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Substituent Constants (σ_p^-) of the Rotated Nitro Group. The Interplay Between the Substituent Effect of a Rotated $-NO_2$ Group and H-Bonds Affecting π-Electron Delocalization in 4-Nitrophenol and 4-Nitrophenolate Complexes: a B3LYP/6-311+G** Study*

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Abstract. The geometries of a series of nine 4-substituted nitrophenols and 4-substituted nitrophenolates (X = H, $CONH_2$, CHO, COOH, $COCH_3$, COCl, CN, NO_2, NO) and of their conformers, where the nitro group rotates by 10º from $\phi = 0°$ to $\phi = 90°$, were optimized at the B3LYP/6-311+G** DFT level. These data were used to analyse the effect of rotating of the nitro group on π-electron delocalization in the ring. It has been shown that the substituent effect stabilization energy (SESE) estimated for *p*-substituted phenolates correlates very well with σ_p^- constants. Based on this dependence the σ_p^- constants for the nitro group as a function of the out-of-plane dihedral angle ϕ were obtained. Application of the model simulating varying strength of H-bond by approaching F^- (HF) group to OH (O^-) group of the 4-nitrophenol (4-nitrophenolate) with the rotating nitro group allowed to show interrelation between changes in aromaticity of the ring due to both rotation of the nitro group and changes in the strength of H-bonding. Two indices of aromaticity: Nucleus-Independent Chemical Shifts (NICS), and the Harmonic Oscillator Model of Aromaticity (HOMA) were used to quantify the aromatic character of the benzene fragment.

Keywords: nitrophenols, DFT calculations, aromaticity, hydrogen bonding, Hammet parameters

INTRODUCTION

The nitro group is both one of the most typical and most important substituents in organic chemistry.[1] Its substituent effect in a classical Hammett scale[2] is mostly inductive in nature. Consequently, the σ_I substituent constant equals to 0.70,[3] whereas the constants for *meta* and *para* positions, σ_m and σ_p, are 0.71 and 0.78, respectively.[4] Thus for the reference reaction, *i.e.* benzoic acid dissociation, the resonance component is very small. Indeed, the reported resonance and field substituent constants,[4] *R* and *F* for nitro group are 0.13 and 0.65, respectively. However for reactions with an electron-donating reaction site, the resonance power of the nitro group increases dramatically: $\sigma_p^- = 1.27$,[5] whereas the pure resonance constant $R^- = 0.62$.[4] The Domenicano group electronegativity[6] for the coplanar and perpendicular nitro group estimated for monosubstituted benzene derivatives are fairly similar: 4.00 and 4.19, respectively. This indicates that the σ-electron withdrawing power is not changed appreciably by twist of the group.

The nitro group is not very rigid. Since the barrier of rotation is rather small (*ca.* 6 kcal mol^{-1}) the weak intermolecular interactions in the crystal lattice may efficiently distort it from planarity. In nitrobenzene derivatives without steric interactions in *ortho* position the nitro group is rotated by up to *ca.* 39º, which is observed in β''-tetrakis(bis(ethylenedithio)tetrathiafulvalene)hydroxoniumtris(oxalato-*O*,*O*')-gallium(III) nitrobenzene clathrate.[7] The mean value of twist is about 7.2º with a standard deviation of 5.6º (Based on 5376 molecular fragments of nitrobenzene derivatives, Cambridge Structural Database).[8] As might be expected, steric interactions in *ortho* position to the nitro group lead to much higher values of distortion. For instance in bis(2,4,6-tris(4-bromophenoxy)-1,3,5-triazine)trinitromesitylene clathrate[9] the group is perpendicular to the ring. An *ortho* substitution is an extreme factor to enforce nonplanarity; however, it is worth noting that even in the crystal structure of nitrobenzene the nitro group is twisted by *ca.* 2º from the plane of the benzene ring.[10] Contrary to general expectations based on reaction mechanisms in organic chemistry[11] (*e.g.* electrophilic substitution) the above observations strongly support the

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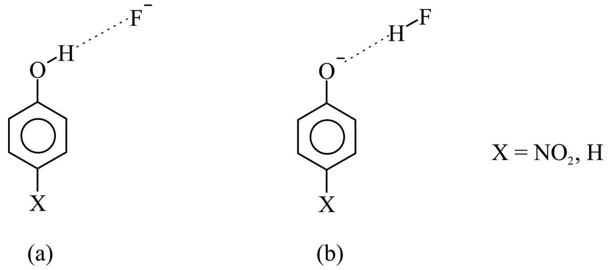
* Dedicated to Professor Zvonimir Maksić on the occasion of his 70th birthday.

