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Tautomeric equilibria, H-bonding and π-electron delocalization in *o*-nitrosophenol. A B3LYP/6–311+G(2df,2p) study†

Ewa D. Raczyńska,[1]* Tadeusz M. Krygowski,[2] Joanna E. Zachara,[2] Borys Ośmiałowski[3] and Ryszard Gawinecki[3]

[1]Department of Chemistry, Agricultural University (SGGW), Nowoursynowska 159c, 02-776 Warsaw, Poland
[2]Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland
[3]Department of Chemistry, Technical and Agricultural University, Seminaryjna 3, 85-326 Bydgoszcz, Poland

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ABSTRACT: Tautomeric interconversions (keto–enol and nitroso–oxime combined according to the 1,5-proton shift into nitrosoenol–ketoxime) and related variations of π-electron delocalization were studied for *o*-nitrosophenol at the B3LYP/6–311 + G(2df,2p) level. The geometry- and magnetism-based indices (HOMA and NICS) were applied to estimate π-electron delocalization. The relative electronic (ΔE) and Gibbs free energies (ΔG) between the tautomers–rotamers were calculated to estimate tautomeric equilibrium and percentage content of the tautomeric mixture. Aromaticity of the phenyl ring and intramolecular H-bonding were found to be the main factors stabilizing tautomeric forms (two isomeric nitrosoenols and one ketoxime) via increasing π-electron delocalization in the chelating (*quasi*) ring and lowering push–pull interaction between *ortho* substituents. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: *o*-nitrosophenol; nitrosoenol–ketoxime tautomerism; π-electron distribution; HOMA; NICS; intramolecular H-bonding

INTRODUCTION

π-Electron delocalization is an internal factor playing a principal role in tautomerization processes. In the case of cyclic π-electron systems, delocalization is related to a few physico-chemical properties: (i) aromatic stabilization energy, (ii) bond length equalization and (iii) special magnetic properties.[1,2] Of these properties, energies of tautomerization (or tautomeric equilibrium constants) are most frequently used in discussions of the stability of various tautomers.[3–6] Aromatic stabilization energies are often considerably larger than energies of tautomerization, and in such cases (e.g. in phenol) aromaticity decides tautomeric preferences.[7] In some cases, tautomerization processes lead to the formation of a *quasi* ring built of the π-electron chain with an H-bond involved.[8,9] The *quasi* ring may be a part of a greater π-system, e.g. *o*-hydroxy Schiff bases,[10] salicylaldehyde[11] or *o*-nitrosophenol.[12] In these *quasi* rings, some π-electron delocalization is also observed[13–15] that may be interrelated with delocalization in the aromatic part.[16,17]

**Correspondence to:* E. D. Raczyńska, Department of Chemistry, Agricultural University (SGGW), Nowoursynowska 159c, 02-776 Warsaw, Poland.
E-mail: raczynskae@delta.sggw.waw.pl
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In all these cases, geometry may provide reliable information about electron distribution that is related to π-electron delocalization. Following the Hellmann–Feynman theorem,[18] the distribution of electronic density in the molecule determines the forces acting on the nuclei, which in turn define the geometry of the molecule in question. Hence, employing appropriate references, molecular geometry may be used to describe π-electron delocalization. The geometry-based aromaticity index HOMA[19] (harmonic oscillator model of aromaticity) describes π-electron delocalization in principle for cyclic systems.[20,21] However, cyclicity is not necessary; the HOMA index may also be used to quantify π-electron delocalization for linear π-electron systems.[22–24] In this paper, HOMA will also be used in this sense. The magnetism-based descriptor of aromaticity NICS (nucleus independent chemical shift) is another index widely used to describe π-electron delocalization.[25] However, this index is used mainly for cyclic π-electron systems.

The purpose of this work was to analyze the interrelation between stabilization and π-electron delocalization for eight tautomers–rotamers of *o*-nitrosophenol. The stability of tautomers–rotamers was measured by means of the energy of isomerization, ΔE(0 K) and ΔG(298 K). The HOMA index and all three forms of NICS were applied to describe π-electron distribution.

