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Joint QTAIM and Hirshfeld Study of the *σ* and *π* Charge Distribution and Electron Delocalization in Carbonyl Compounds: A Comparative Study with the Resonance Model

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Atomic charges and delocalization indexes (DIs) for a series of carbonyl compounds comprising dimethyl ketone, acetaldehyde, acetic acid, methyl acetate, acetamide, methyl vinyl ketone, divinyl ketone, and benzoic acid were studied using two different atomic partitionings: the QTAIM and the Hirshfeld (stockholder) scheme. The resonance model, traditionaly employed to explain the reactivity of these compounds, is not in line with the total atomic charges and DIs calculated by both methodologies. However, the resonance model is supported to some extent by the π charges and π DIs calculated by both schemes, but the calculated values indicate that the π population delocalizes only to a small degree. Although the absolute values of QTAIM and stockholder atomic charges are significantly different, the π charges and the values of the DIs show similar trends for all the atoms and molecules of this study; this is especially the case for the π DIs. A study of the electron density on the level of a single MO performed for CO, H_2CO, F_2CO, and H_2CS reveals that the differences in the atomic σ charges computed with both partitionings can be traced back to their different treatment of interatomic regions.

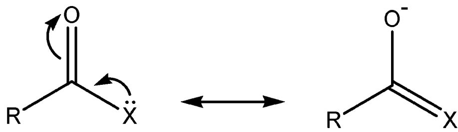
Introduction

The resonance model is generally considered as one of the simplest and most useful models employed in chemistry.[1,2] In fact, it allowed the rationalization of many chemical processes and structural properties of molecules successfully and easily, without having to resort to any calculation. The delocalization of electron charge through concerted movements of electron pairs is essential in this model. These movements give rise to formal charges on the atoms that have been considered meaningful and have been used to describe electrophilic and nucleophilic sites in organic molecules. Thus, the resonance model proposes the delocalization of a lone pair of an atom X toward the oxygen atom of carboxylic acids, esters, and amides through a concerted movement of electron pairs that involve both the lone pair of X and the double bond of the carbonyl group (Scheme 1). Therefore, a resonance form with a double bond between C and X atoms is commonly drawn for these compounds.[3]

When the X atom is replaced by a C═C group the delocalization involves two π bonds and gives rise to the resonance forms shown in Scheme 2 for divinyl ketone. They indicate that a certain positive charge would be placed on the beta carbons leaving an equivalent but negative charge on the oxygen atom. This displacement of the charge is used in the resonance model to explain why hydride reduction of the C═C group is preferred to that of the C═O bond,[4−8] though both C═C reduction and C═O reduction are possible experimentally.[9−12]

Benzoic acid is another example where the resonance model has been useful to justify its reactivity. In this molecule five different resonance forms can be drawn (Scheme 3). These forms are generated by the delocalization between the π electrons of the ring and the π electrons of the carbonyl group.

SCHEME 1



Atomic charges computed by high quality quantum chemical methods are also considered useful tools for obtaining chemical reactivity data.[13] One of the most important groups of methods calculates charges using numerical integration of the electron density, $\rho(\mathbf{r})$, over a certain region of space. Two of these methods, the Quantum Theory of Atoms in Molecules (QTAIM)[14,15] and the Hirshfeld scheme,[16] have been employed in several reactivity studies during the last years.[17−21]

A number of studies in which QTAIM charges were computed for several systems have challenged the reliability of the resonance model and their formal atomic charges.[22−27] Also, delocalization indexes (DIs) defined within the framework of the QTAIM theory[28] were also recently employed (complementing atomic charges) to discuss the inapplicability of the resonance model and the role played by π delocalization to explain the acidity of phenol derivatives[29] and the stability of the protonated forms of pyrimidinic bases.[30] More recently a study employed QTAIM atomic energies for the explanation of the sequence of proton affinities in pyrimidinic bases,[31] thereby providing a new and more realistic interpretation than the one obtained from the resonance model.

Looking for firmer evidence on the limitations of the resonance model, QTAIM and Hirshfeld atomic partitionings were used together in a recent study on the protonation of oxygen and nitrogen containing compounds.[32] We found that Hirshfeld charges were in line with the conclusions previously obtained from the QTAIM charges, both pointing to the inadequacy of the resonance model for explaining the protonation of these compounds.[26,27,29,30]

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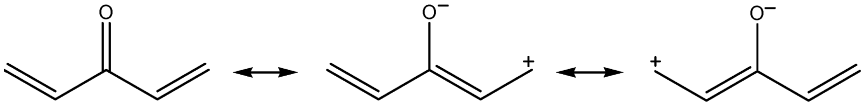
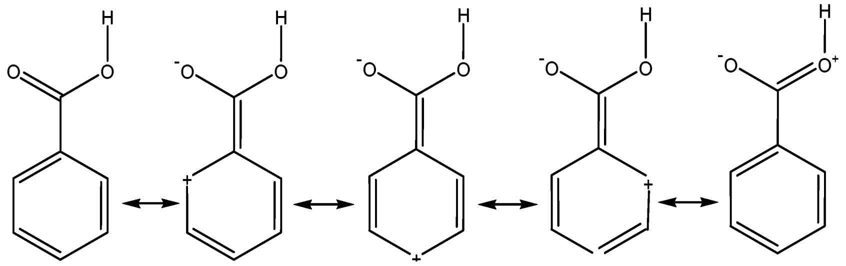
SCHEME 2



SCHEME 3



In the present work we performed another joint QTAIM and Hirshfeld study, in which, besides atomic charges, also DIs are computed with both methodologies. DIs previously only available within the QTAIM framework are extended in this study to the Hirshfeld scheme. In a recent paper Mayer et al.[33] proposed similar calculations for 'fuzzy atoms' by using either Becke's or Hirshfeld's recipe for the weight function, although in this work these indexes were called 'bond orders' instead of DIs. In both partitioning schemes, atomic charges and DIs can be split into σ and π contributions when the molecule has a symmetry plane. The hydride addition process to a series of carbonyl compounds is studied, comparing the results obtained with both partitionings and thereby testing the reliability of the resonance forms shown in Schemes 1−3, which are so often used in organic chemistry, though they have not been confirmed by charge calculations employing modern quantum methodologies.