** Author to whom correspondence should be addressed. (E-mail: chamis@chem.uw.edu.pl) point that the nitro group does not conjugate effectively with the benzene ring.[12] It was shown that rotation of the $-NO_2$ group relative to the plane of the benzene ring in *N,N'*-dimethyl derivatives of *p*-nitroaniline affected significantly geometry of the ring, indicating a decrease of the weight of the quinoid-type canonical structure.[13]

Substituent effects on π-electron delocalization in monosubstituted benzene derivatives are considered to be very weak.[14,15] Much stronger is the substituent effect in disubstituted systems, particularly for the *para* position in benzene[16] or related systems.[17] Obviously, the substituent effect of nitro group depends on the electron donating power of the group in *para* position.[5,18] Among the most effective electron-donating counter substituents for the nitro group are hydroxy and (in particular) the oxo group. Their substituent constants σ_p^+ are −0.92 and −2.3, respectively.[4]

As previously mentioned, the substituent effect on π-electron delocalization of the substituted ring is rather weak, except for cases when the counter substituent in the *para* position has an opposing property. In other words, the substituent should be strongly electron-donating from one side of the ring and strongly electron-accepting from the other side.[19] Obviously, the character of a substituent can be modified by intermolecular interactions.[20,21] Recently, substantial (and systematic) changes in cyclic π-electron delocalization pattern of the ring were observed for *p*-substituted phenol, and particularly for *p*-substituted phenolate involved in H-bonding of the type: OH…base or O^-…H(acid).[22,23] In these cases the substituents were fixed, and the strength of H-bonding was modified within the model[24] in which a HF molecule approached the oxygen fragment in *p*-substituted phenolate or alternatively, F^- anion approached the hydroxyl group in *p*-substituted phenol. This idea is summarized in Scheme 1.

The changes in π-electron delocalization of the ring of *p*-nitrophenol and *p*-nitrophenolate involved in hydrogen bond formation were quantified using a geometry-based index of aromaticity HOMA,[25] which registered changes ≈0.1 and ≈0.3 for case (a) in Scheme 1 (fluoride approaching to hydroxyl group) and case (b) in Scheme 1 (hydrofluoric acid approaching the O^- fragment), respectively. To put these numbers in perspective: HOMA changes by 1 unit going from a model non-aromatic system (the Kekulé structure: 1,3,5-cyclohexatriene) to fully aromatic (benzene). Changes in the magnetism-based aromaticity index $\mathrm{NICS}(1)_{zz}$,[26,27,28] due to the H-bond formation, particularly for O^-…HF interactions, were also found to be very substantial: for $\mathrm{NICS}(1)_{zz}$ the range was equal to ≈10 ppm.[29] For formal definitions of HOMA and NICS see below. There is no doubt that H-bond formation may affect significantly π-electron delocalization in the ring.



Scheme 1. (a) Fluoride approaches the oxygen atom in hydroxyl group; (b) Hydrofluoric acid approaches the oxygen atom in phenolate anion.

This paper is focused on two main problems:

(i) Estimation of the values of substituent constant σ_p^- of the NO_2 group as a function of the $-NO_2$ group dihedral angle. Many quantitative structure activity relationships (QSAR)[30,31] used in modeling of various biologically-based phenomena rely on substituent constant values, so a proper description of the behaviour of group is very important.

(ii) A systematic study of the extent to which nitro group rotation in *p*-nitrophenols and *p*-nitrophenolates affects π-electron delocalization in the ring. As the OH and O^- groups are classical donors or acceptors of hydrogen bond, respectively, the analysis is extended to the influence of a rotated nitro group on the strength of the H-bond formed by F^- or HF approaching the OH or O^- fragment.