COMPUTATIONAL DETAILS

Geometries of all eight tautomers–rotamers of *o*-nitrosophenol were obtained using the Becke-style three-parameter[26] density functional theory[27] method using the Lee–Yang–Parr correlation functional[28] and the 6–311 + G(2df,2p) basis set as previously chosen for simple pentad tautomeric systems[14] (Gaussian 03[29]). Relative electronic (ΔE) and Gibbs free energies (ΔG) were calculated to estimate relative stabilities and percentage contents of all tautomers–rotamers in the mixture.

The HOMA index[19,21,22,30] was estimated from the theoretically derived bond lengths using the equation

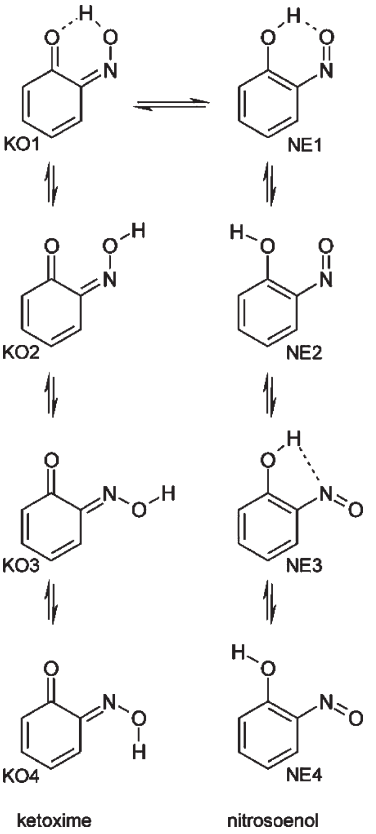
$$\mathrm{HOMA} = 1 - \frac{\alpha}{n}\sum(R_{\mathrm{opt}} - R_{\mathrm{i}})^2 \qquad (1)$$

where n is the number of bonds taken into account, α is a normalization constant, R_{opt} is the optimum bond length assumed for the full electron delocalized system (the R_{opt} value is estimated empirically by use of the harmonic potential applied to determine the energy of extension of the double bond and the energy of compression of the single bond, on condition that for R_{opt} these energies are equal) and R_{i} is the real bond length. According to this assumption, HOMA = 1 for the system with all bonds equal to the optimal values (with complete π-electron delocalization) and HOMA ≤ 0 for the non-aromatic (non-delocalized) system.

NICS is defined as a negative value of absolute shielding estimated in the center of the aromatic moiety in question,[25] whereas NICS(1)[31] estimates the shielding 1 Å above the center. Additionally, the perpendicular component of the NICS(1) tensor, named NICS(1)$_{zz}$,[32] was used. The more negative is the value of NICS, the more aromatic, i.e. delocalized, is the π-electron system. NICSs were calculated at the HF/6–31 + G* level of theory using the GIAO (gauge-independent atomic orbital) method[33] included in Gaussian 03.[29] The geometric center of aromatic rings was determined with the use of the Diamond program.[34]

RESULTS AND DISCUSSION

o-Nitrosophenol (Scheme 1) displays two types of prototropic tautomerism, nitroso–oxime combined with keto–enol tautomerism. Combination of these tautomeric interconversions, running according to the 1,5-proton shift, leads to two tautomers, ketoxime (KO) and nitrosoenol (NE). In turn, rotational isomerism that is possible for the *ortho* substituents allows one to distinguish four rotamers for each tautomeric form (KO1–4 and NE1–4), of which three are intramolecularly H-bonded, one ketoxime (KO1) and two nitrosoenol isomers (NE1 and NE3).



Scheme 1. Rotational isomerism, tautomeric equilibria and H-bonding in *o*-nitrosophenol

Formation of the intramolecular H-bond seems to facilitate tautomeric interconversion. However, there is some debate between Kržan and co-workers[35] and Enchev and co-workers[36] concerning the tautomeric and conformational preferences of *o*-nitrosophenols. The discrepancies between the results obtained by different laboratories may be a consequence of low energies of tautomerization, i.e. low energy barriers for proton transfer in the O—H···O bridge. In the solid state there is no doubt that *o*-nitrosophenols exist in the form of non-chelated ketoxime tautomers.[12]

Analysis of the HOMA (Table 1) and NICS (Table 2) values estimated for all eight tautomers–rotamers (KO1–4 and NE1–4) of *o*-nitrosophenol leads to a few interesting findings. Only one of the four ketoxime rotamers (the chelated structure KO1) displays some electron delocalization [low but positive HOMA values for the phenyl and *quasi* rings, and negative NISC(1) and NICS(1)$_{zz}$ values]. For other ketoxime isomers (KO2–4), which are non-chelated, the π-electron structure is strongly localized in both the OCCNO moiety and the phenyl ring. Hence the HOMA values are negative and NICSs are positive or close to zero.