Methodology and Computational Details

The series of molecules studied (Figure 1) comprises a number of different carbonyl compounds: one ketone (dimethyl ketone), one aldehyde (acetaldehyde), two carboxylic acids (propanoic acid and benzoic acid), one ester (methyl propanoate), and one amide (acetamide) as well as methyl vinyl ketone and divinyl ketone. The products obtained from the hydride addition process were also studied in order to quantify the differences experienced by the total DIs. The distribution of QTAIM and stockholder total atomic charges upon hydride addition in these compounds was studied in a previous work.[34] All geometries were optimized at the B3LYP/6-311++G(d,p) level. The same computational level was employed to obtain the electron density.

According to the QTAIM, an atom A is delimitated by zero-flux surfaces for $\nabla \rho(\mathbf{r})$ in solids and atoms in cages and also by an isocontour where the electron density vanishes in other cases. The atomic charge, $q(A)$, is obtained by eq 1, where Z_A is the atomic number, through the numerical integration of the electron density within the Ω_A atomic basin.[14]

$$q(A) = Z_A - \int_{\Omega_A} \rho(\vec{r}) \cdot d\vec{r} \qquad (1)$$

Similarly, within the Hirshfeld scheme, an atomic charge on an atom is calculated as

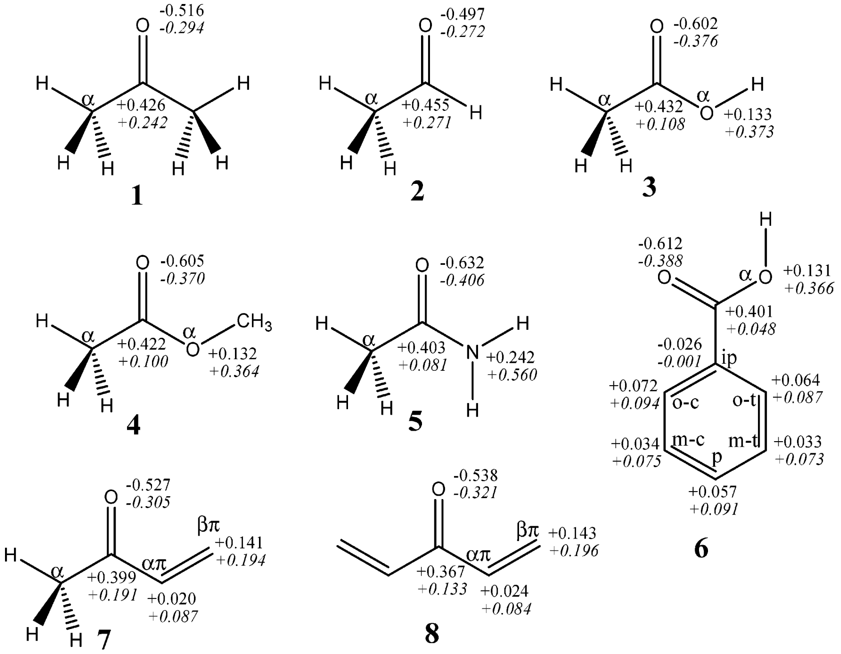


Figure 1. QTAIM and stockholder π atomic charges. The stockholder charges are shown in *italics* below the QTAIM results. Molecules studied and nomenclature employed throughout the work is included.

$$q(A) = Z_A - \int \frac{\rho_A(\vec{r})}{\sum_X \rho_X(\vec{r})} \rho(\vec{r}) \cdot d\vec{r} \qquad (2)$$

a formula analogous to (1), in which $\rho_X(\vec{r})$ is the density of the isolated atom X, placed at the same position occupied by its nucleus in the molecule.[16]

All the oxidized forms of the compound studied possess a symmetry plane which allows the separation of the electron density into σ and π contributions. Calculated σ and π atomic charges were denoted by q^σ and q^π, respectively.

As was found previously in the study of the protonation of oxygenated compounds,[32] large differences exist for the σ charges between both partitionings. Trying to trace the origin of these significant differences, the electron population of each molecular orbital was studied using both partitionings. The molecules chosen for this comparison were formaldehyde, carbonyl fluoride, thioformaldehyde, and carbon monoxide.

The QTAIM DIs, $\delta(\Omega,\Omega')$, are defined by eq 3, which was derived from the integration of the density of the Fermi hole over the two atomic basins Ω and Ω'.[28] $S_{ij}(\Omega)$ denotes the overlap integral of a pair of occupied molecular spin−orbitals, *i* and *j*, integrated within the atomic basin Ω (eq 4). $\delta(\Omega,\Omega')$ represents the extent to which the electrons in the Ω basin are delocalized into Ω' and vice versa. $\lambda(\Omega)$, the autocorrelation index (eq 5), measures the degree to which the electron density of atom Ω is localized. The relevant expressions are

$$\delta(\Omega,\Omega') = |F(\Omega,\Omega') + F(\Omega',\Omega)| = 2\sum_i \sum_j S_{ij}(\Omega) S_{ij}(\Omega') \qquad (3)$$

$$S_{ij}(\Omega) = \int_\Omega \phi_i(\vec{r}) \phi_j(\vec{r}) d\vec{r} \qquad (4)$$

$$\lambda(\Omega) = \delta(\Omega,\Omega) = \sum_i \sum_j S_{ij}(\Omega) S_{ij}(\Omega) \qquad (5)$$

Equations 3 and 5 can easily be used for calculating the delocalization and localization indexes within the Hirshfeld scheme. In this case the integration over the QTAIM basin Ω of a given atom A in (4) needs to be replaced by an integration over the whole of space using the atomic weight factor for atom A as in (2).

$$S_{ij}(A) = \int \frac{\rho_A(\vec{r})}{\sum_X \rho_X(\vec{r})} \phi_i(\vec{r}) \phi_j(\vec{r}) d\vec{r} \qquad (6)$$

Total DIs were determined in oxidized and reduced forms, whereas the σ and π DIs were only calculated for the oxidized forms for obvious symmetry reasons.