METHODOLOGY

p-Nitrophenol-fluoride complexes and *p*-nitrophenolate-hydrofluoric acid complexes were optimized at the B3LYP/6-311+G** DFT level of theory. The fluoride anion or hydrofluoric acid was approaching the molecule of *p*-nitrophenol or *p*-nitrophenolate, respectively, both along the line of a prolongation of O−H or H−F bond direction and in plane of the ring, as shown in Scheme 1. The O…F distance in both cases was frozen and gradually changed by 0.2 Å starting from 4.0 Å down to the distance where hydrogen transfer took place (2.580−2.523 Å for *p*-nitrophenol complexes with planar and perpendicular nitro group, respectively). The *p*-nitrophenolate complexes were optimized down to a O^-…H−F distance of 2.5 Å, but no proton transfer occurred. In both cases (complexes of *p*-nitrophenol and *p*-nitrophenolate) 10 frozen conformers with rotated $-NO_2$ groups were obtained. The optimized (dihedral) rotation angles with respect to the plane of the phenyl ring ranged from 0° to 90°. For comparison, phenol-fluoride and phenolate-hydrofluoric acid complexes were also optimized using the same constraints as the nitro derivatives. Additional species which were fully geometry-optimized at the same level to determine the relationship between SESE[32] (Substituent Effect Stabilization Energy, see below) and the substituent constant σ_{p}^{-} [4] were $^-$O−Ph−X, where X = $CONH_2$, CHO, COOH, $COCH_3$, COCl, CN, NO_2, NO. The reference compounds *p*-nitrophenol, *p*-nitrophenolate anion, phenol and phenolate anion have also been fully optimized at the same (B3LYP/6-311+G**) level of theory. To estimate the extent of π-electron delocalization,[33] two indices of aromaticity were used: the geometry-based HOMA[25,34,35] and the magnetism-based NICS.[26,27,36]

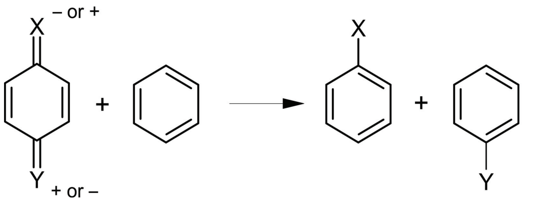
The Harmonic Oscillator Model of Aromaticity (HOMA) is defined as follows:

$$\mathrm{HOMA} = 1 - \frac{\alpha}{N}\sum\left(R_{\mathrm{opt}} - R_{\mathrm{i}}\right)^2$$ (N is the number of bonds taken into the summation; α is an empirical constant fixed to give HOMA = 0 for a model non-aromatic system[25] and HOMA = 1 for a system with all bonds equal to an optimal value R_{opt}, assumed to be realised for fully aromatic systems. R_{i} stands for a running bond length. For CC bonds $\alpha = 257.7$, $R_{\mathrm{opt}} = 1.388$ Å).

NICS is defined as the negative value of absolute magnetic shieldings calculated at centre of a ring system.[26] It may also be calculated at other interesting points inside or around molecules.[37] Rings with negative NICS values are qualified as aromatic: more negative values of NICS correspond to more aromatic rings. NICS calculated at 1 Å above molecular plane is denoted as NICS(1). This value has been considered as a better descriptor of the π-electron effects, because the local, σ-electron, contributions diminish relative to the ring current effects. $\mathrm{NICS(1)}_{zz}$ denotes the component of NICS(1) corresponding to the principal axis perpendicular to the ring plane.[38] The GIAO/B3LYP/6-311+G** method was used for the NICS calculations. All calculations were performed using the Gaussian03 program.[39]

RESULTS AND DISCUSSION

The substituent effect of the nitro group in different conformations with respect to the phenyl ring can be explained using of the idea of SESE (the Substituent Effect Stabilization Energy)[32a] presented in Eq. (1). The enthalpy change associated with this homodesmotic reaction[40] measures an increase in the stability of a system due to X. . .Y interactions both with the ring and through the ring.



(1)

For phenols it has been shown that gas-phase SESE values calculated using quantum chemical methods correlate with experimentally estimated substituent constants σ_{p}.[16] In the case of electron-accepting substituents, a good dependence should be observed for the relationship between the SESE values estimated for *p*-substituted phenolates (Y = O^- in reaction (1)) and the σ_{p}^{-} substituent constant. As mentioned, this type of constants is usually used to describe the "resonance power" of a substituent interacting with an electron-donating reaction site in a *para* position. Table 1 presents the estimated SESE values and the σ_{p}^{-} substituents constants for a few model systems, and Figure 1 shows the dependence between these two quantities. The correlation coefficient is R = 0.994 and the linear regression for this dependence reads as follows:

$$\sigma_{\mathrm{p}}^{-} = 0.0507 \cdot \mathrm{SESE} - 0.0277 \qquad (2)$$

This closely linear relationship can be used now to estimate the σ_{p}^{-} values for an $-NO_2$ group which is rotated with respect to the plane of the benzene ring. The SESE values estimated for *p*-nitrophenolates via reaction (1) (where the $-NO_2$ group rotates to the same degree on both sides of the reaction) and the resulting σ_{p}^{-}, obtained from equation (2) are given in Table 2. The σ_{p}^{-} value for a planar $-NO_2$ group is 1.32, which is very close to the experimentally-obtained value (1.27, see Table 1). While rotating the group a progressive decrease of the resonance character is observed. For a perpendicular nitro group the σ_{p}^{-} is equal to 0.72, which is slightly smaller value than the original Hammett substituent constant (σ_{p} = 0.78).[4] In this geometrical arrangement the resonance effect should be completely absent, while the inductive effect should remain. Indeed

