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Theoretical Analysis of Molecular Structure, Hydrogen Bond Strength, and Proton Transfer Energy in O−H··O Aromatic Compounds

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Molecular geometries for a set of 2-hydroxybenzoyl compounds were obtained at B3LYP/6-31G** level and analyzed in view of a parametric model of intrinsic substituent effects by Taft and Topsom. The structural study of the non- and hydrogen-bonded species, together with proton transferred forms, resulted as very useful in understanding the different factors determining the intramolecular hydrogen bond strength and the proton transfer process in this family of molecules. In addition, the previous study was extended to a sequence of other related six-membered hydrogen-bonded structures (alkane, naphthalene, and alkene derivatives) with increasing aromaticity. The results clearly showed the influence of the covalent and electrostatic (acid−base) nature of the hydrogen bond system on its commonly related chemical properties, hydrogen bond strength, and proton-transfer energy. A significant finding in this paper is the approach between the oxygens that yields the internal hydrogen bond, which occurs in the midpoint of the proton transfer, depends on the acid−base characteristics of the proton donor and acceptor groups, and it is not substantially affected by the aromaticity of the system.

1. Introduction

Organic molecules as 2-hydroxybenzoyl compounds (see Scheme 1) possess a strong intramolecular hydrogen bond (IMHB) (Chart 1) as a result of they bearing a hydroxyl group and a carbonyl group that act as a proton donor (acid) and acceptor (base), respectively, in adjacent positions. It is widely accepted that the presence of this strong IMHB is partly responsible for the characteristic photophysics properties of these compounds.[1,2] According to the mechanism proposed by Weller,[3,4] the changes in the acid−base properties of the hydroxyl and carbonyl groups on the aromatic ring by the effect of electronic transitions may give rise to the mechanism shown in Scheme 1. Proton transfers (PT) take place via the IMHB, and therefore, its characteristics should mainly influence these processes.

The nature of the intramolecular hydrogen bond of 2-hydroxybenzoyl derivatives has been studied by several experimental techniques such as infrared (IR),[5−14] Raman,[15] nuclear magnetic resonance (NMR),[16−18] and X-ray and neutron diffraction[19−23] spectroscopies. Theoretical calculations nowadays provide a complementary way to study these molecular systems containing an IMHB. The development of density functional theory (DFT) at present has allowed one to obtain accurate information on these medium-size IMHB compounds. In fact, they predict molecular properties, such as geometries, IR or Raman frequencies, and chemical shifts, which match outstandingly well the available experimental data.[24−34]

Historically, IR spectroscopy has been the most used method to detect and characterize hydrogen bonds.This technique has shown that 2-hydroxybenzoyl compounds only form strongly internal hydrogen-bonded isomers in inert media.[5−14] In addition, IR measurements proved that the IMHB strength for a series of related aromatic compounds increased with the double bond character of the bond that connects the functional groups ($C_3{=}C_4$; see Chart 1).[6] In this sense, IR data have been commonly used for evaluating the strength of the hydrogen bond of the type −O−H··O=, taking into account the frequency shift of the characteristic donor (O−H) or acceptor (C=O) stretching bands, $\Delta\tilde{\nu} = \tilde{\nu}_{\text{non-IMHB}} - \tilde{\nu}_{\text{IMHB}}$, by the influence of the IMHB.[5,8] The problem of both frequently used criteria is the

SCHEME 1

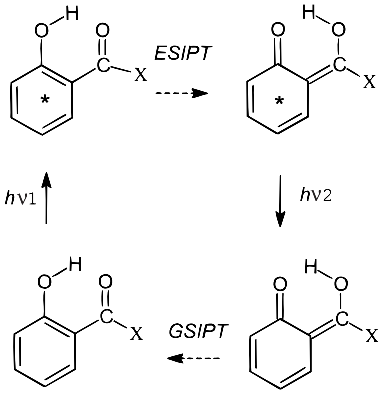
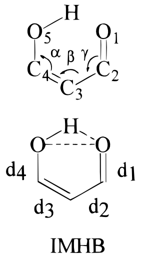


CHART 1



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10.1021/jp994067o CCC: $19.00

CHART 2

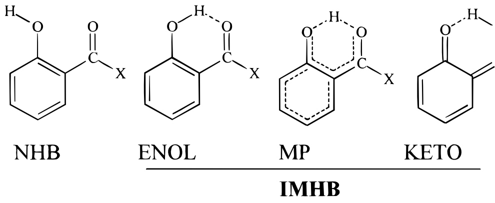
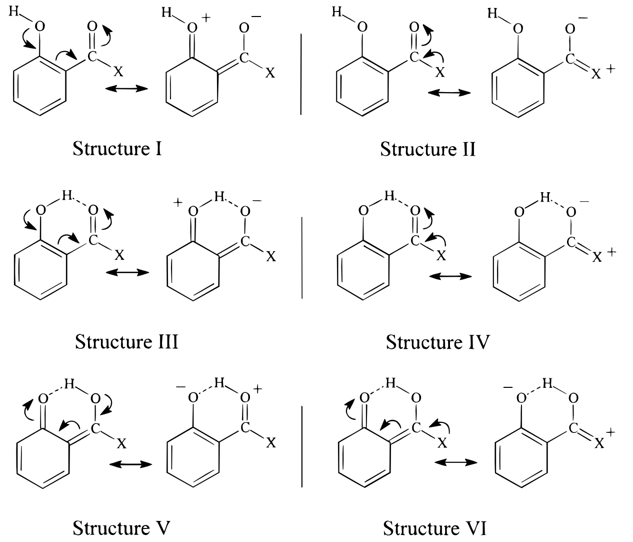


CHART 3



fact by which frequencies of the corresponding non-IMHB molecules are not experimentally available for *2*-hydroxybenzoyl compounds, almost 100% internally hydrogen bonded. Intuitively, the IMHB strength for one family of molecules of O−H proton donors (i.e. phenols, naphthols, etc.) should depend both on the basicity of the carbonyl groups and on the spatial arrangement of the bonds that are formed.[12,25] It is well-known that the chemistry of the carbonyl groups is dominated by lone pair interactions and electronegativity changes.[35,36] Kallie et al.,[37] using natural bond orbital (NBO) analysis, proved that −Me, −Ph, −OR, and $-NR_2$ substituents donate electrons into the π^*(C═O) antibonding orbital of the carbonyl group to an increasing amount, yielding an increasing resonance for this group. A new concept of competing π-electron donating X fragment was introduced, which explains the high resonance stabilizations of benzamides and urea. Steinwender et al.[12] studied the substituent effects on the IMHB for a number of 2-hydroxybenzoyl compounds. They found the sequence of ν(O−H) frequencies could roughly be related to the ν(C═O) frequencies of the corresponding simple benzoyl compounds. However, the values of the $\Delta\nu$(C═O), using these non-IMHB references, could not reasonably be related to ν(O−H) data. It was explained as a consequence of the observed $\Delta\nu$(C═O) values also including the opposing electron-donating effect of the phenolic fragment on the carbonyl group. On the other hand, Lampert et al.[25] showed that a theoretical aproximation of the hydrogen bond energy, $E_{\mathrm{IMHB(NO)}}$, (defined as the difference between the B3LYP/6-31G** energy of the ENOL isomer and that for this structure with the O−H rotated 180°, NHB; see Chart 2) excellently parallel the trends of ν(O−H) frequencies for the 2-hydroxybenzoyl series. Later, our group[29] found that the same E_{IMHB} approximation, but obtained with fully optimization of both NHB and ENOL structures, $E_{\mathrm{IMHB(O)}}$, showed an almost perfect consistency with the corresponding Lampert's values for this family of compounds. The dependence of $E_{\mathrm{IMHB(O)}}$ values on the X substituent was successfully analyzed using a parametric model of intrinsic substituent effects by Taft and Topsom:[38,39]

$$E_{\mathrm{IMHB(O)}} = \rho_{\mathrm{R+}}\sigma_{\mathrm{R+}} + \rho_{\mathrm{F}}\,\sigma_{\mathrm{F}} + \rho_{\alpha}\sigma_{\alpha} + C \qquad (1)$$

Here $\sigma_{\mathrm{R+}}$, σ_{F}, and σ_{α} are the constants of the resonance, inductive field, and polarizability effects, respectively, which characterize the behavior of the X substituent.