QTAIM charges and DIs were calculated employing the AIMPAC program series.[35] The STOCK program, as included in the BRABO program package,[36,37] was employed to calculate stockholder charges and DI’s.

Results and Discussion

***σ* and *π* Atomic Charges and Electron Delocalization Indexes.** The three resonance schemes proposed in the Introduction are discussed separately. Also, for the sake of clarity, the QTAIM and stockholder results are presented and commented on independently.

(i) Scheme 1 (QTAIM): q^π(O) values are around 0.1 au more negative in molecules **3**−**5** than in **1** and **2** (Figure 1). Though this agrees essentially with Scheme 1, 0.1 au is a very small value compared to the total QTAIM charge on the oxygen atom or to its π charge. Therefore, the QTAIM results do not indicate that π delocalization between X and O atoms to be a leading factor of the electron density in molecules **3**−**5**.

q^π(X) values are positive (+0.13 au and +0.24 au for O and N, respectively), which is also in agreement with Scheme 1. Nevertheless, the variation of this π charge within the series **3**−**5** is much larger than the one displayed by the carbonylic oxygen in the same compounds, contradicting the idea that X−O delocalization is the only factor affecting the π electron distribution in these molecules.

q^π(C) displays large positive values (always larger than +0.4 au), much larger than q^π(X), and display small differences along the series **1**−**5**. This indicates the largest values of the π charge are found on the O and C atoms even in molecules containing a π electron donor (**3**−**5**). Although the differences in the q^π(C) values are small, the largest value corresponds to the amide, in agreement with the q^π(X) values commented on above.

QTAIM σ charges (Figure 2) compensate the trends displayed by the π charges. Thus, q^σ(O) values are more negative (around 0.05 au) in molecules **1** and **2** than in molecules **3**−**5**. q^σ(X) displays large negative values (exceeding in absolute value the corresponding q^π(X) positive charges). The largest value corresponds to amide **5** (compensating the differences found between amide and carboxylic acid or ester in the π charge). The result being the following: the charge distribution proposed by Scheme 1 is found to be wrong when we add the σ and π contributions to get the total charges.

As expected, q^σ(C) values in molecules **3**−**5** reflect the presence of the X atom. These charges are almost double the respective values in **1** and **2** due to the electronegativity of oxygen or nitrogen.

QTAIM π DIs in molecules **1**−**5** (Table 1) are in line with the results of the π charges commented above. Thus, the largest π delocalization is found between the C and O atoms. The corresponding DI, δ^π(C,O) decreases for **3**−**5** with regard to **1** and **2**, especially in amide **5**. Both δ^π(C,X) and δ^π(O,X) values indicate an important π delocalization among these atoms, mostly between C and X in molecule **5**. Total DIs decrease significantly upon hydride addition, which is assumed to be a process that decreases π electron delocalization.

(ii) Scheme 1 (stockholder): The stockholder π charges are also shown in Figure 1. Although stockholder q^π(O) and q^π(X) values present similar signs and variations along molecules **1**−**5** than those computed with QTAIM, they differ in their absolute values (by approximately 0.23 au). Stockholder q^π(O) and q^π(O$^\alpha$) display similar absolute values in **3** and **4** (with opposite signs) and a positive value for q^π(N) larger than the negative value of q^π(O) in molecule **5**. Moreover, the stockholder q^π(C) values are much smaller than the QTAIM ones and display an important decrease for molecules **3**−**5**. All these facts reflect that stockholder π charges are in agreement with Scheme 1 both in signs and in absolute values, whereas the QTAIM charges present disagreements in the absolute values as commented above.

Figure 2 contains the stockholder σ charges. It can be observed that the main differences between both methodologies are found in these charges. This was also one of the conclusions of a previous study on the protonation of oxygenated compounds.[32] The Hirshfeld scheme places a small σ charge at the O and C atoms (always positive for O, whereas it is negative