For all ketoxime structures, a strong push–pull interaction between a very strong electron-donating —O$^-$ group ($\sigma^+ = -2.3$)[37] and a very strong electron-accepting —NOH$^+$ group (for —NO $\sigma^- = 1.63$,[37] but for the

Table 1. HOMA indices estimated for the phenyl ring (Ph) and OCCNO moiety in rotamers of the ketoxime (KO) and nitrosoenol (NE) tautomers of *o*-nitrosophenol

Isomer	HOMA(Ph)	HOMA(OCCNO)	Isomer	HOMA(Ph)	HOMA(OCCNO)
KO1	0.253	0.395	NE1	0.909	0.686
KO2	−0.408	−0.328	NE2	0.961	0.462
KO3	−0.490	−0.458	NE3	0.946	0.604
KO4	−0.506	−0.396	NE4	0.968	0.467

Table 2. NICS, NICS(1) and NICS(1)$_{zz}$ estimated for the phenyl ring in rotamers of the ketoxime (KO) and nitrosoenol (NE) tautomers of *o*-nitrosophenol

Isomer	NICS	NICS(1)	NICS(1)$_{zz}$	Isomer	NICS	NICS(1)	NICS(1)$_{zz}$
KO1	0.69	−3.11	−6.44	NE1	−9.57	−9.91	−24.87
KO2	4.62	−0.46	3.59	NE2	−10.71	−10.60	−27.64
KO3	6.26	0.52	5.43	NE3	−9.00	−9.83	−24.84
KO4	5.80	0.20	4.95	NE4	−10.19	−10.46	−26.39

protonated nitroso group this property must be much greater) is possible. In the case of KO1, an electron-withdrawing effect of the protonated nitroso group is partly decreased by intramolecular H-bonding. This is not the case for KO2–4, where the electron-accepting effect of —NOH$^+$ is not weakened by H-bonding. Hence the push–pull interaction leads to partly double C—O and C—N bonds (∼1.25 and 1.32 Å, respectively) in KO1, whereas for the KO2–4 rotamers, they are much closer to a typical double bond (∼1.22 and 1.30 Å, respectively). It may also be rationalized that the proton attached to the nitroso oxygen atom in KO1 bears some electrostatic field, leading to a different electron distribution in the *quasi* ring displayed by the value of aromaticity index HOMA. The lack of these interactions in the case of KO2–4 leads to a more localized structure due to enhanced push–pull effect of *ortho* substituents. In consequence, it decreases π-electron delocalization. In all these cases, the C—O and C—N bond lengths are more double bonds in nature and imply a more localized π-electron structure, the quinoid-like structure in the phenyl ring. This kind of reasoning was previously used to explain π-electron delocalization in pyrazoles[38] and porphyrines.[39]

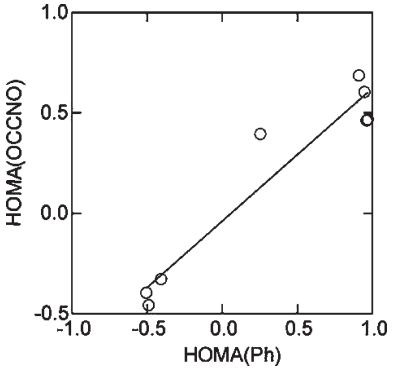


Figure 1. Scatter plot of HOMA values of the phenyl ring (Ph) and the OCCNO moiety (OCCNO). Correlation coefficient 0.954

The π-electron delocalization of the phenyl ring in rotamers of the nitrosoenol form is dramatically higher than that in the ketoxime form. In all nitrosoenol structures (NE1–4), the phenyl ring has a strong aromatic character (HOMA $\geq$ 0.91; NICS values resemble those for benzene[25,40]). π-Electrons in the OCCNO moiety are partialy delocalized (HOMA $\geq$ 0.46), even for the non-chelated structures (NE2 and NE4).

