of the principal component analysis[17] to geometry (bond angles) of the ring in monosubstituted benzene derivatives. The first principal component, directly related to electronegativity, accounts for most of the variance and depends almost entirely on variation in $\alpha$ and $\beta$ angles (for labeling see Chart 1).

Since the changes in $\alpha$ and $\beta$ angles depend on each other for geometric reasons because of the constraint of the planar hexagon,[18] it might be reasonable to consider $\alpha$ as a sufficient geometrical parameter describing the electronegativity of the group in question. To check this hypothesis, we have plotted $\alpha$ angles versus Domenicano's electronegativity. The regression of $\chi$ versus $\alpha$ for 53 monosubstituted benzene derivatives with "first row" substituents (that is, substituents linked to the benzene ring through an element of the Li−F row) with a few cases considered in orthogonal, planar, and pyramidal conformations taken from papers by Domenicano et al.[1] is shown in Figure 1.

**CHART 1**



The regression line reads

$$\chi = -41.00 + 0.3678\alpha \qquad (1)$$

with correlation coefficient cc = 0.998.

This means that, as a good approximation, $\alpha$ values may be used to estimate the electronegativity of the groups for which this angle is known, and also that the greater the $\alpha$ angle is for a given monosubstituted benzene derivative, the greater the group electronegativity for the substituent is.

It has been observed recently that in phenol/phenolate systems involved in H-bond formation the ipso angle, $\alpha$, changes within a great range.[19,20] Thus, following the Domenicano et al.[1] treatment on group electronegativity, these changes may be interpreted as representing the changes in electronegativity of OH/O$^-$ groups involved in an H-bond. Obviously, the magnitude of electronegativity is dependent on the nature and strength of H-bonding. The main purpose of this paper is to show how the above factors affect the electronegativity of the OH and O$^-$ groups in cases when they are involved in H-bonded complexation, and to describe these effects in a more quantitative way.

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* To whom correspondence should be addressed. E-mail: halina@chemix.ch.pw.edu.pl. Fax: (+48) 22-628-27-41. Phone: (+48) 22-660-77-55.

10.1021/jp0605496 CCC: $33.50

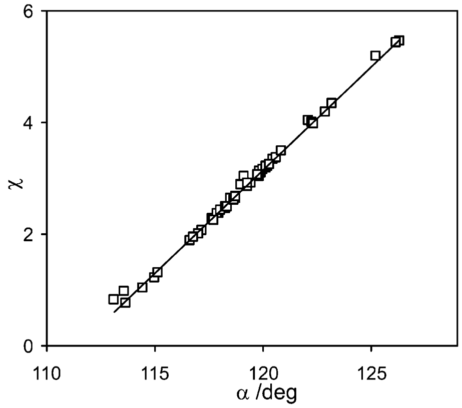


**Figure 1.** Linear regression for the electronegativity,[1] $\chi$, vs ipso angle,[16] $\alpha$. For labeling, see Chart 1.

**CHART 2**

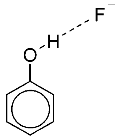
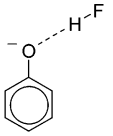


**CHART 3**



## Methodology

To simulate a wide range of H-bond strength, a simplified model system [PhO$\cdots$H$\cdots$F$^-$] with controlled O$\cdots$F distance was used.[20,21] The idea is shown in Chart 2 for OH$\cdots$F$^-$ and Chart 3 for O$^-\cdots$HF.

The fluoride anion approaches the molecule of phenol along the line of prolongation of the O−H bond direction (Chart 2). The O$\cdots$F distance was controlled, and the linearity of O$\cdots$H$\cdots$F and planarity of the phenyl ring were assumed. For the PhOH$\cdots$F$^-$ complexes, the O$\cdots$F distance was varied from 4.0 Å up to a distance when the proton transfers from phenol to F$^-$. In the case of the PhO$^-\cdots$HF complexes (Chart 3), the range of the O$\cdots$F distance was slightly wider and started from the distance for the optimal geometry of the system.