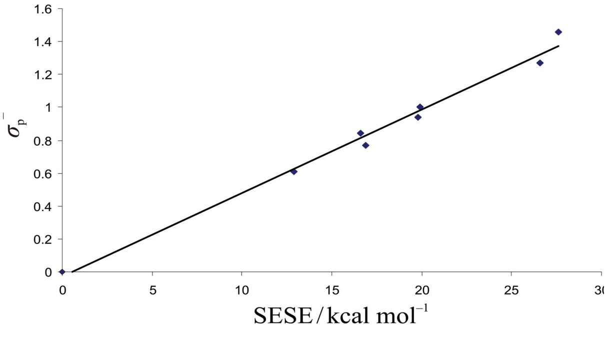


Figure 1. Dependence between σ_{p}^{-} and SESE values estimated for *p*-substituted phenolates with use of the reaction (1). Correlation coefficient R = 0.994, 8 points.

Table 1. The SESE values (expressed in kcal/mol) estimated with use of the Eq. (2) and experimental σ_p^- values[3,4]

	SESE	σ_p^-
H	0.00	0.00
$CONH_2$	12.9	0.61
CHO	19.8	0.94
COOH	16.9	0.78
$COCH_3$	16.6	0.84
CN	19.9	1.00
NO_2	26.6	1.27
NO	27.6	1.46

the estimated substituent value is consistent with σ_I for the nitro group ($\sigma_I = 0.70$).[4] It is worth noting that small deviations from planarity (within *ca.* 10°) practically do not reduce the resonance power of the group. Therefore small deviations from planarity are well-tolerated and therefore most nitrobenzene derivatives have non-planar $-NO_2$ groups while adapting to the intermolecular interactions in the solid state. Support for the presented values of σ_p^- comes from the dependences of the parameters describing cyclic π-electron delocalization: HOMA or NICS and σ_p^-. If the parameters are calculated for benzene fragment in nitrophenolates with rotated $-NO_2$ groups and their values for $\phi = 0°$ and $\phi = 90°$ are used to calculate two-point linear equations using σ_p^- (1.27) and σ_I (0.70), respectively, then based on these regressions (see Supplement for details) we may estimate values of σ_p^- for other ϕ angles. The resulting data are presented in Table 2. It is clear that they are in very good agreement with the values of σ_p^- estimated from the Eq. (2). Hence a very good linear dependence between SESE and σ_p^- for *p*-substituted phenolates supports the idea that SESE values may serve as a source of information on σ_p^- for molecules with variously rotated $-NO_2$ substituents. We would argue that σ_p^- values calculated in this way would be better for applications (*e.g.* in QSARs) since they should more accurately reflect the behaviour of the $-NO_2$ group as it responds to different geometries.

Changes in electron-accepting power of "rotated" nitro groups due to the decrease of the resonance effect lead to substantial changes in π-electron delocalization in the ring of both *p*-nitrophenol and *p*-nitrophenolate. Figure 2 presents the aromaticity indices HOMA, NICS and NICS(1) as a function of $-NO_2$ group dihedral angle (ϕ) for the systems involved in the hydrogen bonds, as well as for the parent compounds. We note that the dependences for NICS(1)$_{zz}$ are fairly similar to NICS and NICS(1), so for brevity they are not shown here.

As expected the changes in π-electron delocalization are significantly smaller for *p*-nitrophenols as compared with *p*-nitrophenolates, because the hydroxy group is a much weaker π-donating system than the oxo group (σ_p^+ for OH is −0.92 and for O^- is −2.3).[4] This may be exemplified by the values of HOMA for systems involved in strong hydrogen bond (at O...F distance of 2.6 Å), which change by 0.06 in the former case and by 0.12 in the latter. Importantly for *p*-nitrophenol the differences, Δ, of NICS's and HOMA values between $\phi = 0°$ and $= 90°$ are the greatest for cases where O…F interatomic distance is the smallest, since then the H-bond strength for OH…F^- is the strongest and the mobility of the electrons at the oxygen

