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Comparison of the AIM and Hirshfeld Totals, σ, and π Charge Distributions: A Study of Protonation and Hydride Addition Processes

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A comparison of atomic charges has been carried out using two different atomic partitionings: one provided by the theory of Atoms in Molecules (AIM) and one based on the Hirshfeld scheme. The systems studied were the neutral and protonated forms of O- or N-containing compounds, some of them bearing two functional groups. The results obtained with both partitionings display important discrepancies, in particular, for the charges of the C−X groups (X = O or N), for their variation upon protonation, and for the final charge of the proton. However, separating the σ from the π changes upon protonation, and a clear correlation was found for the π contributions that were calculated using the AIM and Stockholder schemes. This allowed the conclusion that the classical resonance forms do not agree with the π charge variations (obtained with both the AIM and Hirshfeld methods) that are produced by protonation. In fact, though the π charges calculated with both methods are different, they provide the same conclusions about the π charge redistribution upon protonation. The main difference between the results obtained with both partitionings pertains to how the σ electron population is distributed among the atoms of the molecule.

Introduction

Atomic charges are considered useful tools for obtaining chemical insights from structural and chemical reactivity data.[1] There are many definitions of atomic charge. The most important we can mention include the traditional Mulliken population analysis method,[2] the density matrix-based normal population analysis developed by Reed et al.,[3−5] and the method based on the atomic polar tensor developed by Cioslowski.[6] Another group of methods obtains the atomic charges through the numerical integration of the electronic density, $\rho(\mathbf{r})$. The results provided by two of these methods are compared in this work; one is based on the AIM theory[7,8] and the other on the Hirshfeld scheme.[9−14] Since both methods have been adequately described in the literature, only the expressions relevant to this study will be given in order to clarify the notation used. According to the AIM theory, an atom (with a few exceptions)[15] consists of a nucleus which acts as an attractor for the trajectories of the gradient of the charge density vector field, $\nabla\rho(\mathbf{r})$, and its associated atomic basin, Ω, throughout which these trajectories spread. An atom, A, is delimited by zero-flux surfaces for $\nabla\rho(\mathbf{r})$ and an isocontour where the electron density vanishes. The atomic charge (q_A) is obtained by eq 1, where Z_A is the atomic number, through the integration of the electronic density within the atomic basin.

$$q_A = Z_A - \int_\Omega \rho(\mathbf{r})\, d\mathbf{r} \tag{1}$$

The Hirshfeld scheme calculates the atomic charge (eq 2) by using the atomic deformation density, $\delta\rho_A(\mathbf{r})$, which is related to the molecular deformation density, $\Delta\rho(\mathbf{r})$, by eq 3. $\Delta\rho(\mathbf{r})$ is defined by eq 4, where ρ^{mol} is the molecular electron density and ρ^{pro} is the promolecule density given by eq 5, where $\rho^{at}(\mathbf{r})$ represents the charge density of the isolated atom, A, placed at the same position occupied by its nucleus in the molecule. Finally, the function $w_A(\mathbf{r})$ in eq 3 gives the relative contribution of atom A to the promolecule in the point $\mathbf{r}$ and is expressed by eq 6.

$$q_A = -\int \delta\rho_A(\mathbf{r})\, d\mathbf{r} \tag{2}$$

$$\delta\rho_A(\mathbf{r}) = w_A(\mathbf{r})\Delta\rho(\mathbf{r}) \tag{3}$$

$$\Delta\rho(\mathbf{r}) = \rho^{mol}(\mathbf{r}) - \rho^{pro}(\mathbf{r}) \tag{4}$$

$$\rho^{pro}(\mathbf{r}) = \sum \rho_A{}^{at}(\mathbf{r}) \tag{5}$$

$$w_A(\mathbf{r}) = \rho_A{}^{at}(\mathbf{r})/\rho^{pro}(\mathbf{r}) \tag{6}$$

AIM and Hirshfeld charges (also called Stockholder charges) were only compared for a series of diatomic molecules in previous work.[10] The dependence of the basis sets used for different methods was investigated using a series of hydrocarbons and other simple organic molecules using the Hartree−Fock level.[11] Rousseau et al.[12] studied the influence of the basis set, the atomic spectroscopic state used for the evaluation of the weight factors, and the electron correlation upon the calculated Hirshfeld charges. Their work proved that calculated charges can be considered as converged upon use of a sufficiently large basis set and computational method, as is the case in this study. De Proft et al. investigated the relationship between the atomic dipole of the H and Cl in H−X and Cl−X bonds with the electronegativity of X.[14]