Becke-style 3 parameter density functional theory using the Lee−Yang−Parr correlation functional and 6-311+G** basis set (B3LYP/6-311+G**) were used to optimize the geometries of the molecules and complexes and to calculate vibrational frequencies. Optimal geometries of molecules and H-bond complexes (without the O$\cdots$F distance constrained) and PhO$^-\cdots$HF complexes with O$\cdots$F distance in the range 2.4−2.8 Å have no negative frequencies. Only one negative frequency was found for the other complexes, indicating the proper route of the proton on the path realized by H-bonding of the system under consideration.

All calculations were performed using the *Gaussian98* series of programs.[22]

To estimate the interaction energy, eq 2[21] is used, employing the counterpoise correction method which eliminates basis set superposition errors:

$$E = E_{AC}(\text{basis}_{AC}; \text{opt}_{AC}) - E_{A}(\text{basis}_{AC}; \text{opt}_{A}) - E_{C}(\text{basis}_{AC}; \text{opt}_{C}) \quad (2)$$

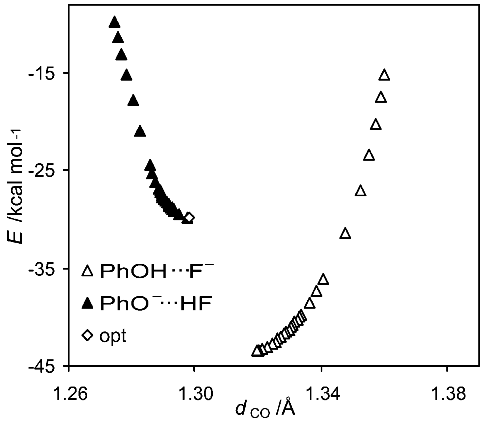


**Figure 2.** Dependence of energy of interaction, $E$, on CO bond lengths, $d_{CO}$ (opt denotes the optimal H-bonded complex).

where, for interactions described by Chart 2, A is phenol and C is F$^-$. $E_A$(basis$_{AC}$; opt$_A$) means that the energy of molecule A, $E_A$, was calculated using internal coordinates of the A and C molecules, basis$_{AC}$, and for the geometry obtained during optimization of molecule A, opt$_A$. The other terms in eq 2 should be understood in the same way. For interactions described by Chart 3, A is phenolate anion and C is hydrofluoric acid.

Geometries of H-bonded complexes of phenol and phenolate anion with various oxygen and nitrogen bases/acids were retrieved from CSD.[2] The searches were performed for phenol (phenolate) interacting with a nitrogen or oxygen base (acid) with an intermolecular contact between the oxygen of phenol (phenolate) and the nearest O or N atom in base (acid) equal to or less than the sum of their van der Waals radii.[23] In the case of phenolate H-bonded complex the angle between the oxygen of phenolate, the proton and O or N of the acid (proton donor) was limited from 90 to 180 degrees. The searches were restricted to structure measurements with the reported mean estimated standard deviation (esd) of the CC bond $\leq$ 0.01 Å (there is no structure of the phenolate with esd $\leq$ 0.005 Å in the database), not disordered, without errors and 3D coordinates determined. Sometimes the molecules of the solvent were present in the crystal lattice.

## Results and Discussion

The CO bond lengths may be considered as an estimate of H-bond strength. For PhOH$\cdots$F$^-$ interactions,[21] the shorter the CO bond length is, the stronger the H-bond is. However, in the case of CO$^-\cdots$HF interactions, a reverse situation occurs: the longer the CO bond length is, the stronger the H-bond is. This is shown in scatter plots in Figure 2, where the energy of interaction, $E$, described by eq 2 is plotted against CO bond length, $d_{CO}$.