It results from the above discussion that the changes in aromaticity indices for the phenyl ring and the OCCNO moiety should be correlated with each other. The scatter plot of HOMA values for the phenyl ring and the OCCNO moiety presented in Fig. 1 supports this point of view. It is clear that qualitatively the increase in π-electron delocalization in the phenyl ring is associated with the increase of delocalization in the OCCNO moiety. This relationship also suggests that the changes in aromaticity indices for phenyl ring, HOMA and NICS, may be correlated with those of the C—O and C—N bond lengths (Table 3). Figures 2 and 3 show the scatter plots that fully support the above point of view.

In both cases (Figs 1 and 2) the dependences are monotonic, but for HOMA vs *R*(C—O) and *R*(C—N) the relationships are non-linear since the bond lengths in HOMA are used as squared quantities. Of the three forms of NICS, NICS(1)$_{zz}$ was chosen as the most reliable one since the other two NICSs are scalar representatives of the tensor magnitude.[32,41] For all NICSs in Table 2, intercorrelation gives linear regressions with the correlation coefficient at a level better than 0.997. Undoubtedly, owing to π-electron delocalization it may be expected that the changes in C—O and C—N bond lengths are correlated. Figure 4 presents the scatter plot of *R*(C—N) vs *R*(C—O).

Table 3. C—O and C—N bond lengths (Å) in tautomers–rotamers of *o*-nitrosophenol

Isomer	*R*(C—O)	*R*(C—N)	Isomer	*R*(C—O)	*R*(C—N)
KO1	1.251	1.318	NE1	1.330	1.391
KO2	1.219	1.297	NE2	1.348	1.429
KO3	1.216	1.291	NE3	1.342	1.406
KO4	1.214	1.295	NE4	1.350	1.431

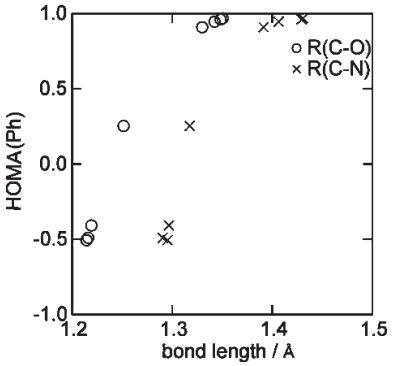


Figure 2. Scatter plots of HOMA for phenyl ring vs. *R*(C—O) and *R*(C—N)

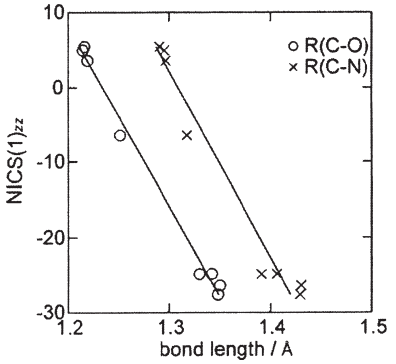


Figure 3. Scatter plots of NICS(1)$_{zz}$ vs *R*(C—O) and *R*(C—N). Correlation coefficient for the first line is −0.996 and for the next −0.982

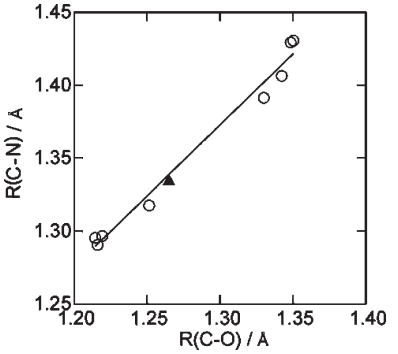


Figure 4. Dependence of *R*(C—N) on *R*(C—O). The black triangle represents the point of *R*(C—N)$_{opt}$ and *R*(C—O)$_{opt}$ taken from HOMA modeling

Interestingly, for the point for *R*(C—N)$_{opt}$ and *R*(C—O)$_{opt}$ (closed triangle in Fig. 4), the optimal bond lengths of the HOMA[19] index lie close to the line (inclusion of this point in the regression decreases the correlation coefficient insignificantly, from 0.9839 to 0.9835). Since all R_{opt} values in the HOMA model are estimated empirically, the finding is a good support for this way of estimation of R_{opt}.