We obtained that the resonance of the electronic donor X fragment yields the increase of the basicity in the carbonyl group and, consequently, the strength of the IMHB. On the other hand, the inductive effect of X deactivates the lone pair of the carbonylic oxygen and, therefore, weakens the hydrogen bond. In addition, Berthelot et al.[13] used Taft's substituent constants as well to research IR results of a number of 2-hydroxybenzoyl compounds. They noted that the IMHB strength was influenced not only by the electron-donating effect of X but also by the electron-withdrawing effect of COX, increasing the acidity of the hydroxyl group and the steric effects of bulky substituents. Recent B3LYP/6-31G** results by our group[33] for some 2-hydroxybenzoyl derivatives showed that, using NHB rotamers as a reference, the $\Delta\nu$(C═O) values are lineraly correlated to the $E_{\mathrm{IMHB(O)}}$ data. However, an inverse relation between both parameters compared to that presented by Zadarozhnyi was found.[8] We concluded that the vibrations of the acceptor C═O group mainly depend on the resonance effects of the substituent, which contribute to the electrostatic interaction of the hydrogen bond. But, at the same time, a π-donor X group hinders the increase of electronic delocalization due to hydrogen bond formation, which slightly diminishes the covalent contribution to the IMHB stability and, in addition, the acidity of O−H group.

NMR parameters widely used for characterizing the type of IMHBs studied are the O−H chemical shifts, δ_{OH}, primary isotope effects, or secondary deuterium isotope effects on chemical shifts (as for ^{13}C, $^{n}\Delta C$(OD)).[12,16−18,32] Thus, it was shown that δ_{OH} as well as $^{2}\Delta C$(OD) isotope effects reflects the strength of the IMHB in the family of 2-hydroxybenzoyl compounds. However, different correlations were found between δ_{OH} and $^{2}\Delta$C(OD) for different benzene-substituted hydroxybenzoyl compounds, which was explained because $^{2}\Delta$C(OD) depends on the bond order of d_3 (Chart 1) (i.e., on the electronic rearrangements in the molecular skeleton of the IMHB system) whereas δ_{OH} increases with the acidity of O−H group.

X-ray and, particularly, neutron diffraction spectroscopies provide accurate structural data for IMHB geometries.[19−23] Through studies of a great number of related IMHB molecules, it was proved that experimental O−H lengths are good descriptors of IMHB strength. Moreover, O••O and H••O distances were also shown as adequate parameters for quantifiying the hydrogen bond interaction, since both were found proportional to the mutually intercorrelated magnitudes ν(O−H), δ_{OH}, and O−H length. On the basis of crystallographic studies, Gilli et al.[21] concluded that there is a class of strong hydrogen bonds, noted as ••O═C−C═C−O−H•• (resonance-assisted hydrogen bonding, RAHB), which is due to the fact that the neutral donor and acceptor atoms are connected by a system of π-conjugated double bonds. Taking into account only the relation existing between the bond lengths of the IMHB system shown in Chart 1, the authors proposed a model in which the special stability of this structure is associated with the great extent of π-delocation along the chain, i.e, to the capacity of the system to form the polar structure (zwitterion) written as structure III in Chart 3. This phenomenon is essentially a synergistic reinforcement of the hydrogen bonding and π delocation: the partial charges generated by resonance increase the hydrogen bond interaction, and then the proton is moved toward the carbonyl group compensating the opposite charges and favoring the π system. According to this model, the strongest IMHB occurs in those systems with strong covalent character, where ENOL and KETO forms (Chart 2) are practically equivalent, giving minimal O··O distances and a hydrogen atom approximately symmetrical between the oxygens. An additional conclusion is that the role played by the acid−base properties of the donor and acceptor groups in these systems is almost irrelevant.

A discussion about the connection between the existence and the magnitude of the barrier to proton transfer and the strength of the IMHB exists in the literature. A tight relationship between both parameters was found for different electronic states of malonaldehyde and similar compounds.[41−44] Recently, the ground-state proton−transfer (GSIPT) curves were obtained by our group at the B3LYP/6-31G** level for a number of 2-hydroxybenzoyl compounds.[29] In all cases our results provided a GSIPT curve with a single minimum in the enol zone, where structures evolve from a typical enol form to the keto form by an approach of the atoms that yield the IMHB in the midpoint (MP) of the transfer (see Chart 2). For the molecules studied, no correlation was found between the IMHB energy, E_{IMHB}, and the proton-transfer barrier, E_{barrier}. This finding could be understood from the different dependences on Taft and Topsom's substituent constants.[38,39] Thus, according to the results of the adjustment

$$E_{\mathrm{barrier}} = \rho_{\mathrm{R+}}\sigma_{\mathrm{R+}} + \rho_{\mathrm{F}}\,\sigma_{\mathrm{F}} + \rho_{\alpha}\sigma_{\alpha} + C \qquad (2)$$

E_{barrier} was acceptably described only by the inductive field effect of X. Recently, Lee et al.[44] published a theoretical study on keto−enol tautomerization involving carbonyl derivatives. Analysis of the relative isomer stabilities by a substituent parameter model showed that the keto form is always lowered in energy and strongly stabilized by a π-donor, whereas the enolization is less unfavorable for π-acceptor substituents.

In this work we analyze the substituent dependence of the structures for a number of 2-hydroxybenzoyl compounds (X = H, CH_3, OCH_3, NH_2, CN, NO_2, Cl, and F). For this purpose, we perform a multiple linear regression analysis of substituent effects on the IMHB distances (Chart 1)

$$d_{\mathrm{IMHB}} = \rho_{\mathrm{R+}}\sigma_{\mathrm{R+}} + \rho_{\mathrm{F}}\,\sigma_{\mathrm{F}} + \rho_{\alpha}\sigma_{\alpha} + C \qquad (3)$$

using molecular geometries obtained at the B3LYP/6-31G** level. This study will be carried out in ENOL and NHB forms and through the proton-transfer curves (MP and KETO forms; see Chart 2). Previous analysis will prove an useful way for understanding the different factors determining the strength of the hydrogen bond, E_{IMHB}, or the proton-transfer barrier, E_{barrier}, in this family of IMHB compounds. To analyze the influence of the aromaticity on this type of internal hydrogen-bonded system, the previous study will be extended to related six-membered IMHB structures with a different nature of the bond joining the hydroxyl and carbonyl groups. The results of this work will definitively show the main influence of the electrostatic and covalent nature of the IMHB interaction on relevant chemical properties of this type of O−H··O intramolecular hydrogen-bonded compound.

2. Theoretical Procedure

All the molecular geometries have been calculated by means of the B3LYP[46,47] method in conjunction with a 6-31G** basis set. ENOL and NHB geometries (see Chart 2) have been obtained with a full energy optimization at the B3LYP/ 6-31G** level. An O−H bond distance of 1.6 Å is assigned to the KETO form, and the remaining coordinates were optimized at the B3LYP/ 6-31G** level. An intermediate structure, MP, with $R_{\mathrm{O-H}}$ = 1.3 Å, was obtained for each compound by this theoretical procedure as a representative geometry for the midpoint of the proton transfer. In Table 1 are collected the bond distances of the NHB, ENOL, MP, and KETO structures for the 2-hydroxybenzoyl compounds studied. It should be noted that planar geometries are obtained except for X = NH_2, whose ENOL form and, especially, NHB form have the amide group deviated out of the molecular plane.