The two different physical situations mentioned above are represented by different changes in energy of H-bonding as a function of CO bond lengths. The limiting cases of the CO bond length are in the PhOH (the maximal value) and in the PhO$^-$ (the minimal one) not complexed by a hydrogen bond. In our model system, it means that F$^-$ and HF, respectively, are in infinity. For OH$\cdots$F$^-$ interactions, an increase in energy of H-bonding is associated with a shortening of the CO bond. This is due to the fact that the fluoride approaching the proton in the OH group causes lengthening of the OH bond leading to a more negative charge settled at the oxygen. This may cause mesomeric interactions with the $\pi$-electron structure of the ring. In consequence, the CO bond may become shorter. A reverse situation occurs for PhO$^-\cdots$HF interactions. The shorter the

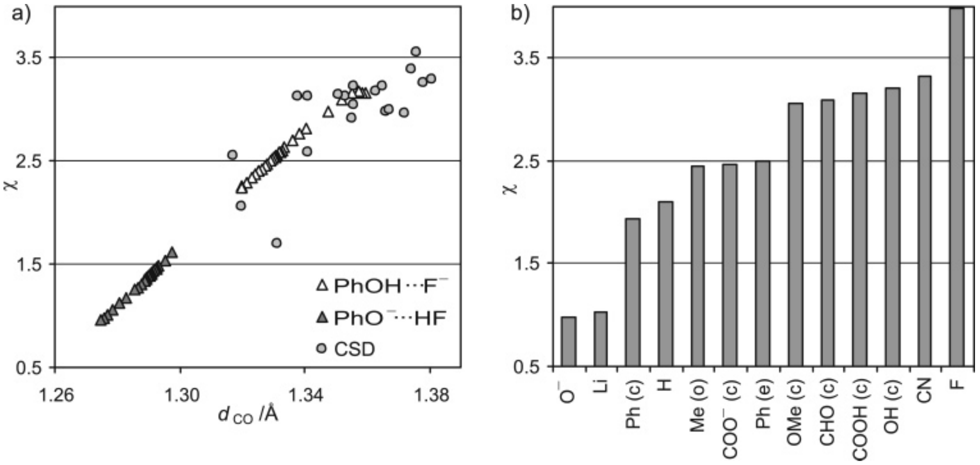


**Figure 3.** (a) Dependence of group electronegativity, $\chi$, for various H-bonded complexes of phenol and phenolate anions with Brönsted bases and acids (as shown in the box, CSD indicates experimental geometry retrieved from CSD[2]) on CO bond length, $d_{CO}$. (b) For comparison, a histogram of $\chi$ values[1] for various groups known as typical substituents is shown.

distance between the proton of HF and the oxygen of phenolate is, the stronger the H-bond and the longer the CO bond become. The approaching proton attracts electrons from the partly double bond leading to elongation of the CO bond.

Undoubtedly, the different kind of H-bonding in those two cases generates different possibilities of electron delocalization from the oxygen atom toward the CO bond and further to the benzene ring. Nevertheless, the CO bond lengths and electronegativity of the OH/O$^-$ groups involved in H-bonding are mutually related, as shown by Figure 3. The range of variation of $\chi$(O$^-$) in O$^-$⋯HF complexes is between ~0.9 and 1.6. For OH⋯F$^-$ complexes, $\chi$(OH) ranges from 2.2 to 3.2. For OH and O$^-$ not interacting with anything, i.e., for isolated (ab initio optimization) phenol and phenolate, the values of $\chi$ are known, being equal to 3.21 and 0.98, respectively.[1] Thus, the observed $\chi$ values for interaction schemes as in Charts 2 and 3 should be in the range 0.98−3.21.

Figure 3a presents the variation of $\chi$ values, depending on CO bond length, $d_{CO}$, which in turn depends on the nature of OH⋯F$^-$ and O$^-$⋯HF interactions: the scale of the magnitude is from 0.9 to 3.2. The circles denote the electronegativities of phenol and phenolate H-bonded complexes estimated from experimental geometries.[2] It should be noted that in these cases variation in H-bond strength depends only on the nature of base (acid) in the complex. The observed variation of electronegativity for H-bonded complexes of phenol and phenolate is not large (2.7−3.5 and 1.7−2.0, respectively). Despite a reasonable picture of the observed changes in electronegativity, for crystal diffraction determination of geometry it should always be taken into account that the geometry may be affected by crystal packing forces,[24] particularly in the case of bond angles,[25] and random and systematic errors in X-ray crystal structure determination (including, e.g., uncorrected thermal motion effects). Figure 3b presents the changes of electronegativity for typical substituents; for comparison, there is the same range of variation in electronegativity as that for model data of Figure 3a.