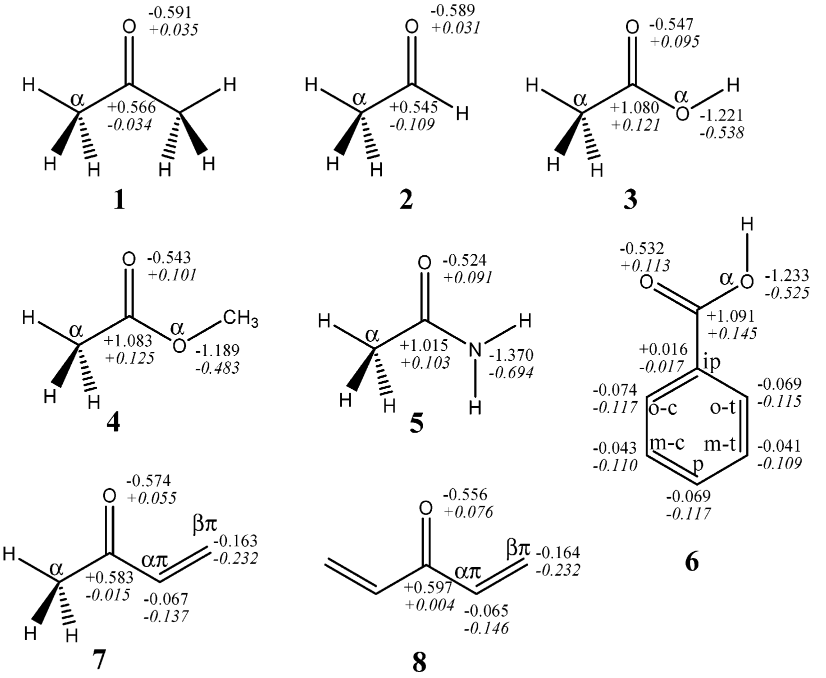


Figure 2. QTAIM and stockholder σ atomic charges. The stockholder charges are shown in *italics* below the QTAIM results.

TABLE 1: QTAIM Total and π DIs for Molecules 1−5[a]

	δ(O,C)		δ(O,X)		δ(O,C$^\alpha$)		δ(C,X)		δ(C,C$^\alpha$)	
	total	π	total	π	total	π	total	π	total	π
1	1.447	0.641			0.131				0.953	
	(−0.363)				(0.001)				(−0.070)	
2	1.502	0.680			0.132				0.978	
	(−0.392)				(0.005)				(−0.084)	
3	1.328	0.538	0.303	0.126	0.111		0.875	0.210	0.939	
	(−0.240)		(−0.075)		(0.015)		(−0.134)		(−0.059)	
4	1.318	0.527	0.277	0.125	0.111		0.878	0.221	0.935	
	(−0.201)		(−0.092)		(0.015)		(−0.194)		(−0.053)	
5	1.302	0.503	0.289	0.149	0.122		1.024	0.281	0.929	
	(−0.226)		(−0.082)		(0.007)		(−0.190)		(−0.052)	

[a] The values shown are obtained for oxidized forms and their variations upon hydride addition (in brackets).

TABLE 2: Stockholder Total and π DIs for Molecules 1−5[a]

	δ(O,C)		δ(O,X)		δ(O,C$^\alpha$)		δ(C,X)		δ(C,C$^\alpha$)	
	total	π	total	π	total	π	total	π	total	π
1	2.222	0.749			0.206				1.079	
	(−0.638)				(−0.004)				(−0.105)	
2	2.317	0.791			0.209				1.132	
	(−0.657)				(−0.011)				(−0.103)	
3	2.202	0.707	0.283	0.117	0.183		1.448	0.377	1.083	
	(−0.500)		(−0.023)		(0.056)		(−0.357)		(−0.149)	
4	−2.170	0.693	0.264	0.115	0.182		1.420	0.375	1.077	
	(−0.432)		(−0.044)		(0.044)		(−0.446)		(−0.131)	
5	2.144	0.671	0.286	0.135	0.193		1.441	0.418	1.064	
	(−0.521)		(−0.086)		(0.036)		(−0.377)		(−0.127)	

[a] The values shown are obtained for oxidized forms and their variations upon hydride addition (in brackets).

for C in molecules **1** and **2** and positive in **3**−**5**). These values and their differences with respect to the QTAIM results are thoroughly analyzed for each MO in the section below. Although stockholder and QTAIM σ charges display very different values, they display similar trends. Moreover, the values obtained for q^σ(X) with the Hirshfeld scheme present a negative sign which compensates largely the π charge, invalidating Scheme 1 as it was found above with the QTAIM results.

Table 2 contains the stockholder DIs for molecules **1**−**5**. We notice that the description of the π electron delocalization provided by the Hirshfeld scheme for these systems is quite similar to that deduced from QTAIM DIs. This is true both for the values obtained for each molecule as well as for the trends shown in their variations along the series of molecules. Stockholder results indicate a larger π delocalization between O and C, and C and X, but not between O and X (compare δ^π(O,C), δ^π(C,X), and δ^π(O,X) values in Table 2). The same can be said about the total electron delocalization. It must be pointed out that δ(O,C) and δ(C,X) experience large variations upon hydride addition, which are double the QTAIM values and amount for the π DIs before the process. In resume, the stockholder results from Table 2 support similar conclusions

TABLE 3: QTAIM Total and π DIs for Vinyl Ketones 7 and 8[a]

7	δ(O,C)	δ(O,C$^{\alpha\pi}$)	δ(O,C$^{\beta\pi}$)	δ(C,C$^{\alpha\pi}$)	δ(C,C$^{\beta\pi}$)	δ(C$^{\alpha\pi}$,C$^{\beta\pi}$)	δ(C,C$^{\alpha}$)
total	1.420	0.130	0.092	0.991	0.080	1.803	0.957
	(−0.327)	(−0.003)	(−0.037)	(−0.082)	(−0.028)	(0.009)	(−0.073)
π	0.614	0.038	0.064	0.115	0.047	0.797	

8	δ(O,C)	δ(O,C$^{\alpha\pi}$)	δ(O,C$^{\beta\pi}$)	δ(C,C$^{\alpha\pi}$)	δ(C,C$^{\beta\pi}$)	δ(C$^{\alpha\pi}$,C$^{\beta\pi}$)
total	1.395	0.127	0.092	0.998	0.081	1.795
	(−0.292)	(−0.003)	(−0.038)	(−0.103)	(−0.028)	(0.020)
π	0.584	0.038	0.064	0.120	0.047	0.789

[a] Variations experienced by the total DIs upon the hydride addition are shown in parentheses.