Table 2. SESE values (expressed in kcal/mol) calculated for nitrophenolate with rotating $-NO_2$ group (from $\phi = 0°$ to $\phi = 90°$). σ_p^- from Eq. (2) are denoted as σ_p^- (1), they are recommended values, given in bold; σ_p^- from the dependence $\sigma_p^- = -0.2828 \cdot \text{HOMA} + 0.8715$ are denoted as σ_p^- (2) Supplement;[(a)] and σ_p^- from the dependence $\sigma_p^- = 6.15 \cdot \text{NICS} - 10.234$ are denoted as σ_p^- (3)[(a)]

ϕ	SESE	σ_p^-(1)	HOMA	σ_p^-(2)	NICS	σ_p^-(3)
0	26.6	**1.32**	0.51	1.27	−2.4	1.27
10	26.4	**1.31**	0.51	1.27	−2.5	1.26
20	25.7	**1.28**	0.52	1.23	−2.7	1.22
30	24.6	**1.22**	0.55	1.15	−3.1	1.15
40	23	**1.14**	0.56	1.09	−3.6	1.08
50	21.1	**1.04**	0.59	1.00	−4.1	0.99
60	19.1	**0.94**	0.62	0.89	−4.7	0.91
70	17	**0.84**	0.64	0.81	−5.2	0.82
80	15.4	**0.76**	0.66	0.75	−5.7	0.74
90	14.8	**0.72**	0.67	0.70	−5.9	0.70

[(a)] See Supplement for details.