In many cases, the strength of intermolecular H-bonding is approximated by an interatomic distance between heavy atoms participating in a joint interaction with the proton in between.[26] Figure 4 presents the dependence of energy of interaction, $E$, on O⋯F interatomic distance, $d_{O\cdots F}$. Again, we observe two lines, one for OH⋯F$^-$ interactions and the other for O$^-$⋯HF interactions, the former being stronger H-bonding.

The way of estimating electronegativity of the OH group involved in H-bond presented above is now applied to experimental geometries of phenol in its H-bonded complexes with various bases. The data were retrieved from CSD.[2]

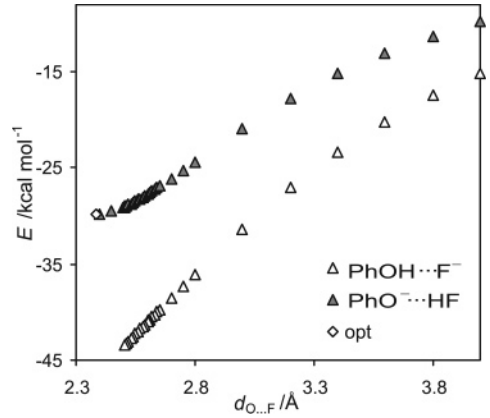


**Figure 4.** Dependence of energy of interaction, $E$, on O⋯F interatomic distance, $d_{O\cdots F}$ (opt denotes the optimal H-bonded complex).

**CHART 4**

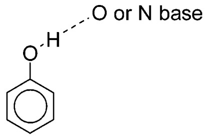
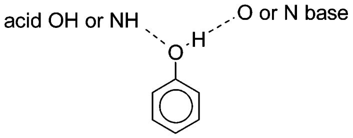


**CHART 5**



Two cases have to be distinguished:

(i) The hydroxyl group of phenol is proton donating in the H-bonded complex with bases (Chart 4).

(ii) The hydroxyl group of phenol is involved in two H-bonding interactions; in one, the OH of phenol is proton donating, and in the other, the oxygen of the OH group is proton accepting (Chart 5).

In the second case (the OH group involved in both kinds of interactions, Chart 5), the same value of the estimated $\chi$ is associated with two values of $d_{O\cdots O(N)}$: one (labeled d2, Figure 5) for the hydroxyl acting as the proton donor and the other (labeled a2, Figure 5) for the OH, i.e., the oxygen, acting as the proton acceptor in the H-bonded complex.

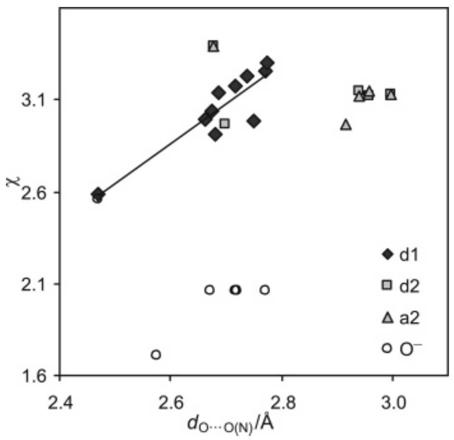


**Figure 5.** Estimated values of electronegativity, $\chi$, (eq 1) plotted against interatomic distance, $d_{O\cdots O(N)}$ (experimental geometry retrieved from CSD[2]). d1 stands for $d_{O\cdots O(N)}$ in the case of an OH group involved in one H-bond with OH being the proton donating group; d2 and a2 are the cases where $d_{O\cdots O(N)}$ stands for the distances of interactions where oxygen in the OH group is proton accepting a2 and OH is proton donating d2. The circles are for phenolate anion involved in one or more H-bonds.