The strength of the intramolecular hydrogen bond (IMHB), E_{IMHB}, in the stable form of each molecule studied was estimated as the difference between the energies for the fully optimized ENOL and NHB forms. The proton-transfer barrier, E_{barrier}, was evaluated as the difference between the energy corresponding to KETO and ENOL structures. The energy value for the midpoint (MP) of the GSIPT curves was denoted by E_{MP}. Table 2 shows the calculated values of those parameters for the 2-hydroxybenzoyl compounds studied, together with the field-inductive (σ_{F}), resonance ($\sigma_{\mathrm{R+}}$), and polarizability (σ_{α}) substituent parameters.[38−40]

All the calculations have been performed with the Gaussian 94 program.[48]

Statistical analysis have been adequately stablished since $\sigma_{\mathrm{R+}}$, σ_{F}, and σ_{α} parameters are nearly independient variables in the multiple linear regression, having tolerances up to 0.9.

3. Results

3.1. Structural Analysis of Non-IMHB Isomers of 2-Hydroxybenzoyl Compounds. First, we study the effect of the substituent (X) on the structures NHB (Chart 2). In Table 1 are recollected the bond distances of the NHB isomers for the eight 2-hydroxybenzoyl compounds studied. As can be observed, the complete structure is affected by the substituent, and those effects are greatest on the bonds of the carbonyl carbon, d_1 and d_2. As an exception, the bonds d_4 and O−H, which compose the C−O−H group, are practically identical for all of the compounds.

We analyze these effects by fitting the bond lengths of the NHB molecules studied (Table 1) and the parameters $\sigma_{\mathrm{R+}}$, σ_{F}, and σ_{α} of the substituent (Table 2). Table 3 gathers the results of the analysis. We find that, in contrast to the rest of X, the effects produced by CN and NO_2 cannot be adequately described by the substituent parameters used. This fact was noted previously,[29] and it will be studied in section 3.6 of this paper.

From the coefficients obtained for eq 3, shown in Table 3, the observations a−d follow:

(a) The inductive field effect has as a principal consequence the reduction of the adjacents bonds to C−X. In the case of the C═O group, this fact results from the strong polarization in the direction $C^{+}-O^{-}$. The electron acceptor substituents increase the positive charge of the carbon atom, which results in a greater Coulombic interaction between the C_2 and O_1 atoms, with the consequent decreasing of the bond length. Due to the tendency of C_3 to be charged negatively, an analogous behavior of the d_2 bond with respect to the inductive field is expected.

(b) The substituent resonance effect increases the length of the bonds of the carbon to which it is bonded. Taking into account the π donor character of X, the lengthening of C═O would be produced by the participation of the canonic form described as structure II in Chart 3, which must be competitive

TABLE 1: Bond Distances (Å) of the IMHB System for 2-Hydroxybenzoyl Structures (See Chart 1 and 2)

	d_1				d_2				d_3				d_4				O−H		O••O				H••O		
X	NHB	ENOL	MP	KETO	NHB	ENOL	MP	KETO	NHB	ENOL	MP	KETO	NHB	ENOL	MP	KETO	NHB	ENOL	NHB	ENOL	MP	KETO	ENOL	MP	KETO
NH_2	1.220	1.246	1.286	1.310	1.505	1.481	1.443	1.423	1.410	1.421	1.443	1.461	1.359	1.339	1.296	1.272	0.966	0.996	2.863	2.552	2.405	2.540	1.645	1.153	1.021
CH_3	1.220	1.242	1.284	1.310	1.498	1.470	1.422	1.401	1.419	1.425	1.450	1.470	1.355	1.337	1.291	1.266	0.967	0.994	2.651	2.556	2.395	2.535	1.656	1.144	1.018
NO_2	1.191	1.213	1.267	1.296	1.469	1.449	1.405	1.389	1.428	1.437	1.471	1.495	1.350	1.336	1.283	1.258	0.968	0.983	2.597	2.575	2.387	2.519	1.709	1.144	1.014
H	1.214	1.235	1.279	1.304	1.479	1.452	1.406	1.386	1.415	1.422	1.450	1.469	1.353	1.339	1.290	1.265	0.967	0.990	2.774	2.620	2.402	2.535	1.730	1.153	1.022
OCH_3	1.213	1.234	1.275	1.303	1.490	1.469	1.429	1.408	1.415	1.420	1.443	1.461	1.356	1.342	1.298	1.272	0.967	0.987	2.694	2.606	2.421	2.543	1.720	1.173	1.027
CN	1.217	1.238	1.287	1.314	1.476	1.451	1.408	1.391	1.419	1.426	1.457	1.477	1.351	1.336	1.286	1.261	0.968	0.987	2.696	2.606	2.394	2.530	1.724	1.169	1.024
F	1.193	1.212	1.265	1.287	1.475	1.455	1.411	1.388	1.415	1.421	1.447	1.468	1.353	1.341	1.294	1.267	0.967	0.982	2.727	2.657	2.427	2.539	1.793	1.185	1.030
Cl	1.190	1.212	1.263	1.295	1.476	1.458	1.413	1.392	1.421	1.427	1.457	1.477	1.351	1.339	1.291	1.264	0.967	0.982	2.643	2.613	2.413	2.535	1.750	1.169	1.024

TABLE 2: Substituent Effect Parameters of Resonance (σ_{R+}), Inductive Field (σ_F), and Polarizability (σ_α) and Calculated Energy Values (kcal mol^{-1}) (See text) of 2-Hydroxybenzoyl Compounds

X	σ_{R+}	σ_F	σ_α	E_{IMHB}	E_{MP}	$E_{barrier}$
NH_2	−0.52	0.14	−0.16	15.4	8.7	13.2
CH_3	−0.08	0.00	−0.35	14.2	8.3	11.3
NO_2	0.00	0.65	−0.26	9.7	11.7	15.7
H	0.00	0.00	0.00	12.3	9.2	11.5
OCH_3	−0.42	0.25	−0.17	12.3	12.1	17.6
CN	0.00	0.60	−0.46	11.0	9.6	12.0
F	−0.25	0.44	0.13	10.1	14.2	19.3
Cl	−0.17	0.45	−0.43	9.6	13.6	18.6

with the other resonance present in the system (structure I in Chart 3). The effects of σ_{R+} on the distance d_2 are indirect and competitive with the canonic structure that governs this bond. Thus, a greater σ_{R+} value means a greater impediment for structure I (Chart 3) and, consequently, the d_2 length increases. The participation of different resonances in the final geometry justifies the lower correlation coefficient found between the distance d_2 and the parameters of X.

(c) Regarding the remaining distances in the system, they slightly depend on the propagation of the substituent effects through the molecular structure. The results obtained in our analysis (Table 3) show that d_3 increases with σ_F, as consequence of the electron density displacement toward the C_2 atom. On the opposite side, d_3 is shortened by σ_{R+}, whose effect prevents the resonance between the carbonyl and benzene fragments (structure I in Chart 3). It should be noted that the polarizability effect of X is negligible in the carbon−oxygen bonds, but it is not so on the bonds between carbon atoms, d_2 and d_3.

(d) The separation between oxygens, O••O, must depend not only on the substituent effects on the bond distances but also on the steric interactions between X and the benzene ring. As is expected, the O••O distance does not bear a linear relation with the parameters of X. The fit indicates that the resonance effect prevails over the inductive one, broadening the system, since the substituent resonance hinders structure I. O••O is reduced by σ_F, because of the bond length shortenings in the structure.

3.2. Structural Analysis of Systems with IMHB. Now we analyze the effects of the substituent on systems where an intramolecular hydrogen bond (ENOL in Chart 2) exists in the structure.

In Table 1, it can be observed the changes of the bond distances produced by the hydrogen bond for the structures studied (i.e., the difference between NHB and ENOL isomers). Thus, the IMHB interaction increases d_1 and O−H and decreases d_2; moreover, d_3 lengthens and d_4 shortens, though in a minor amount. It can be concluded that the internal hydrogen bond causes a greater participation of the aromatic system resonance (structure III in Chart 3) in the final geometry of the molecule. Concerning the O••O distance, we find that it is strongly shortened with the IMHB formation. For the species with X = NH_2, the great difference in the O••O distance arises from the NHB form, whose amide group is strongly out of the plane.