TABLE 4: Stockholder Total and π DIs for Vinyl Ketones 7 and 8[a]

7	δ(O,C)	δ(O,C$^{\alpha\pi}$)	δ(O,C$^{\beta\pi}$)	δ(C,C$^{\alpha\pi}$)	δ(C,C$^{\beta\pi}$)	δ(C$^{\alpha\pi}$,C$^{\beta\pi}$)	δ(C,C$^{\alpha}$)
total	2.178	0.201	0.105	1.107	0.195	1.834	1.084
	(−0.599)	(−0.032)	(−0.023)	(−0.097)	(−0.038)	(0.023)	(−0.143)
π	0.720	0.064	0.058	0.159	0.087	0.674	

8	δ(O,C)	δ(O,C$^{\alpha\pi}$)	δ(O,C$^{\beta\pi}$)	δ(C,C$^{\alpha\pi}$)	δ(C,C$^{\beta\pi}$)	δ(C$^{\alpha\pi}$,C$^{\beta\pi}$)
total	2.130	0.199	0.106	1.115	0.195	1.827
	(−0.552)	(−0.020)	(−0.026)	(−0.130)	(−0.039)	(0.030)
π	0.689	0.064	0.059	0.164	0.087	0.668

[a] Variations experienced by the total DIs upon the hydride addition are shown in parentheses.

than the QTAIM results from Table 1, an important π electron delocalization between C and X atoms larger in molecule **5** than in **3** and **4**, and a decreasing of π electron delocalization between the O and C atoms in molecules **3**−**5**.

(iii) Scheme 2 (QTAIM): According to Scheme 2 the charge at the oxygen in molecules **7** and **8** should become more negative than in molecule **1**, and C$^{\beta\pi}$ atoms should present positive charges. Certainly, q^{π}(O) values computed with QTAIM for molecules **7** and **8** are more negative, by −0.011 and −0.022 au, respectively, than those obtained for **1**. These variations are smaller than those found for molecules **3**−**5**. Also, positive QTAIM values are obtained for q^{π}(C$^{\beta\pi}$) (+0.141 and +0.143 in molecules **7** and **8**, respectively). All of this is in agreement with the charge displacement proposed by Scheme 2 as long as considering only the π electron density. Anyway, as found for Scheme 1, when one looks at the values of q^{π}(C) on molecules **7** and **8**, it is clear that these charges are significantly larger than the q^{π}(C$^{\beta\pi}$), and the differences with regard to molecule **1** are very small. It means that the main polarization of the π charge remains between the O and C atoms of the carbonyl group, which is only slightly affected by the attachment of vinyl groups.

QTAIM π electron DIs (Table 3) indicate a large delocalization between C and O (δ^{π}(O,C) values are 0.614 and 0.584 au in **7** and **8**, respectively) and between the C$^{\alpha\pi}$ and C$^{\beta\pi}$ (δ^{π}(C$^{\alpha\pi}$,C$^{\beta\pi}$) values are 0.797 and 0.789 au in **7** and **8**, respectively). The former are smaller than those in **1** and **2** molecules but are larger than those in molecules **3**−**5**. This proves again that Scheme 2 has a smaller weight on the π charge of molecules **7** and **8** than Scheme 1 on the π charge of molecules **3**−**5**. It is also interesting to compare the values of π delocalization in molecule **7** with the corresponding values in ethylene and acetaldehyde; in this way we can also measure the weight of Scheme 2 on the π charge distribution of vinyl ketones. The values of δ^{π}(C,O) and δ^{π}(C,C) in acetaldehyde and ethylene are 0.680 and 0.885 au, respectively. One can see that these are not very different than those displayed by molecule **7**. Moreover, Scheme 2 proposes a large π electron delocalization between C and C$^{\alpha\pi}$, nevertheless it is very small compared with δ^{π}(C,O) and δ^{π}(C$^{\alpha\pi}$,C$^{\beta\pi}$) values commented on above (δ^{π}(C,C$^{\alpha\pi}$) values are 0.115 and 0.120 au in molecules **7** and **8**, respectively). It must be noted that π DIs between C$^{\beta\pi}$ and the carbonyl group are also very small (Table 3).

The variations shown by the total DIs only strengthen the conclusions presented above. The variations in δ(C,O) are much larger than the remaining values, δ(C$^{\alpha\beta}$,C$^{\beta\pi}$) almost do not change upon the hydride addition process, and the variation in δ(C,C$^{\alpha\pi}$) is similar to that of δ(C,C$^{\alpha}$) in molecule **7**, where π delocalization does not exist. Once more, Scheme 2 agrees with the QTAIM π DIs. Nevertheless it has a small weight on the π charge distribution and becomes wrong when the total DIs are considered.

(iv) Scheme 2 (stockholder): The stockholder π charges of molecules **7** and **8** (Figure 1), like the QTAIM ones, do not contradict the charge distribution of Scheme 2. Negative and positive charges are placed on the O and C$^{\beta\pi}$ atoms, respectively. Differences between both methodologies are found again on the absolute values of q^{π}(O), which are approximately 0.22 au. Stockholder q(C$^{\beta\pi}$) is larger than the QTAIM ones, but differences are quite small. On the contrary, the results of both methodologies again differ for q^{π}(C). QTAIM q^{π}(C) are large and positive, indicating that the main polarization of the π distribution is around the carbonyl group, and stockholder q^{π}(C) is also positive but slightly smaller than q(C$^{\beta\pi}$) strengthening the validity of Scheme 2.

The stockholder σ charges of molecules **7** and **8** display positive values for O and a value of almost zero for C (Figure 2). q^{σ}(C$^{\beta\pi}$) and q^{σ}(C$^{\alpha\pi}$) are negative with absolute values larger than the π ones, compensating the trends shown by the π charges and invalidating Scheme 2. In resume, as previously commented for Scheme 1, the stockholder π charges are in good agreement with the charge distribution suggested by Scheme 2 as long as the π contributions are considered separately from the σ.