Figure 5 presents the dependence of estimated electronegativity, $\chi$, on the interatomic distance O (from OH/O$^-$ groups) and oxygen or nitrogen atoms from bases/acids, $d_{O\cdots O(N)}$.

It follows from Chart 4 that the stronger the H-bond is, approximated by interatomic distance, $d_{O\cdots O(N)}$,[26] the more negative charge is on the oxygen atom and the lower the value of electronegativity should be. This is in line with the regression line in Figure 5 for points labeled by d1 for which correlation coefficient cc = 0.90. The $\chi$ values are mostly lower than the value for phenol itself ($\chi = 3.21$) and drop down to ∼2.6.

In the case of the OH group involved in two H-bonds, Chart 5, the consequence may be a lowering of electron charge at oxygen and hence an increase of electronegativity of the OH. It is worth mentioning that $\chi$ for $PhOH_2^+$ is 5.46[1] and hence the approach of the proton donating group to the oxygen atom of OH (shorter however than the sum of van der Waals radii[23]) should lead to an increase of electronegativity. Note that another H-bond in which OH is proton donating acts in the opposite direction. In a real crystal structure, one of these interactions may be superior to the other one, and then, the appropriate $d_{O\cdots O(N)}$ value may be substantially shorter. This interaction may determine the electronegativity of the OH group. For these cases, there are two values of $d_{O\cdots O(N)}$ given, indicated in Figure 5 by different symbols: d2 and a2. For clarity, two examples are discussed more in detail. One of them is the low-temperature measurement (123 K) crystal data for phenols.[27] Its molecules form a hydrogen-bonded chain where the phenols are arranged in approximately 3-fold helices. In this case, three independent molecules of phenol are in the asymmetric part of the elementary cell, and hence, three pairs of $d_{O\cdots O(N)}$ and angles values are given: (2.655, 2.664, and 2.693 Å) and (121.2°, 120.7°, and 120.2°). However, precision of measurements is not sufficiently high, and therefore, the mean values of $d_{O\cdots O}$ and $\alpha$ were taken into account. The resulting value of the angle leads to an electronegativity ($\chi = 3.40$) value that is higher than the value for phenol (3.21). Thus, it seems that in this case with two kinds of interactions (OH···O and O···HO) the accepting interaction of the oxygen is dominant. This kind of interaction was already analyzed on the basis of experimental and computational results.[28] Another three pairs of points ($d_{O\cdots O(N)} = 2.940$, 2.957, and 2.996 Å) are for polymorphs of crystalline phenol measured under high pressure (0.16 GPa).[29] The crystal structure of this polymorph is completely different from that of the former one. Both H-bonding interactions (d2 and a2, Figure 5) are weaker (the ambient pressure hydrogen bond[27] strength is approximately 8% greater[29] than that in the high-pressure phase), characterized as a longer O···O interatomic distance. This leads to $\chi$-values close to the one obtained for an isolated molecule of phenol ($\chi = 3.21$).

## Conclusions

The most important conclusion of this report is that the substituent property as the group electronegativity depends strongly on interactions with the environment and that H-bond complexation may cause substantial changes in this property. This kind of effect was already discussed earlier[30] in regard to specific substituent−solvent interactions affecting the acidity of phenol derivatives. Differences in acidities in the gas phase and solution measurements of phenols have been attributed to the specific solvent−substituent interactions.

In the present report, the changes in substituent property due to H-bonded complexation of OH/O$^-$ are given numerically by group electronegativity expressed in the Pauling scale.[3] The important thing to add is that these changes are very big and depend on the nature and strength of H-bonding.

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**Supporting Information Available:** Details of the molecular modeling, supplementary references, and information concerning H-bonded complexes of phenol and phenolate retrieved from CSD (see ref 2). This material is available free of charge via the Internet at http://pubs.acs.org.

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