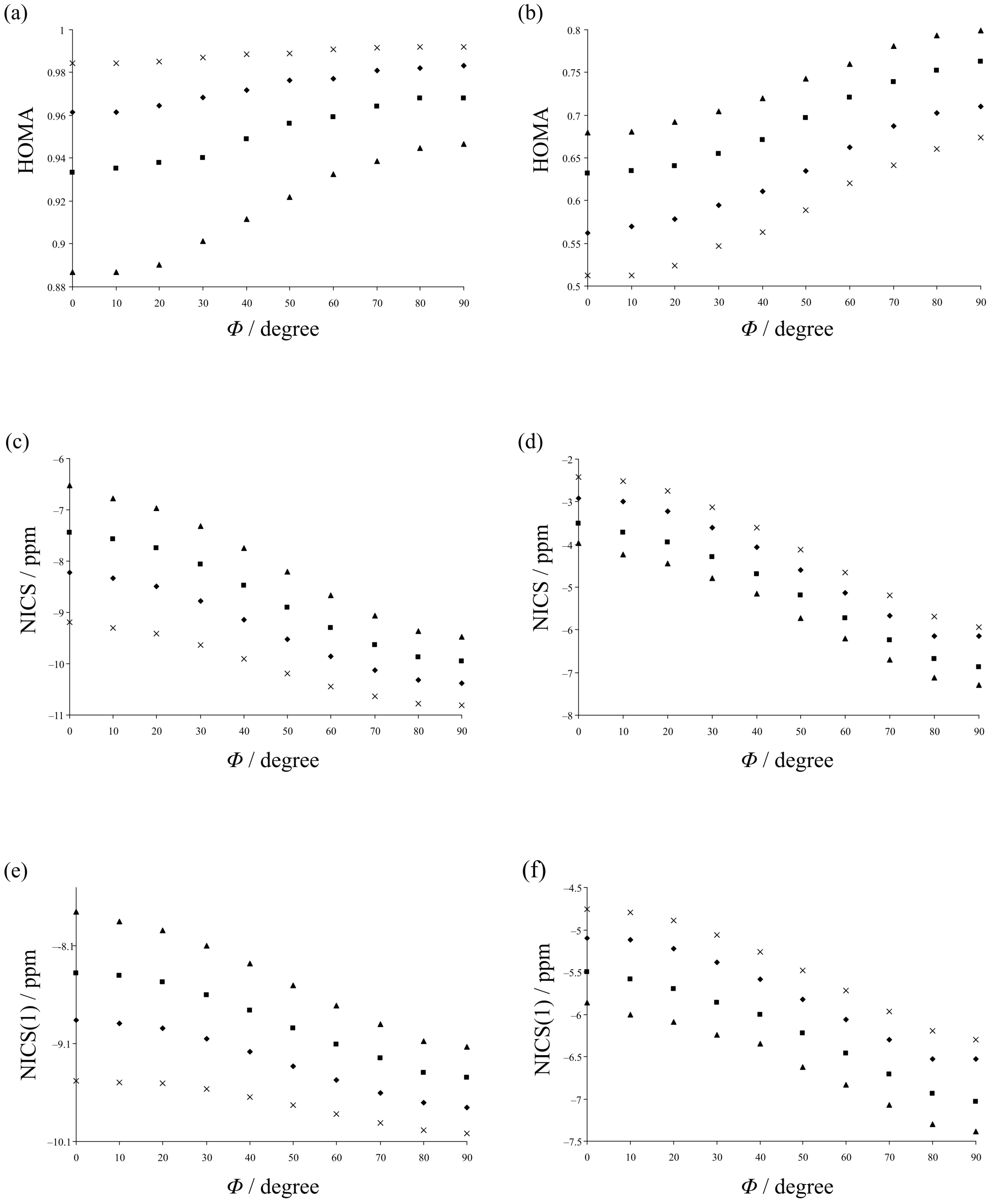


Figure 2. Dependences of HOMA, NICS and NICS(1) on bend angle ϕ for four interatomic O…F distances: infinity (*i.e.* systems not involved in H-bond − points denoted by ×), 4 Å (points denoted as ♦), 3 Å (points denoted by ■), and 2.6 Å (points denoted by ▲) for p-nitrophenol (a), (c), (e) and p-nitrophenolate (b), (d), (f).

atom susceptible for intramolecular charge transfer to nitro group is the largest. Consequently, the differences Δ(HOMA) and Δ(NICS) are the greatest for O…F distance $d_{(\mathrm{O...F})} = 2.6$ Å and smallest for the case where this distance is infinite, *i.e.* for *p*-nitrophenol itself. Hence the changes of π-electron delocalization due to the rotation of the $-\mathrm{NO}_2$ group are most effectively seen for the former case and then gradually decrease. A reverse situation is observed for *p*-nitrophenolate. The Δ(HOMA), Δ(NICS) values are the greatest for *p*-nitrophenolate, and gradually decrease with a decrease of the O…F interatomic H-bond distance. The shorter the O…F distance, the stronger the H-bond with HF, so the electrons are more efficiently immobilized for intramolecular charge transfer to the nitro group. Thus the values of Δ(HOMA), Δ(NICS) are smaller. The most aromatic ring is for $\phi = 90^\circ$ as documented by HOMA = 0.67, NICS = −5.93 ppm and NICS(1) = −6.30 ppm.

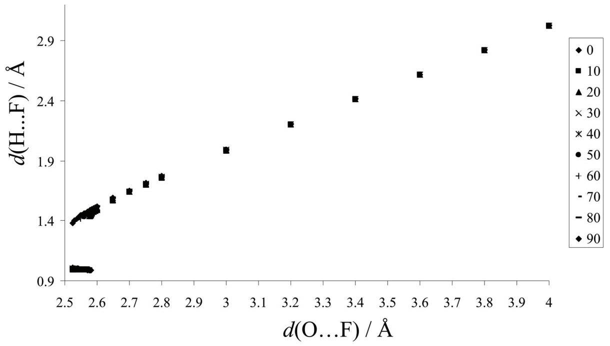


Figure 3. The dependence between d(H…F) on d(O…F) for p-nitrophenol (upper line) and p-nitrophenolate (bottom line). Data for different angles are represented by the symbols shown on the right of the Figure.

Obviously this is due to the weakest resonance effect in this case. For phenolate, where there is no counter substituent, the aromaticity of the ring is: HOMA = 0.68, NICS and NICS(1) are −4.17 and −5.91 ppm, respectively. Thus, the ring aromaticity estimated by HOMA and NICS(1) is in both cases almost the same, but NICS in phenolate shows a lower aromatic character of the ring than in the case of the perpendicular rotamer of *para* nitrophenolate.

SESE values, which are reliable measures of these substituent effects, can be used to show how the rotation of the nitro group depends on the H-bond strength. The strength is usually approximated by the distance between the hydrogen of the proton donating group (OH in our case) and the acceptor atom (F^- in our case), *i.e.* $d_{(H...F)}$. In our model the O…F interatomic distance was fixed in computation but gradually changed from one model to the next leading to a decrease of the $d_{(H...F)}$ distance. These changes are described by a linear relation with H…F optimized distance, and therefore represent the "strength" of the H…F interaction. Figure 3 presents dependence of $d_{(H...F)}$ on $d_{(O...F)}$, which supports the use of $d_{(O...F)}$ as a quantitative estimate of H-bonding strength. Note that for all values of ϕ the dependence is practically the same − the data points form one curve.