Stockholder π electron DIs for molecules **7** and **8** (Table 4) display only slight variations with regard to the QTAIM ones. Total indexes only present significant differences on the δ(O,C) values and their variations upon the hydride addition process; these are larger for the stockholder results, but this fact does not change the conclusions. Therefore, the stockholder DIs lead

TABLE 5: QTAIM Total and π DIs for Benzoic Acid (6)[a]

	$\delta(O,C)$	$\delta(O,C^{ip})$	$\delta(O,C^{o-t})$	$\delta(O,C^{o-c})$	$\delta(O,C^{p})$	$\delta(O,C^{m-t})$	$\delta(O,C^{m-c})$	$\delta(O,O^{\alpha})$
total	1.303	0.106	0.031	0.048	0.014	0.005	0.004	0.297
	(−0.210)	(0.009)	(−0.011)	(0.002)	(−0.010)	(0.001)	(0.002)	(−0.074)
π	0.514	0.030	0.021	0.020	0.013	0.003	0.002	0.121

	$\delta(C,C^{ip})$	$\delta(C,C^{o-t})$	$\delta(C,C^{o-c})$	$\delta(C,C^{p})$	$\delta(C,C^{m-t})$	$\delta(C,C^{m-c})$	$\delta(C,O^{\alpha})$
total	0.970	0.052	0.056	0.011	0.009	0.009	0.871
	(−0.105)	(−0.013)	(−0.018)	(−0.007)	(−0.001)	(−0.001)	(−0.121)
π	0.114	0.021	0.023	0.011	0.002	0.003	0.207

	$\delta(C^{ip},C^{o-t})$	$\delta(C^{ip},C^{o-c})$	$\delta(C^{o-t},C^{m-t})$	$\delta(C^{o-c},C^{m-c})$	$\delta(C^{m-t},C^{p})$	$\delta(C^{m-c},C^{p})$
total	1.342	1.334	1.398	1.402	1.384	1.380
	(0.002)	(0.022)	(0.002)	(−0.012)	(−0.002)	(0.012)
π	0.388	0.382	0.430	0.432	0.418	0.414

[a] Variations experienced by the total DIs upon the hydride addition are shown in parentheses.

TABLE 6: Stockholder Total and π DIs for Benzoic Acid (6)[a]

	$\delta(O,C)$	$\delta(O,C^{ip})$	$\delta(O,C^{o-t})$	$\delta(O,C^{o-c})$	$\delta(O,C^{p})$	$\delta(O,C^{m-t})$	$\delta(O,C^{m-c})$	$\delta(O,O^{\alpha})$
total	2.153	0.175	0.031	0.067	0.012	0.007	0.006	0.277
	(−0.469)	(0.032)	(−0.005)	(−0.001)	(−0.008)	(0.001)	(0.002)	(−0.016)
π	0.679	0.055	0.019	0.023	0.011	0.004	0.003	0.112

	$\delta(C,C^{ip})$	$\delta(C,C^{o-t})$	$\delta(C,C^{o-c})$	$\delta(C,C^{p})$	$\delta(C,C^{m-t})$	$\delta(C,C^{m-c})$	$\delta(C,O^{\alpha})$
total	1.077	0.138	0.150	0.016	0.017	0.018	1.437
	(−0.173)	(−0.024)	(−0.031)	(−0.007)	(−0.003)	(−0.004)	(−0.341)
p	0.161	0.045	0.048	0.014	0.008	0.008	0.373

	$\delta(C^{ip},C^{o-t})$	$\delta(C^{ip},C^{o-c})$	$\delta(C^{o-t},C^{m-t})$	$\delta(C^{o-c},C^{m-c})$	$\delta(C^{m-t},C^{p})$	$\delta(C^{m-c},C^{p})$
total	1.381	1.374	1.452	1.456	1.442	1.439
	(−0.009)	(0.004)	(0.002)	(−0.007)	(0.006)	(0.017)
p	0.362	0.358	0.394	0.396	0.386	0.383

[a] Variations experienced by the total DIs upon the hydride addition are shown in parentheses.

to parallel conclusions about the electron delocalization in vinyl ketones to those obtained from the QTAIM results.

(v) Scheme 3 (QTAIM): All the QTAIM π charges of the carbons of the benzene ring in molecule **6** are positive except that of C^{ip} (Figure 1), which is slightly negative. As Scheme 3 proposes, the values of $q^{\pi}(C^{o})$ and $q^{\pi}(C^{p})$ are positive and larger than $q^{\pi}(C^{m})$, although the differences are small and never surpass 0.04 au. On the other hand, the positive charges of the carbons of the ring are reflected by the small electron population gained by the carbonyl group with regard to molecule **3** (0.010 au and 0.031 au for the O and C, respectively), which also agrees with Scheme 3. Nevertheless, this effect is extremely small and is larger on C than on O, which is not reflected by Scheme 3. Moreover, the QTAIM σ charges included in Figure 2 show negative values for $q^{\sigma}(C^{o})$ and $q^{\sigma}(C^{p})$ that are larger than $q^{\sigma}(C^{m})$. They compensate the π charges leading to differences in the total charge that do not exceed 0.01 au among the carbons of the ring.