Considering the structural data for ENOL structures in Table 1, we find that the effects of substituents are very similar to those observed for the NHB structures. However, the O−H bond now depends on the nature of X. On the other hand, we find that the O••O distance is less affected by X, while the H••O distance behavior parallels that of O••O in the ENOL form.

The analysis of the bond distance dependency on the substituent parameters of the IMHB system provides the

TABLE 3: Multiple Linear Regression Equations between the Bond Distances (Å) of the IMHB Structure Drawn in Chart 1 for 2-Hydroxybenzoyl Compounds and the Substituent Effect Parameters

	NHB	ENOL
d_1	$1.215 - 0.030(\pm 0.005)\sigma_{R+} - 0.068(\pm 0.005)\sigma_F$ ($r = 0.99$; Sd $= 0.001$)	$1.235 - 0.037(\pm 0.002)\sigma_{R+} - 0.074(\pm 0.002)\sigma_F - 0.008(\pm 0.002)\sigma_\alpha$ ($r = 1.0$; SD $= 0.001$)
d_2	$1.483 - 0.047(\pm 0.014)\sigma_{R+} - 0.047(\pm 0.014)\sigma_F - 0.019(\pm 0.012)\sigma_\alpha$ ($r = 0.95$; SD $= 0.006$)	$1.455 - 0.049(\pm 0.011)\sigma_{R+} - 0.029(\pm 0.011)\sigma_F - 0.020(\pm 0.010)\sigma_\alpha$ ($r = 0.96$; SD $= 0.005$)
d_3	$1.416 + 0.014(\pm 0.004)\sigma_{R+} + 0.009(\pm 0.004)\sigma_F - 0.010(\pm 0.003)\sigma_\alpha$ ($r = 0.97$; SD $= 0.002$)	$1.422 + 0.008(\pm 0.003)\sigma_{R+} + 0.004(\pm 0.003)\sigma_F - 0.010(\pm 0.003)\sigma_\alpha$ ($r = 0.96$; SD $= 0.001$)
d_4		
O−H		$0.991 - 0.013(\pm 0.006)\sigma_{R+} - 0.028(\pm 0.006)\sigma_F$ ($r = 0.96$; SD $= 0.003$)
O··O	$2.742 - 0.240(\pm 0.177)\sigma_{R+} - 0.196(\pm 0.174)\sigma_F - 0.199(\pm 0.162)\sigma_\alpha$ ($r = 0.82$; SD $= 0.075$)	$2.612 + 0.101(\pm 0.043)\sigma_{R+} + 0.145(\pm 0.042)\sigma_F + 0.112(\pm 0.039)\sigma_\alpha$ ($r = 0.96$; SD $= 0.018$)
H··O		$1.721 + 0.148(\pm 0.052)\sigma_{R+} + 0.235(\pm 0.051)\sigma_F + 0.122(\pm 0.048)\sigma_\alpha$ ($r = 0.97$; SD $= 0.022$)
	MP	KETO
d_1	$1.280 - 0.021(\pm 0.006)\sigma_{R+} - 0.048(\pm 0.005)\sigma_F$ ($r = 0.99$; SD $= 0.002$)	$1.304 - 0.018(\pm 0.002)\sigma_{R+} - 0.042(\pm 0.002)\sigma_F - 0.016(\pm 0.002)\sigma_\alpha$ ($r = 1.0$; SD $= 0.001$)
d_2	$1.408 - 0.068(\pm 0.008)\sigma_{R+} - 0.030(\pm 0.008)\sigma_F - 0.018(\pm 0.007)\sigma_\alpha$ ($r = 0.99$; SD $= 0.003$)	$1.387 - 0.069(\pm 0.007)\sigma_{R+} - 0.034(\pm 0.006)\sigma_F - 0.020(\pm 0.001)\sigma_\alpha$ ($r = 0.99$; SD $= 0.003$)
d_3	$1.449 + 0.021(\pm 0.005)\sigma_{R+} + 0.011(\pm 0.005)\sigma_F - 0.010(\pm 0.004)\sigma_\alpha$ ($r = 0.96$; SD $= 0.002$)	$1.469 + 0.026(\pm 0.006)\sigma_{R+} + 0.016(\pm 0.006)\sigma_F - 0.011(\pm 0.005)\sigma_\alpha$ ($r = 0.97$; SD $= 0.002$)
d_4	$1.290 - 0.015(\pm 0.003)\sigma_{R+}$ ($r = 0.92$; SD $= 0.002$)	$1.265 - 0.017(\pm 0.003)\sigma_{R+} - 0.006(\pm 0.003)\sigma_F$ ($r = 0.97$; SD $= 0.001$)
O··O	$2.404 + 0.049(\pm 0.012)\sigma_F + 0.024(\pm 0.012)\sigma_\alpha$ ($r = 0.93$; SD $= 0.006$)	$2.534 - 0.0140(\pm 0.004)\sigma_{R+}$ ($r = 0.86$; SD $= 0.002$)
H··O	$1.153 + 0.065(\pm 0.010)\sigma_F + 0.028(\pm 0.015)\sigma_\alpha$ ($r = 0.96$; SD $= 0.007$)	$1.022 + 0.016(\pm 0.005)\sigma_F + 0.011(\pm 0.005)\sigma_\alpha$ ($r = 0.94$; SD $= 0.002$)

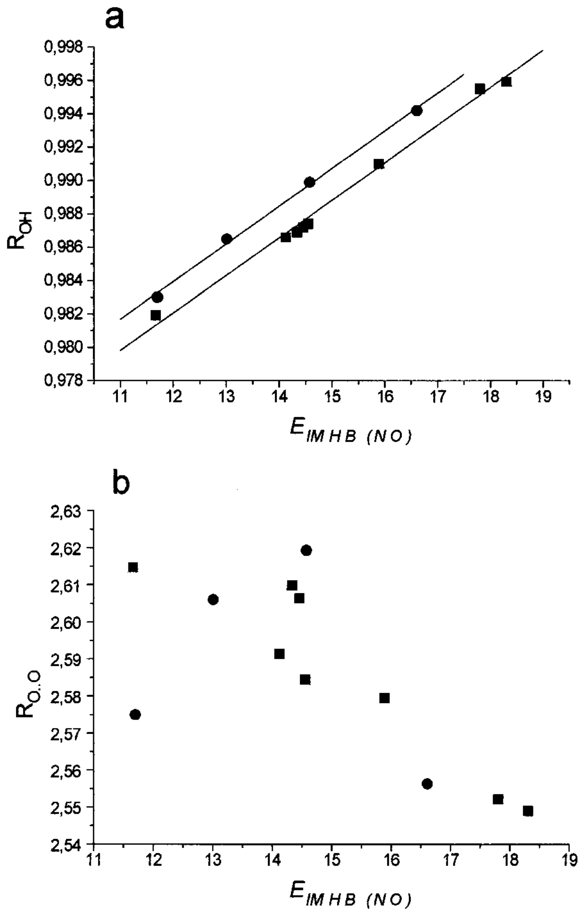


Figure 1. (a) OH and (b) O··O bond distances (Å) vs $E_{IMHB(NO)}$ values (kcal mol^{-1})[26,29] for a set of 2-hydroxybenzoyl compounds calculated at the B3LYP/6-31G** level.

following information (Table 3): (a) The bond length of the carbonyl group, d_1, for the series of 2-hydroxybenzoyl compounds mainly depends on the resonance and inductive field effects of the substituent; therefore, qualitatively identical changes are produced independently of the IMHB formation. (b) The bond length d_2 is described by the parameters of X in a similar way to that of the open form, NHB. However, because the resonant form of the chain (structure III in Chart 3) is now favored, the distance d_2 is more sensitive to the competitive effect of the resonance between X and the carbonyl group (structure IV in Chart 3). (c) For the remaining structure, we find that the distances of the IMHB structure depend on X, like those of the NHB structures. However, worse statistical correlation and smaller changes in the bond distances with the nature of X for ENOL than for NHB isomers could indicate competitive structural effects occurring through the carbon chain and the hydrogen bond. (d) The changes in the distance of the hydroxyl group are adequately described by the X parameters, depending mainly on σ_F, which shortens this distance, while the σ_{R+} effects lengthens it. Thus, the O−H distance in the system IMHB clearly depends on how X affects the carbonyl oxygen. On the other hand, the correlation between the O··O distance and σ_{R+}, σ_F, and σ_α is improved when a IMHB occurs in the molecule. For these structures, the O··O distance principally increases by inductive field effects and is reduced by resonance effects of the substituent. Thus, it is clear that this distance is determined by the effects of X through the hydrogen bond as well.