Figure 4(a) presents the dependences between the SESE values (see Eq. 1) for p-nitrophenols involved in hydrogen bond with fluoride and the nitro group dihedral angle, ϕ. For clarity three arbitrary interatomic distances d(O…F): 4 Å, 3 Å and 2.6 Å have been chosen. Figure 4(b) presents complementary dependences for three ϕ values: 0º, 50º and 90º.

It is apparent that the most steep dependence is observed for the case with d(O…F) = 2.6 Å and changes from 15 kcal/mol to 10 kcal/mol for $\phi = 0º$ and $\phi = 90º$, respectively (see Figure 4a). At this distance the system is very close to proton transfer from hydroxy group to fluoride. The oxygen atom in OH group has a highly negative partial charge because of the longer distance to the parent proton, which leads to effective through-resonance interaction with the nitro group. The scale of the effect obviously depends on the dihedral angle ϕ. Simultaneously with an increase of H-bonding strength, as estimated by the H…F distance d(H…F), the OH bond length becomes weaker, (*i.e.* longer). Figure 5 presents this dependence.

It is shown in Figure 5 that upon decreasing the O…F distance a lengthening of the OH bond is observed. At some $d_{(O...F)}$ distance proton is transferring to fluoride, what is accompanied with another H-bond formation, where hydrofluoric acid interacts with an oxo group of the nitrophenolate system. Note that the transfer depends clearly on $-NO_2$ group dihedral angle ϕ (see

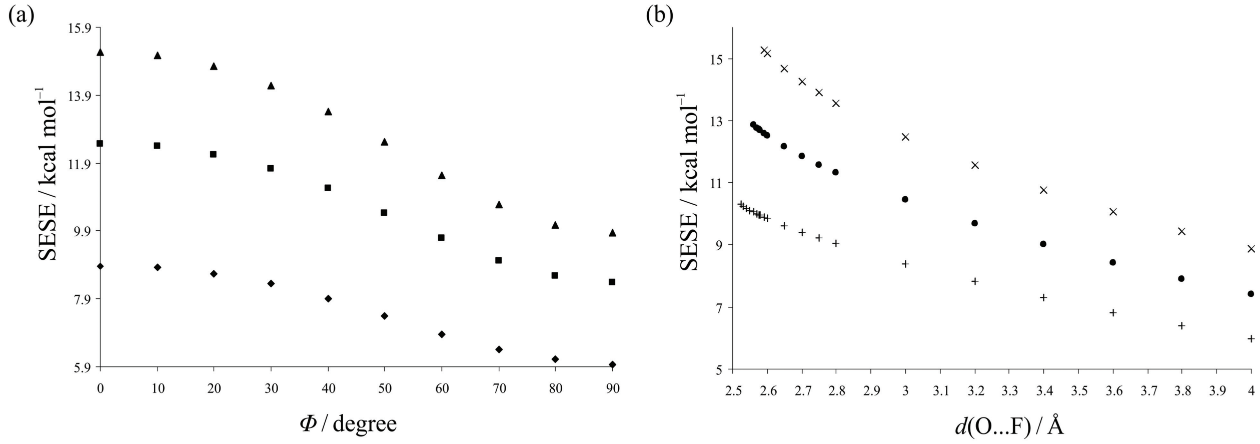


Figure 4. (a) Dependence of SESE (in kcal/mol) on bend angle ϕ for d(O…F) = 4 Å (points denoted as ◆), 3 Å (points denoted by ■), and 2.6 Å (points denoted by ▲) for p-nitrophenol interacting with F^-. (b) Dependence of SESE (in kcal/mol) on the distance between O...F for three selected bend angles ϕ: 0º (denoted as ×), 50º (denoted as ●) and 90º (denoted as +).

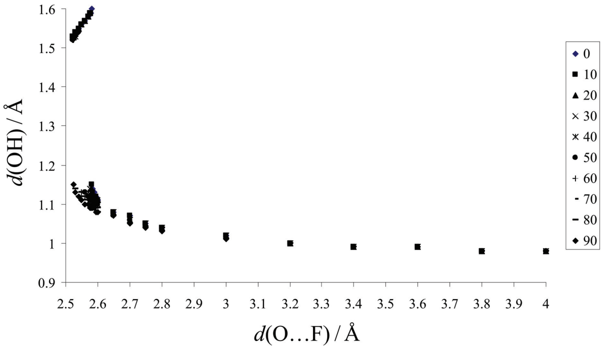


Figure 5. Dependence of *d*(OH) on *d*(O…F), simulating H-bond strength. The upper line is for *p*-nitrophenolates, the bottom line for *p*-nitrophenols. Data for different angles are represented by various symbols shown on the right of the Figure.