Another interesting aspect relates to energetics (Table 4). The point is that owing to the strong H-bond, the NE1 structure has the lowest energy [the relative electronic energy $\Delta E(0\,\mathrm{K})$ and the relative Gibbs free energy $\Delta G(298\,\mathrm{K})$ is $0.0\,\mathrm{kcal\,mol^{-1}}$ ($1\,\mathrm{cal} = 4.184\,\mathrm{J}$); reference structure], its NE2 rotamer without H-bonding is less stable by 10.5 [$\Delta G(298\,\mathrm{K}) = 10.0$] $\mathrm{kcal\,mol^{-1}}$. Roughly, this may be a qualitative measure of H-bond

Table 4. Relative indices of aromaticity [ΔHOMA(Ph), ΔHOMA(OCCNO) and ΔNICS(1)$_{zz}$][a], energies of isomerization [relative electronic $\Delta E(0\,\mathrm{K})$ and Gibbs free $\Delta G(298\,\mathrm{K})$ energies in $\mathrm{kcal\,mol^{-1}}$][a] and percentage contents (%) of tautomers–rotamers of *o*-nitrosophenol

Isomer	ΔHOMA(Ph)	ΔHOMA(OCCNO)	ΔNICS(1)$_{zz}$	$\Delta E(0\,\mathrm{K})$	$\Delta G(298\,\mathrm{K})$	%
KO1	−0.656	−0.291	18.43	3.2	3.2	0.4
KO2	−1.317	−1.014	28.46	12.4	11.9	<0.001
KO3	−1.399	−1.144	30.30	11.2	10.5	<0.001
KO4	−1.415	−1.082	29.82	18.3	17.2	<0.001
NE1	0.000	0.000	0.00	0.0	0.0	98.4
NE2	0.052	−0.224	−2.77	10.5	10.0	<0.001
NE3	0.037	−0.082	0.03	2.8	2.6	1.2
NE4	0.059	−0.219	−1.52	9.0	8.5	<0.001

[a] All parameters relative to that found for the NE1 structure.

strength in NE1. In the rotamer NE3 there is another H-bond, —OH towards the nitrogen atom in the nitroso group. Its $\Delta E(0\,\mathrm{K})$ value is 2.8 kcal mol^{-1} [$\Delta G(298\,\mathrm{K}) =$ 2.6 kcal mol^{-1}] whereas that of the NE4 rotamer without such interaction is 9.0 (8.5) kcal mol^{-1}. The difference, 6.2 (5.9) kcal mol^{-1}, might suggest that the OH$\cdots$O interaction is stronger by >4 kcal mol^{-1} than the OH$\cdots$N interaction. However, note that the *quasi* ring in NE1 is six-membered whereas in NE3 it is five-membered. Hence a stronger strain may appear in the NE3 *quasi* ring. The O—H—O and O—H—N angles, 144.4° and 114.5°, respectively, support this explanation.

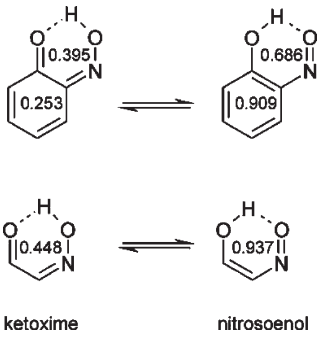
For ketoxime structures, only the KO1 rotamer, where strong push–pull interaction is weakened by the NH$\cdots$O H-bonding, is relatively stable with $\Delta E(0\,\mathrm{K})$ [and $\Delta G(298\,\mathrm{K})] = 3.2$ kcal mol^{-1}, whereas for all other structures strong push–pull interaction between the —NOH$^+$ and —O$^-$ groups leads to clear destabilization. KO2 is a rotamer in which the H-bond of KO1 is broken, and the difference between the relative energies of KO1 and KO2, equal to 9.2 (8.7) kcal mol^{-1}, is often assumed to be a qualitative measure of —NOH$^+\cdots$O$^-$ H-bond strength.[42,43] The change in conformation of the —OH group (owing to its rotation) may also contribute to this energy difference. Note that this energy difference includes the stabilization due both to the H-bond itself and also to a geometry deformation which is associated with an increase in π-electron delocalization. On the other hand, lone pair–lone pair repulsions possible in all non-chelated structures (KO2, KO3, KO4, NE2 and NE4) may be one of the reasons for their high energies. This means that the estimated measures of H-bond strength in the chelated structures (KO1, NE1 and NE3) may be smaller than the difference between the energies of the corresponding rotamers with and without H-bonding (KO1 and KO2, NE1 and NE2, NE3 and NE4).