3.3. IMHB Strength. The fit between the estimated values of the IMHB strength, E_{IMHB}, and the substituent parameters

TABLE 4: Multiple Linear Regression Adjustment Equations between the Calculated Energy Values (kcal mol^{-1}) for 2-Hydroxybenzoyl Compounds and the Substituent Effect Parameters

E_{IMHB}	$12.9 - 6.7(\pm1.8)\sigma_{\mathrm{R+}} - 10.5(\pm1.8)\sigma_{\mathrm{F}}$ ($r = 0.96$; SD $= 0.8$)
E_{MP}	$8.8 + 2.4(\pm2.0)\sigma_{\mathrm{R+}} + 12.9(\pm2.0)\sigma_{\mathrm{F}}$ ($r = 0.97$; SD $= 0.9$)
E_{barrier}	$11.5 + 17.5(\pm2.2)\sigma_{\mathrm{F}}$ ($r = 0.97$; SD $= 1.0$

(Table 4) shows coherent results with the conclusions obtained in previous structural analysis of 2-hydroxybenzoyl compounds (Table 3). Thus, for the IMHB molecules studied, the stability of the hydrogen bond depends mainly on the effect of the inductive field of the substituent, which weakens the IMHB. The resonance effect, on the other hand, strengthens the IMHB. These results indicate that the hydrogen bond system in these compounds is mainly affected by the nature of X through the carbonyl group. Thus, the IMHB strength mainly depends on the basicity of the carbonylic oxygen, which increases with the resonance of the X substituent, while the inductive field of X deactivates the lone pairs of this atom, reducing its acceptor character.

As it is shown in Table 1, the larger the O−H bond, the stronger the IMHB (Table 2). Figure 1a confirms that the O−H distance is linearly correlated with the IMHB strength, E_{IMHB}, for a great number of *o*-hydroxybenzoyl compounds. A parallel behavior, but corresponding to O−H distances slightly larger, is found for substituent with null or almost null $\sigma_{\mathrm{R+}}$ effects (●). It clearly evidences the competing resonances in the IMHB structure. On the other hand, the O••O (and H••O) distances show a worse correlation with E_{IMHB} values (Figure 1b).

3.4. Proton Transfer (PT). Now, we study the effect of the substituent on the distances of the IMHB system along the proton transfer in the ground state of 2-hydroxybenzoyl compounds. As it was shown,[28,29] during the proton transfer process these molecules evolve from a typically ENOL form to a KETO form, which approximately corresponds to an O−H distance of 1.6 Å (see Chart 2).

Analyzing the bond distances of KETO forms in Table 1 for the different molecules studied, it can be concluded that the effects of the substituent are in general similar to those in ENOL forms. However, smaller changes occur in d_1, while d_2−d_4 distances are more affected by the nature of X. These differences are understood since the resonance with the substituent in KETO forms could be written as structure VI in Chart 3. So it would be in competition with the resonant structure of the chain shown as structure V in Chart 3. In contrast to ENOL forms, we find that the O••O (and H••O) distances are almost equal in all KETO species studied.

Following the model previously used, we analyze the bond distances of the IMHB system for KETO forms using $\sigma_{\mathrm{R+}}$, σ_{F}, and σ_{α} parameters. The results of the corresponding adjustments (Table 3) indicate the following: (a) The bond distances d_1 and d_2 qualitatively depend on X like in the ENOL form. However, the distance d_2 correlates in a better way with the substituent constants, showing a greater influence of $\sigma_{\mathrm{R+}}$, while d_1 shows an opposite behavior. (b) The distance d_3 depends on the nature of X as in nontransferred structures. But now, d_4 can be described adequately by $\sigma_{\mathrm{R+}}$ and σ_{F}. (c) On the other hand, the O••O separation depends on the resonance effect on X only, whereas the H••O distance is almost independent of $\sigma_{\mathrm{R+}}$. All noted results indicate that while in the ENOL form the resonance of X contributes directly to the IMHB interaction, now it occurs with the carbon chain (structure VI) and hardly affects the properties of the O_1 atom.

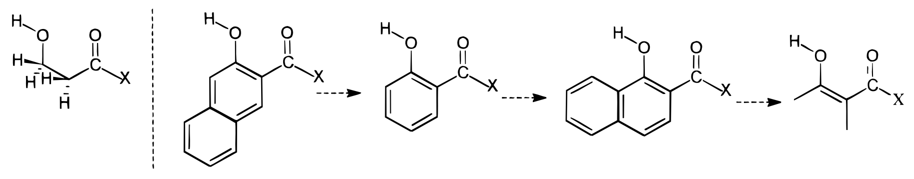
According to our previous work,[29] the energy barrier for the proton transfer, E_{barrier}, in the ground state of 2-hydroxybenzoyl compounds is only described by the parameter σ_{F} (Table 4). The inductive field effect of the substituent increases this E_{barrier} energy. Taking into account our previous structural analysis, this finding must be clearly attributed to the fact that, in the KETO structure, X resounds with the alkene group, the atom O_1 being only indirectly affected. Thus, the properties of the enol oxygen mainly depend on the inductive field effect of X, which determines the characteristics of the IMHB in KETO forms.

As it was shown,[28,29] the analysis of the change undergone by the molecular structure of these compounds as the process progresses gives an interesting result: while the length of O••O is virtually the same for ENOL as for KETO forms, the proton-transfer yields considerable shortening of the O••O distance, which peaks halfway through the transfer (MP form in Chart 2: $R_{\mathrm{O-H}} = 1.3$ Å). As can be observed in Table 1, the bond distances of MP structures do not justify the great approximation between the oxygens that yield the IMHB. However, the shortening of the O••O distance can be explained by the decrease around ≈1−3° of the α, β, and γ angles (see Chart 1) in all the IMHB systems studied. The closer approach of the oxygen atoms at the proton transfer midpoint is relevant because it is energetically favored, giving as a consequence GSIPT curves with a single minimum in the enol zone in the *o*-hydroxybenzoyl compounds studied. On the other hand, the close connection between the O••O approximation and the energy of MP structures was shown earlier to increase both in the same direction.[43,44] This becomes evident when we see the similar dependence between Taft and Topsom's substituent parameters and the former magnitude

$$\Delta \mathrm{O{\cdot\cdot}O}_{\mathrm{ENOL-MP}} = 0.210 + 0.111(\pm0.032)\sigma_{\mathrm{R+}} + 0.099(\pm0.031)\sigma_{\mathrm{F}} + 0.089(\pm0.029)\sigma_{\alpha} \quad r = 0.96;\ \mathrm{SD} = 0.014$$

and the relative energies of the MP structures (Table 4). It is found that the energy of the MP structure depends mainly on σ_{F}, but $\sigma_{\mathrm{R+}}$ now takes some weight in the fit, stabilizing the

SCHEME 2



	C-C	NPh23	Ph	NPh12	C=C
Calculated Bond Order of d_3 (X=CH_3):	0.97	1.21	1.31	1.36	1.73