Scheme 3 indicates that the values of $\delta(O,C^{o})$ and $\delta(O,C^{p})$ should be larger than $\delta(O,C^{m})$, and the same trend should be shown by $\delta(C,C^{o})$, $\delta(C,C^{p})$, and $\delta(C,C^{m})$. This seems to be supported by the values presented in Table 5 (for both the π and the total indexes), although the differences among them are very small and not remarkable. On the other hand, though a very large π electron delocalization between C and C^{ip} atoms can be inferred from the structures drawn in Scheme 3, $\delta^{\pi}(C,C^{ip})$ is almost four times smaller than $\delta^{\pi}(C,O)$. Regarding the electron delocalization among the carbons of the ring, $\delta^{\pi}(C^{o},C^{m})$ and $\delta^{\pi}(C^{m},C^{p})$ values are expected to be larger than $\delta^{\pi}(C^{ip},C^{o})$ in molecule **6** according to Scheme 3. Certainly, this happens also for the total DIs, although once more the differences are not significant.

The differences in the total DIs experienced upon hydride addition are only important for the atoms belonging to the acid group. According to Scheme 3 the electron delocalization between the atoms of the acid group and the carbons of the benzene ring should experience appreciable variations; nevertheless, the values of Table 5 show variations that never exceed 0.02 au indicating the small significance of Scheme 3.

(vi) Scheme 3 (stockholder): Stockholder π charges of molecule **6**, also shown in Figure 1, lead to similar conclusions than the QTAIM ones. Thus, positive π charges are also placed on the carbons of the ring, displaying in this case slightly larger values with smaller differences between $q^{\pi}(C^{o})$, $q^{\pi}(C^{p})$, and $q^{\pi}(C^{m})$ (in this case they never exceed 0.02 au). The differences in the π electron population of O and C with regard to molecule **3** are 0.012 and 0.060 au, respectively, similar to those obtained with QTAIM.

The stockholder σ charges of all the carbons of molecule **6** (Figure 2) are negative, with absolute values larger than the π ones and larger on C^{o} and C^{p} than on C^{m}. The total charges of these carbons are negative with differences that do not exceed 0.013 au, as found by the QTAIM scheme. The most remarkable differences between the stockholder and QTAIM partitionings are found again on $q^{\sigma}(O)$ and $q^{\sigma}(C)$ values, which (as found for the remaining molecules) are positive and small according to the stockholder results.

Stockholder π and total DIs for **6** are collected in Table 6. As for the other molecules studied, differences with the QTAIM DIs are very small. The π and total $\delta(Y,C^{o})$ and $\delta(Y,C^{p})$ ($Y=O,C$) DIs are larger than $\delta(Y,C^{m})$ but show very small differences. $\delta^{\pi}(C,C^{ip})$ is four times smaller than $\delta^{\pi}(C,O)$, and

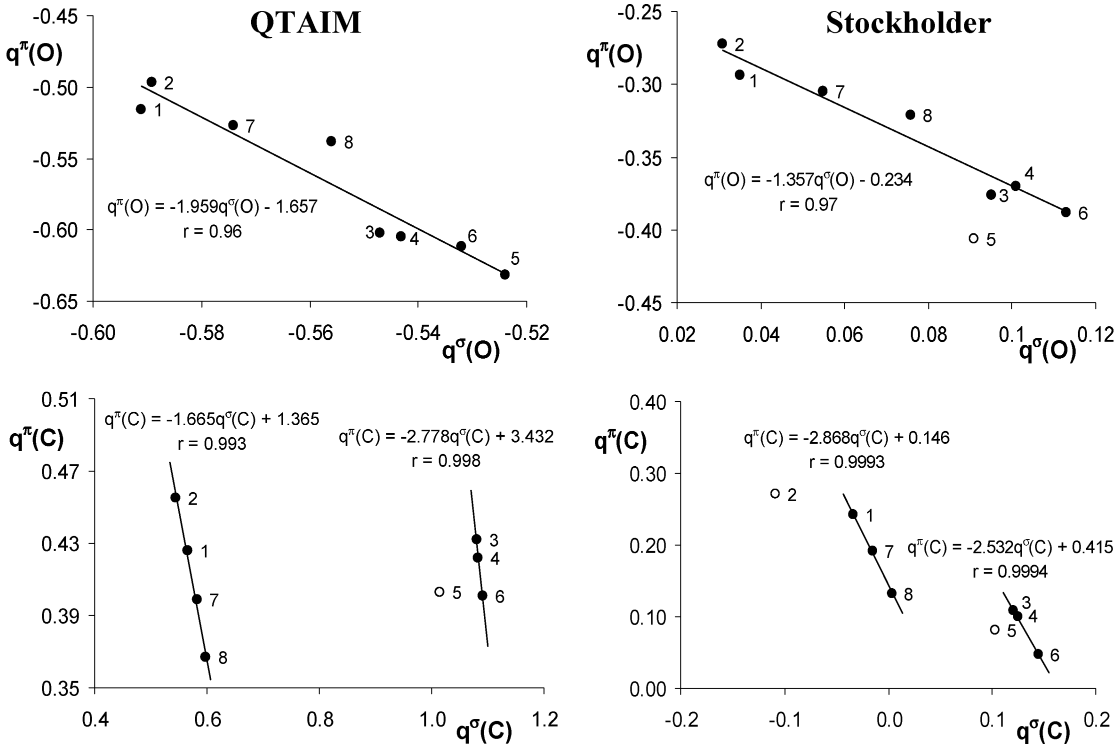


Figure 3. Linear correlations between σ and π atomic charges for the O and C atoms of the carbonyl group. Labels correspond to the nomenclature indicated in Figures 1 and 2.

an increase of $\delta^{\pi}(C^{o},C^{m})$ and $\delta^{\pi}(C^{m},C^{p})$ with regard to the $\delta^{\pi}(C^{ip},C^{o})$ is observed also for the total indexes with no significant differences.