It results from the above discussion that in the case of NE systems the HOMA and NICS values of the phenyl ring do not change significantly for all rotamers and indicate high π-electron delocalization (Tables 1 and 2). The relative changes in HOMA and NICS(1)$_{zz}$ values are not larger than 0.10 and 3.0, respectively (Table 4). Some difference in π-electron delocalization appears in the case of the OCCNO moiety. When the OH$\cdots$O and OH$\cdots$N H-bonds are formed in NE1 and NE3, the HOMA values are equal to 0.686 and 0.604, respectively. On the other hand, the HOMA values for the systems without H-bonds are much lower, 0.462 and 0.467 for NE2 and NE4, respectively. The lack of H-bonding results in a stronger push–pull interaction between the —OH and —NO groups, and in consequence in a more localized π-structure.

In the case of KO rotamers, strong push–pull interaction between the —NOH$^+$ and —O$^-$ groups strongly localizes the π-electron structure, leading to negative HOMA values and close to zero NICSs. The only exception is KO1, where push–pull interaction is weakened by H-bonding between —NOH$^+$ and —O$^-$ groups. For this case $\Delta E(0\,\mathrm{K})$ [and $\Delta G(298\,\mathrm{K})$] is 3.2 kcal mol^{-1} (stabilization comparable to that for NE1 and NE3). For all the other KO rotamers, the relative energies are >11 kcal mol^{-1}.

Thermal corrections (not larger than 0.5 kcal mol^{-1}) and changes in entropy ($T\Delta S$ term not larger than 2 kcal mol^{-1}) are very small for all tautomers–rotamers, and have only a slight effect on their relative stabilities. Interestingly, tautomerization between the most stable ketoxime (KO1) and the most stable nitrosoenol (NE1) tautomer can be considered as the isoentropic process ($T\Delta S = 0$ kcal mol^{-1}) since tautomers do not change the symmetry, both are H-bonded and both possess the six-membered *quasi* ring. Similar isoentropic behavior has recently been observed at the same level of theory for the simplest intramolecularly H-bonded ketoxime–nitrosoenol system (without any additional π-electron substituents as given in Scheme 2).[14] However, interrelation between stabilization and π-electron delocalization of the ketoxime and nitrosoenol tautomers in this system is different from that in *o*-nitrosophenol.

For the simplest ketoxime–nitrosoenol system, shown at the bottom of Scheme 2, π-electron delocalization is not in line with stability of the tautomers. The ketoxime form with less delocalized π-electrons in the *quasi* ring (HOMA 0.448) is more stable than the nitrosoenol form, with exceptionally high (as for the *quasi* ring) π-electron delocalization (HOMA 0.937). In this case, π-electron delocalization is an important but not the main factor that decides about tautomeric preference. H-bonding and stability of functionalities seem to play a principal role. The situation changes dramatically in *o*-nitrosophenol, where the *quasi* ring is part of the phenyl ring. In this case, π-electron delocalization in the phenyl ring seems to be responsible for tautomeric stabilities. Tautomeric equilibrium is shifted strongly towards the more aromatic nitrosoenol form. Although the presence of the phenyl ring decreases π-electron delocalization in the *quasi* ring to a higher degree for the nitrosoenol form than for the ketoxime form in comparison with the simplest system



Scheme 2. Influence of the phenyl ring on tautomeric equilibrium and π-electron distribution (HOMA index) in ketoxime–nitrosoenol H-bonded systems

(HOMA is reduced from 0.937 to 0.686 and from 0.448 to 0.393, respectively), the nitrosoenol form with higher π-electron delocalization in the phenyl ring (HOMA 0.909) than that in the ketoxime form (HOMA 0.253) is favored in the tautomeric mixture. In consequence, π-electron delocalization in both rings (phenyl and *quasi*) is in line with the stability of tautomers.

In conclusion, aromaticity of the phenyl ring plays a principal role in stability of the favored tautomer of *o*-nitrosophenol. Localization of the π-electron structure due to a strong push–pull effect of *ortho* substituents destabilizes the system. H-bonding decreasing the push–pull interaction between the electron-donating group (OH or O^-) and the electron-accepting group (NO or NOH^+) stabilizes the system and increases π-electron delocalization.

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