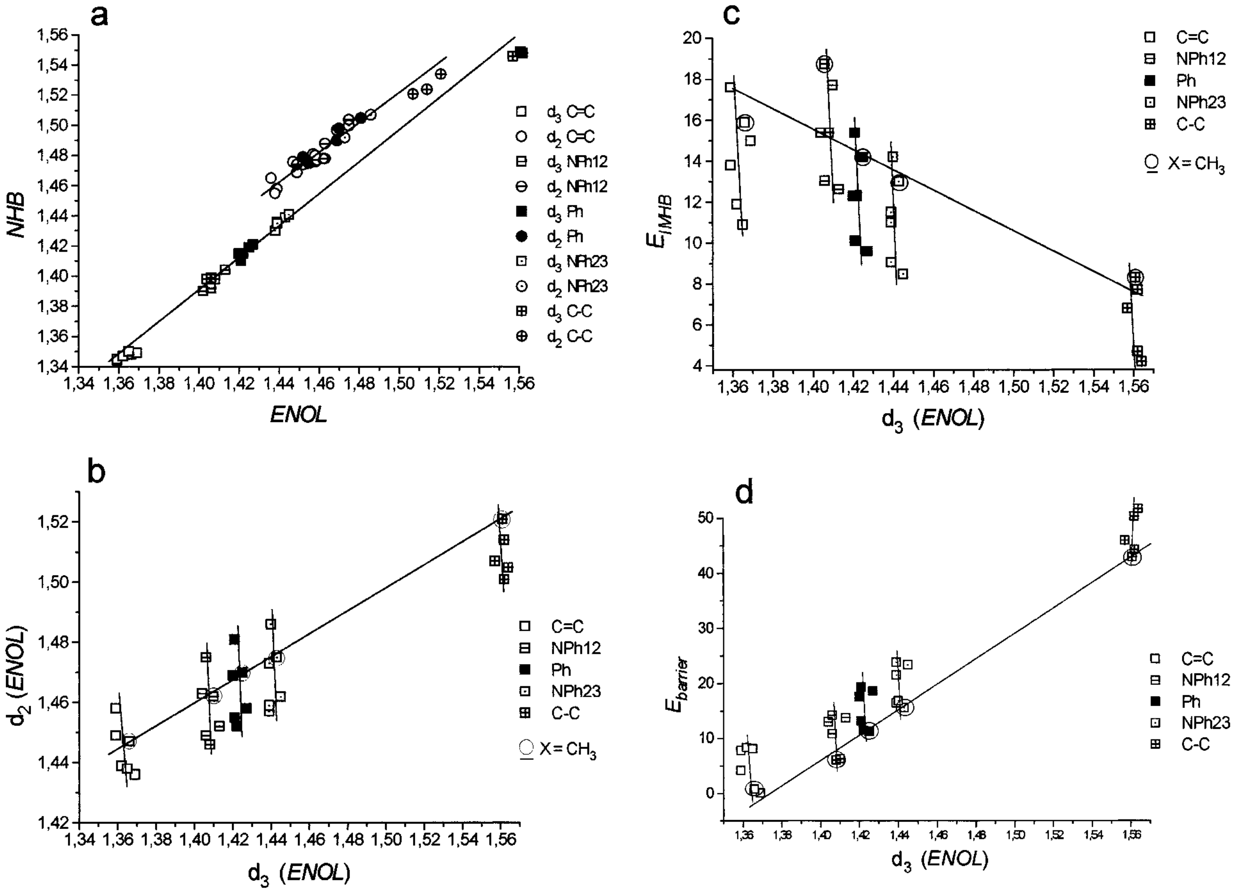


Figure 2. (a) d_2 and d_3 bond distances (Å) of NHB isomers vs the corresponding values of ENOL isomers, (b) d_2 vs d_3 bond distances (Å) of ENOL structures, (c) E_{IMHB} values (kcal mol^{-1}) vs d_3 bond distances (Å), and (d) E_{barrier} values (kcal mol^{-1}) vs d_3 bond distances (Å) for the five families of O−H••O IMHB compounds studied calculated at the B3LYP/6-31G** level.

TABLE 5: Bond Distances (Å) of Methyl-Substituted (X = CH_3) IMHB Structures with Increased Double Bond Character of d_3 (See Scheme 2)

	C−C		NPh23		Ph		NPh12		C=C	
	NHB	ENOL	NHB	ENOL	NHB	ENOL	NHB	ENOL	NHB	ENOL
d_1	1.211	1.222	1.219	1.239	1.220	1.242	1.221	1.247	1.223	1.250
d_2	1.534	1.521	1.500	1.475	1.498	1.470	1.497	1.462	1.476	1.447
d_3	1.549	1.561	1.439	1.443	1.419	1.425	1.402	1.410	1.348	1.366
d_4	1.515	1.410	1.356	1.343	1.355	1.337	1.350	1.332	1.347	1.320
O−H	0.966	0.972	0.968	0.990	0.967	0.994	0.965	1.004	0.965	1.009
O••O	2.708	2.685	2.649	2.574	2.651	2.556	2.622	2.519	2.830	2.540
H••O		1.802		1.678		1.656		1.599		1.622

midpoint zone. So we find that, in this situation in which the hydrogen atom is similarly attracted by both oxygens, the substituent resonance cannot be drawn as one canonic structure, but X donates electron density to the whole pseudoaromatic system, thereby being stabilized.

3.5. Effects Due to the Double Bond Character of the Linkage That Connects the Hydroxyl and Carbonyl Groups in the IMHB System (d_3). Now we analyze thorougly the influence of the conjugation along the IMHB system. For this purpose, we study the IMHB system in the sequence of molecules shown in Scheme 2 with an increasing double bond character of d_3. In Table 5 the corresponding bond distances for those structures with X = CH_3 are shown. In the NHB forms, we find that when the bond order of d_3 increases, the distances d_2 and d_4 decrease and, in a minor amount, d_1 lengthens. Also the O••O distance becomes smaller (in the case of the C=C structure, the proximity of the oxygens causes the repulsion of their lone pairs, increasing the β angle). Clearly, all noted changes can be attributed to the rising participation of the canonic form described as structure I in Chart 3. On the other hand, the O−H bond is hardly affected by the double bond character of d_3. Analogous effects are produced in ENOL species by increasing the double bond character of d_3 (ca. 0.01 Å greater, Table 5). It confirms that the molecular skeleton resonance (structure III in Chart 3) is favored with hydrogen bond formation. As it is observed in Table 5, the O−H distance in ENOL species increases when d_3 shortens, as the carbonyl group does.

Figure 2a shows the effects of the IMHB formation on the bonds d_2 and d_3. For a wide number of related compounds, we find that the presence of an IMHB provokes an increasing of d_3 distance and a shortening of the d_2 distance, in an amount practically proportional to the length of these bonds in the NHB species. So these changes would be closely connected to the aromaticity of the molecular fragment considered (see Chart 1). Figure 2b represents d_2 vs d_3 values for ENOL forms, and it is verified that they are not proportional. However, it is evident that if we choose one substituent, such as X = CH_3, the bond

TABLE 6: Ratio Values of the Coefficients A and B from the Fit $E_X = A\sigma_{R+} + B\sigma_F + C$ for the Families of IMHB Compounds Studied

	A/B			A/B	
	E_{IMHB}	$E_{barrier}$		E_{IMHB}	$E_{barrier}$
C=C	0.59	−0.31	NPh23	0.68	0.18
NPh12	0.60	−0.40	C−C	0.72	0.73
Ph	0.64	0			

distance d_2 linearly diminishes when increasing the double bond character of d_3, showing the rising π-donor properties of d_3. On the contrary, for a family of IMHB molecules, such as the 2-hydroxybenzoyl compounds, d_2 bond changes are almost independent of the d_3 distance. Therefore, d_2 must only depend on substituent effects. Shedding light, Figure 2c shows that for different molecules with the same substituent ($X = CH_3$), a greater bond order of d_3 leads to an increase in the E_{IMHB} value, since it implies greater conjugation on the IMHB system. However, when one family of X-substitued molecules is considered, E_{IMHB} greatly changes for similar d_3 bond length values, as a consequence of the substituent effects on carbonyl basicity.