Interdependency of σ and π Electron Populations. Linear correlations between σ and π electron populations were previously found for compounds such as pyrrole, aminopyridine, and pyridine.[38] Therefore, the relations between σ and π atomic charges have also been investigated. Figure 3 shows the linear correlations obtained between the σ and π charges of the O and C of the carbonyl group, reflecting the interdependency of σ and π electron populations. The slopes of the linear correlations (always more negative than -1) indicate that a decrease on the σ electron population implies a larger increase in the π population. For the C one must distinguish between carboxylic acids (molecules **3**, **4**, and **6**) and ketones and aldehydes (**1**, **2**, **7**, and **8**). The amide (**5**) is a particular case and cannot be included with the rest of the molecules. Acetaldehyde (**2**) is also a special case for the Hirshfeld charges.

MOs Study of QTAIM and Stockholder σ Electron Population. Looking for the origin of the significant differences between QTAIM and stockholder σ charges we have analyzed the contributions for each MO separately for CO, H_2CO, F_2CO, and H_2CS. Figure 4 shows the electron density of the σ MOs with the largest differences between QTAIM and stockholder electron populations. The contribution of these MOs to the σ charge differences represents more than 50% of the total difference in some cases (CO and H_2CS) (Table 7). Looking at Figure 4, we observe that these MOs place most of the electron density in the region between the atoms. On the other hand, Figure 5 shows the electron density associated with the σ MOs of H_2CO and H_2CS where the differences between QTAIM and stockholder are negligible (Table 7). Looking at Figure 5 we observe that these MOs place most of the electron density around the nuclei. All of this indicates that the differences in the charges between both atomic partitionings originate in the region of the interatomic surface. This is indeed logical, if we consider the QTAIM in terms of the Hirshfeld partitioning. The ‘weight factors’ for QTAIM atoms would be always 1 or 0 depending if the point is, respectively, inside or outside of the atomic basin. In contrast, the weight factors for a ‘stockholder atom’ are approximately equal to 1 only in the proximity of its nucleus and only take approximately a value of 0 in the points close to the nuclei of the remaining atoms. Therefore, the differences between the QTAIM and stockholder “weight factors” are actually in the interatomic region.

TABLE 7: Difference between QTAIM and Stockholder Electron Population in the MOs Drawn in Figures 4 and 5[a]

Mol	MO	C	X=O,S
CO	3	70.1	70.1
OCH2	3	39.8	49.0
	4	0.3	0.4
OCF2	7	21.0	47.0
SCH2	7	69.4	52.6
	8	3.8	3.8

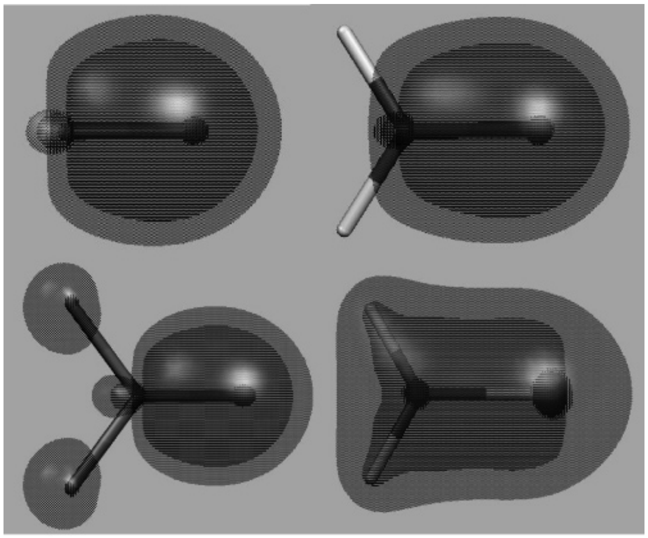
[a] The values are expressed in % with regard to the total difference.

Conclusions

The schemes traditionally proposed by the resonance model for carbonyl compounds are not reproduced by the QTAIM and stockholder total atomic charges and delocalization indexes. However, they are supported to some extent by the π charges and π delocalization indexes calculated by both schemes, although the QTAIM π charges show important discrepancies with regard to the traditional charge distribution on the $q^{\pi}(C)$ values.

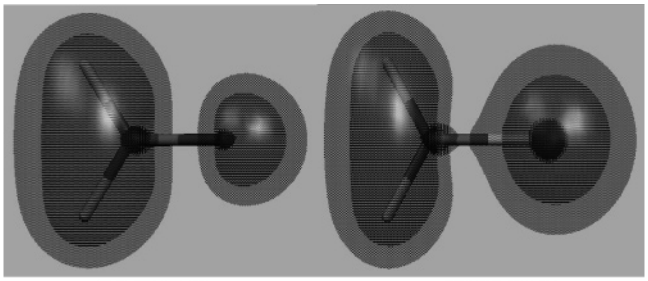
The π charge and π delocalization indexes indicate that the presence of acid, ester, or amide groups has more influence on the π charge of the carbonyl group than the presence of vinyl groups, with the amide as the most influential.

The large differences found in the σ charges between both atomic partitionings originate from their different treatment of



CO (MO 3) H2CO (MO 3)
F2CO (MO 7) H2CS (MO 7)

Figure 4. Plot of the electron density for the MOs with the largest differences of electron population between QTAIM and stockholder partitionings. Internal and external surfaces represent electron density values of 0.1 au and 0.05 au, respectively.



H2CO (MO 4) H2CS (MO 8)

Figure 5. Plot of the electron density for the MOs with negligible differences of electron population between QTAIM and stockholder partitionings. Internal and external surfaces represent electron density values of 0.1 au and 0.05 au, respectively.

the interatomic region. Thus, only MOs with large electron density between the atoms present large differences in the QTAIM and stockholder contribution to the electron population. For instance, more than 50% of these differences are due to only one MO in both CO and H_2CS.

It has to be remarked that, although atomic charges calculated with both methodologies display large differences in many cases, the delocalization indices calculated with both the stockholder and QTAIM schemes are in good agreement for all atoms and molecules here studied.

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