Figure 4b). The values of $d_{(\mathrm{O...F})}$ at which proton does transfer show the strength of the interaction of OH group with the nitro group, which depends on the ϕ angle. For $\phi = 90^\mathrm{o}$ the transfer is at the lowest O…F distance $d_{(\mathrm{O...F})} = 2.523$ Å − it means that for this case the electron attracting power of NO_2 group is the weakest and OH bond the strongest. The smaller is the ϕ value, the more negative charge is withdrawn from OH group, and a weaker interaction from F^- is needed to attract proton − the longer is the O…F distance for proton transfer. For planar *p*-nitrophenol ($\phi = 0°$) the O...F distance is equal $d_{(\mathrm{O...F})} = 2.580$ Å.

CONCLUSION

The substituent effect of the nitro group depends strongly on its conformation. It has been shown that the substituent effect stabilization energy (SESE) estimated for *p*-substituted phenolates correlates very well with σ_p^- constants. Based on this dependence the σ_p^- constants for the nitro group as a function of the $-NO_2$ group dihedral angle ϕ were obtained. They change from 1.32 for $\phi = 0^\mathrm{o}$ to 0.72 for $\phi = 90^\mathrm{o}$, in good agreement with experimental values of σ_p^- and σ_I, respectively. Rotation of the nitro group with respect to the aromatic fragment always reduces the efficiency of the through-resonance interaction with an electron-donating counter substituent. The changes in π-electron delocalization are smaller for *p*-nitrophenols as compared with *p*-nitrophenolates, because the hydroxy group is a much weaker electron donating system than the oxo group. For the systems involved in hydrogen bonding, the values of SESE and descriptors of π-electron delocalization such as HOMA, NICS and NICS(1) strongly depend on the strength of the H-bond. For *p*-nitrophenol the difference in values corresponding to the twist of the nitro group from $\phi = 0^\mathrm{o}$ to 90^o is the greatest for cases where the hydrogen bond is strongest (the O…F interatomic distance is the smallest, *i.e.* 2.6 Å). At this distance the *p*-nitrophenol approaches the point when proton transfer from hydroxyl group to fluoride occurs. Consequently, the oxygen atom in the OH group has a high negative partial charge, and this leads to more effective through-resonance interaction with the nitro group. For *p*-nitrophenolates the tendency is reversed, which can be explained in an analogous way.

Supplementary Materials. – Supporting informations to the paper are enclosed to the electronic version of the article. Total energies and the Cartesian coordinates at B3LYP/6-311+G** for all analysed systems are given. These data can be found on the website of *Croatica Chemica Acta.* (http://public.carnet.hr/ccacaa)

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SAŽETAK

Supstituentske konstante (σ_p^-) rotirajuće nitro skupine. Međudjelovanje supstitucijskog efekta rotirajuće $-NO_2$ skupine i H-veze koje utječe na π-elektronsku delokalizaciju 4-nitrofenolnih i 4-nitrofenolatnih kompleksa: B3LYP/6-311+G** studija

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Primjenom B3LYP/6-311+G** razine teorije optimirane su geometrije serije od devet 4-supstituiranih nitrofenola i 4-supstituiranih nitrofenolata (X = H, $CONH_2$, CHO, COOH, $COCH_3$, COCl, CN, NO_2, NO) i njihovih konformera, u kojima nitro skupina rotira za 10º od $\phi = 0º$ do $\phi = 90º$. Podaci su korišteni u analizi efekata rotacije nitro skupine na π-elektronsku delokalizaciju prema prstenu. Pokazano je kako stabilizacijska energija supstituentskog efekta (engl. *substituent effect stabilization energy*, SESE) određena za *p*-supstituirane fenolate dobro korelira sa σ_p^- konstantama. Na osnovu ove ovisnosti dobivene su σ_p^- konstante za nitro skupinu kao funkcija dihedralnog kuta ϕ. Korištenje modela u kojem se mijenja jakost H-veze nadolazeće F^- (HF) skupine prema OH (O^-) skupini 4-nitrofenola (4-nitrofenolata) s rotirajućom nitro skupinom pokazuje ovisnost između promjene aromatičnosti prstena zbog rotacije nitro skupine i promjene jakosti H-veze. Dva indeksa aromatičnosti NICS i HOMA korišteni su za kvantificiranje aromatskog karaktera benzenskog fragmenta.