Concerning the effect of the nature of the d_3 bond on the proton transfer (PT), Figure 2d shows a clear linear relationship between the double bond character of d_3 and the decrease of the PT barrier, $E_{barrier}$, for different structures with the same X substituent. However, for one family of X-substituted IMHB compounds, $E_{barrier}$ can be considered almost independent of the d_3 distance, mainly changing by the field-inductive substituent effect.

As it is shown in Figure 2a−d, all series of O−H··O compounds are located upon bond order sequence d_3. Moreover, the families of IMHB compounds behave almost identically in those fits. Table 6 presents the coeficient of σ_{R+} (A) divided by the coeficient of σ_F (B) of the corresponding fits between E_{IMHB} or $E_{barrier}$ and the substituent parameters (eqs 1 and 2, respectively) for the five IMHB families studied. First, we find a similar depedence of IMHB energy on the substituent for all series but showing a slightly strong resonance effect with decreasing aromaticity of the IMHB system (i.e. a rising competitive structure IV with respect to structure III). About the substituent effect on the proton-transfer barrier for the different IMHB families, it is found that the sign of the σ_{R+} coefficient (A) changes with the IMHB nature. Thus for very strongly π-conjugated double-bond systems (C=C and NPh12), the substituent resonance hinders the proton-transfer process. In phenyl compounds no resonance effects result on $E_{barrier}$, whereas in weakly or nonconjugated IMHB systems (NPh23 and C−C, respectively), KETO structures are stabilized by the resonance of the substituent.

Considering the approximation between the oxygens that yields the IMHB in the intermediate zone of GSIPT curves, we find, for all five types of compounds studied with $X = CH_3$, similar changes in the bond angles upon going from the ENOL form to the MP form (Table 7). Thus, the approach of the IMHB system during the proton transfer is not affected by the aromaticity of the system. Therefore, it should be attributed to electrostatic interactions between the hydrogen and both oxygen atoms during proton transfer. Figure 3 shows a lack of any direct relationship between ΔO··O and E_{MP} values for the whole of IMHB compound considered, although there exists a trend for each IMHB family.

Right now, we are able to analyze if the parameters R_{O-H}, ν(O−H), δ_{OH}, and $^2\Delta C$(OD), noted in the Introduction, have general application as indicators of the IMHB strength for the structures studied. First, we find that R_{O-H} is linearly correlated to the other three magnitudes ($r \approx 0.98-0.99$). In addition, all of them show a clear trend with the E_{IMHB} values for all of the compounds studied (Figure 4a), although the cases of malonaldehyde and its methyl derivative are greatly deviated. On the other hand, as a rule, the bond distance O−H becomes larger when the energy for the proton-transfer barrier falls (Figure 4b). However, if we only consider one family of IMHB molecules, data appear very scattered, with no clear relationship.

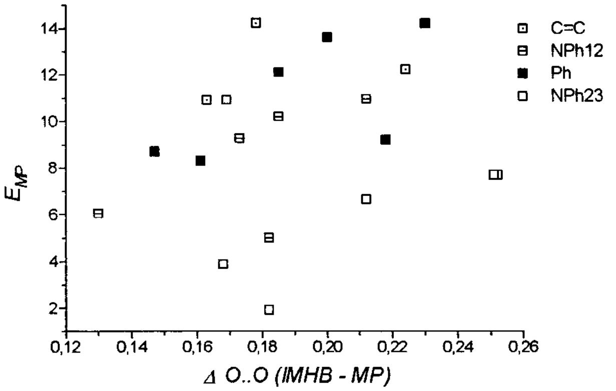


Figure 3. Relative energies of the MP structure, E_{MP} (kcal mol^{-1}), *vs* O··O approach (Å) from ENOL to MP geometries, ΔO··O (ENOL−MP), calculated at the B3LYP/6-31G** level.

TABLE 7: Bond Angle Differences between MP and ENOL Structures for Methyl Substituted ($X=CH_3$) IMHB Structures with Increased Double Bond Character of d_3

	Δ(MP−ENOL)		
	α	β	δ
C=C	−1.8	−2.5	−1.3
NPh12	−2.1	−2.5	−1.3
Ph	−1.3	−2.3	−1.1
NPh23	−1.5	−2.3	−1.2
C−C	−1.5	−1.8	−1.0

3.6. IMHB in 2-Hydroxybenzoyl Species with CN and NO_2 Groups as X Substituents. The CN and NO_2 functional groups were excluded in the previous analysis because they were markedly deviant from the expectation.[29] In fact, these acceptors groups actually behaved as if they were electron donors. Commonly, the substituents CN and NO_2 are regarded as strong with respect to their field/inductive effects. In contrast to the rest of the X studied, CN and NO_2 are not electron donors by resonance but moderate π-acceptors. According to Taft's parameters[40] for this type of substituent, σ_{R-}, the COCN and $CONO_2$ groups would result in better electron acceptors than, for example, the COH fragment for donor species such as *o*-phenol. However, Taft et al.[40] explained that the π-acceptor substituent parameter does not apply generally to strongly π-electron-deficient centers, as it is in fact C_2.

We propose here a model for the resonance of CN and NO_2 with the phenyl structure, described as structure VII in Chart 4. According to this model, the resonance effect of these substituents would not prevent the conjugation along the IMHB system. On the contrary, the electronic demand of CN and NO_2 is supplied with the electron density of the phenol fragment, which would increase its acidity.

In Table 8, the differences between the bond distances of the NHB forms calculated at the B3LYP/6−31G** level (Table 1) and those obtained using the equations in Table 3 for the 2-hydroxybenzoyl derivative with X = CN are shown. We find that the theoretical distances d_1−d_3 are greater than those predicted in function of σ_{R+}, σ_F, and σ_α, which seems to confirm

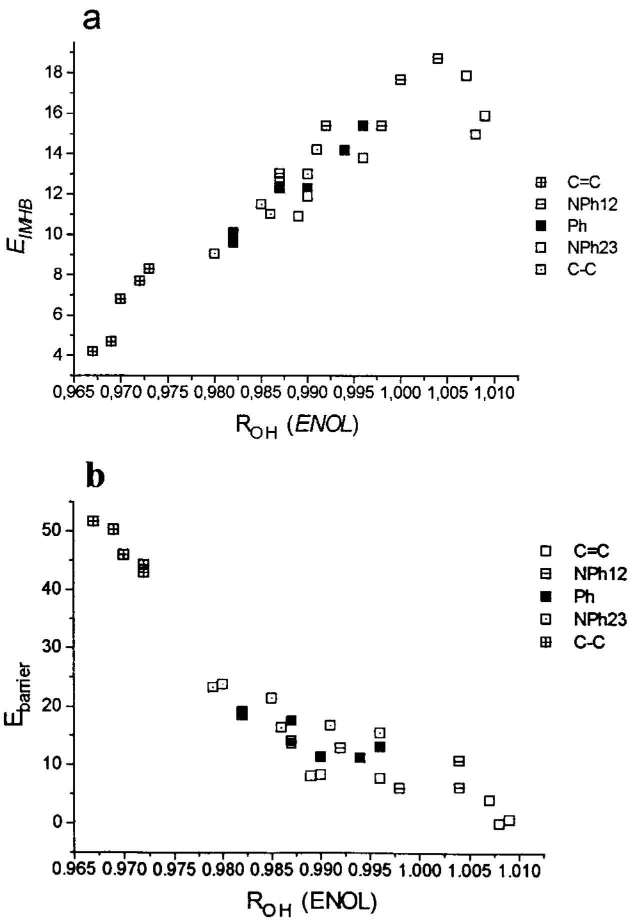
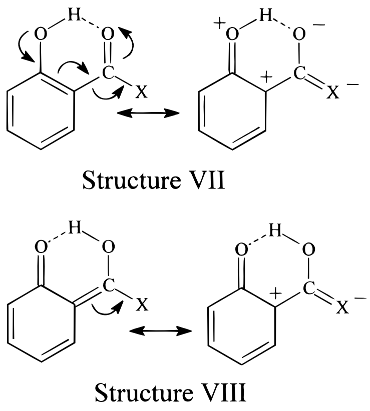


Figure 4. (a) E_{IMHB} and (b) $E_{barrier}$ values (kcal mol^{-1}) vs OH bond distances (Å) for the complete number of O−H••O compounds studied calculated at B3LYP/6-31G** level.

CHART 4



the participation of structure VII in the final NHB geometry. Furthermore, we find greater d_1, d_3, and O−H distances and shorter d_2, d_4, O••O, and H••O distances than in the species with X = H (Table 1). These results can be explained by an increased participation of the structure I in the NHB geometry. Concerning ENOL forms, our results indicate even a greater structure III resonance in the IMHB system (Table 8).

Comparing the E_{IMHB} value obtained at B3LYP/6-31G** level with that obtained using the equation shown in Table 4, we conclude that the resonance effect of these π-acceptor substituents increases the acidity of the hydroxyl group as well as the electron delocalization in the pseudochelate ring, which causes the stabilization of the IMHB system, balancing the strong destabilizing effect of σ_F in the molecular framework.

TABLE 8: Difference between Bond Distances (Å), E_{IMHB} and $E_{barrier}$ (kcal mol^{-1}) Values Calculated at B3LYP Level and Those Obtained Using the Equations in Tables 3 and 4

	CN			
Δ(value$_{B3LYP}$ − value$_{fit}$)	NHB	ENOL	MP	KETO
d_1	0.021	0.022	0.025	0.017
d_2	0.014	0.011	0.015	0.022
d_3	0.007	−0.013	0.015	0.016
d_4			−0.007	−0.003
O−H		0.009		
O••O	−0.027	−0.124	−0.046	−0.015
H••O		−0.153	−0.048	−0.018
E_{IMHB}	4.5 kcal mol^{-1}			
E_{MP}	−6.9 kcal mol^{-1}			
$E_{barrier}$	−10.0 kcal mol^{-1}			

Concerning the influence of CN and NO_2 substituents on the proton transfer (PT) of the *o*-hydroxybenzoyl compounds, the possible substituent resonance in the KETO form, structure VIII in Chart 4, would be competitive with structure V in the final geometry. In good agreement with this model, theoretical d_1−d_3 are sensibly greater, while d_4 is shorter than those obtained using substituent parametric equations (Table 8). If we compare the KETO structures of the species X = H and CN (Table 1), it can be inferred the participation of structure VIII in the molecular structure of the latter compound. According to our analysis, the resonance of the CN group greatly contributes to the stability of the KETO form (Table 8), since it favors the hydroxyl group formed and does not hinder the conjugation along the IMHB system.

4. Conclusions

The parametric model by Taft et al. based on the inductive field, resonance, and polarizability effects of the substituent is able to describe the structural differences of a number of 2-hydroxybenzoyl compounds, obtained from molecular geometries optimized at the B3LYP/6-31G** level of hydrogen- and non-hydrogen-bonded isomers, and proton-transferred species. The previous model gives relevant information about the factors which determine the chemical properties of these IMHB systems.

According to the analysis above, the general effect of the inductive field of the susbtituent in these compounds is to withdraw charge from the carbonyl carbon, thereby shortening its bond distance and displacing electron density from the phenol and carbonyl fragments to the carbon center. The consequent loss of charge that hurts the carbonyl oxygen reduces its basicity and as a result weakens the IMHB system. The resonance of the substituent in the nontransferred forms occurs with the carbonyl group, by increasing its basicity and, therefore, the electrostatic interaction in the intramolecular hydrogen bond. The resonance of X happens in a competitive way with the canonic structure corresponding to the double-conjugated bonds of the molecular chain. On the other hand, we find that the IMHB formation leads to a greater conjugation in the molecule, which at the same time stabilizes the intramolecular hydrogen bond structure. The polarization effect of the substituent on the bond distances and the properties of the IMHB systems studied are, generally, negligible.

The only distance of the IMHB system that is directly related to its energy for the *o*-hydroxybenzoyl compounds studied is that of the O−H group. The O••O and H••O distances also depend on other factors which do not result from the IMHB formation, such as the substituent effect on the molecular skeleton or the steric interactions between the X fragment and the benzene ring.

The ground-state proton-transfer barrier for the *o*-hydroxybenzoyl compounds is determined by the inductive field effect of the substituent on the IMHB in the KETO structure. The resonance of X is established with the carbon chain, by having an weak effect on the stability of the transferred form. The great approximation of the oxygen atoms, which happens in the midpoint of the proton transfer, is favored energetically and arises from the fact that the angles of the carbon chain become narrower in the MP species. It is confirmed that the IMHB approach results as proportional to the stability of that MP structure. In the intermediate zone of PT, the molecular energy is also characterized by the destabilizing effect of the inductive field of the substituent; however, the substituent now transfers electron density to the whole pseudoaromatic structure, thereby stabilizing the MP structure.

The increase of the double bond character of the bond which joins the hydroxyl and carbonyl group in a series of IMHB derivatives with the same substituent reflects a larger aromaticity in the system and indicates a greater contribution of the resonance of the chain to the final geometries. The consequent electron delocalization stabilizes the intramolecular hydrogen bond system. That covalent contribution to the IMHB ranges 10 kcal/mol in energy from aliphatic to alkene compounds. On the other hand, the increased aromaticity in systems with the same substituent strongly reduces the energy barrier to the ENOL−KETO isomerization (ranging 40 kcal/mol). A different behavior is found when one family of X-substituted IMHB compounds is considered. There, the IMHB energy for each O−H··O series mainly depends on the substituent effects on the basicity of the carbonyl group. These changes in the electrostatic character of the hydrogen bond provoke variations in the E_{IMHB} values of 7 kcal/mol. Concerning the proton-transfer process for one family of IMHB compounds, we conclude that the relative energy of the KETO form is determined by the substituent effect on the new hydroxyl group, ranging approximately 8 kcal/mol. Nearly a parallel behavior is observed for all IMHB families analyzed, but an increasing resonance substituent effect in weaker aromatic systems is found. It shows that the molecular properties of these types of IMHB systems also depend on the competing resonances happening in the molecular structure. This fact is especially relevant in ground-state proton-transfer processes, where π-donor substituents increase the potential barrier for strong aromatic structures, whereas it has the reverse effect on weak or nonaromatic compounds.

We find that the O··O approach in the midpoint of the proton transfer does not depend on the aromaticity of the IMHB system. Therefore, this geometrical change should be due to electrostatic interactions between hydrogen and both oxygen atoms.

The parameters $R_{\mathrm{O-H}}$, ν(O−H), δ_{OH}, and $^2\Delta C$(OD) are self-consistent for the whole number of O−H··O systems studied. These magnitudes can be considered as adequate indicators for the hydrogen bond strength, by reflecting the sum of covalent and electrostatic contributions to the interaction. In addition, they show a general linear trend versus the proton-transfer barrier values. However, the poorer correlation for families implies no direct relation between the E_{IMHB} and E_{barrier} magnitudes for all IMHB molecules studied.

The groups CN and NO_2 are deviated from the rest of substituents analyzed, since both behave as π-acceptors instead of as π-donors by resonance. Thus, the substituent interaction increases the phenol group acidity, while it does not hinder the resonant form of the molecular framework. Both facts lead to an increase of the IMHB strength. On the other hand, the resonance of the CN and NO_2 substituents in KETO structure stabilizes its hydroxyl group and contributes to the aromaticy of the system, by reducing the energy barrier for proton transfer.

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