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TABLE 1: Selected Atomic Charges (q) and Their Variations upon Protonation (Δq) in Molecules 1−5 Calculated Using the AIM Theory and the Hirshfeld Scheme (STOCK)[a]

	1		2		3		4		5	
	AIM	STOCK	AIM	STOCK	AIM	STOCK	AIM	STOCK	AIM	STOCK
q										
X[b]	−1.094	−0.233	−1.041	−0.201	−0.898	−0.182	−1.026	−0.209	−1.069	−0.199
C[b]	0.521	−0.002	1.002	0.122	0.374	0.005	0.366	−0.039	0.686	0.026
Δq										
X[b]	0.000	0.294	−0.002	0.280	0.025	0.236	0.005	0.300	−0.094	0.285
C[b]	−0.218	0.108	−0.097	0.225	−0.105	0.119	−0.095	0.080	0.070	0.199
H[c]	0.691	0.274	0.689	0.282	0.668	0.256	0.477	0.206	0.511	0.216

[a] All values are in atomic units (au). [b] Charge differences were calculated as protonated − unprotonated, X = O or N. [c] Charge values for H$^+$.

The main objective of this work is to investigate whether several remarkable conclusions, previously obtained within the framework of the AIM theory, can be reproduced by employing a different atomic charge definition, such as the Hirshfeld scheme. In particular, we want to check if the Hirshfeld charges confirm that (i) hydrogen atoms play a leading role in the stabilization of protonated species providing the charge gained by the proton, as was found in several previous AIM studies,[16−19] (ii) the redistribution of the electron density experienced after protonation by molecules that contain very electronegative atoms, X, is better reproduced by X$^+$−H than by X−H$^+$ forms, as it was previously obtained with the AIM theory for several linear[18,20] and cyclic[19,21] ethers, carbonyl compounds,[22] and pyrimidine bases,[23] and (iii) the redistribution of the electron charge experienced after protonation by molecules with a π delocalized charge is not well-described by the resonance model, as it was also previously found in the above cited AIM study on pyrimidine bases.[23]

Our study also aims at comparing the AIM and Hirshfeld descriptions of the charge redistribution experienced in a hydride addition process, which is compared with the protonation process. The effect of two functional groups over the modifications of the atomic charges in the protonation process was also studied.

Both AIM and Hirshfeld schemes seem to be adequate for rationalizing the reactive processes, including protonation, because they have provided reactivity indexes. Thus, Bader et al. employed the laplacian of the density charge ($\nabla^2\rho$) to rationalize the ability for electrophilic aromatic substitution of benzene derivatives.[24] More recently, the Hirshfeld scheme has been employed for determining the Fukui function,[25−27] which is one reactivity index commonly used in chemistry.

Computational Details

MP2/6-311++G** electronic densities were employed for the calculations of the atomic charges and the electronic populations of all of the molecules studied here. These densities were obtained using Gaussian 98.[28] AIM and Hirshfeld charges and electronic populations were obtained using, respectively, the AIMPAC[29] and STOCK programs.[12,25] When the AIM partitioning was used, the σ and π contributions were calculated by taking into account the natural orbital (NO) symmetries and by performing atomic integrations for every NO within the limits defined by the atomic surfaces. The density matrix is used in the Stockholder calculations, and the σ and π separation is completed over this matrix.

Our study comprises eleven molecules. Five of them were selected for studying the atomic charge redistribution upon the protonation in small molecules: formaldehyde (**1**), methanol (**2**), oxacyclopropane (**3**), methylamine (**4**), and methylenimine (**5**). Thus, five different functional groups containing very electronegative atoms (N or O) with or without π systems are considered for both atomic partitionings, which allows us to study the influence of a double bond and the electronegativity over the atomic charge redistribution. The classical representations of the protonated forms usually employed in organic chemistry are discussed, as well. The effect of two functional groups over the redistribution of the atomic charges was analyzed by considering the groups containing the most electronegative atoms (hydroxyl and carbonyl). Therefore, 4-hydroxy-2-pentanone (**6**) and 2,4-pentadione (**7**) were studied. Since this study is concerned with the mutual interaction of functional groups due to their proximity and not with the specific alterations of the charge density due to hydrogen bonding, we have only considered (for **6**) the conformer where the intramolecular hydrogen bond is not formed. The evolution of the atomic charges upon the hydride and proton addition was compared only for the propanone molecule, **8**. Finally, three aromatic molecules, **9**−**11**, two with C_s symmetry [3-aminocyclopent-2-enone (**9**) and 2,4-cyclopentadien-1-one (**10**)] and the third with C_{2v} symmetry [2-pyridinone (**11**)], were selected for studying the systems with π charge delocalization. It was previously found that some amides experience charge modifica-

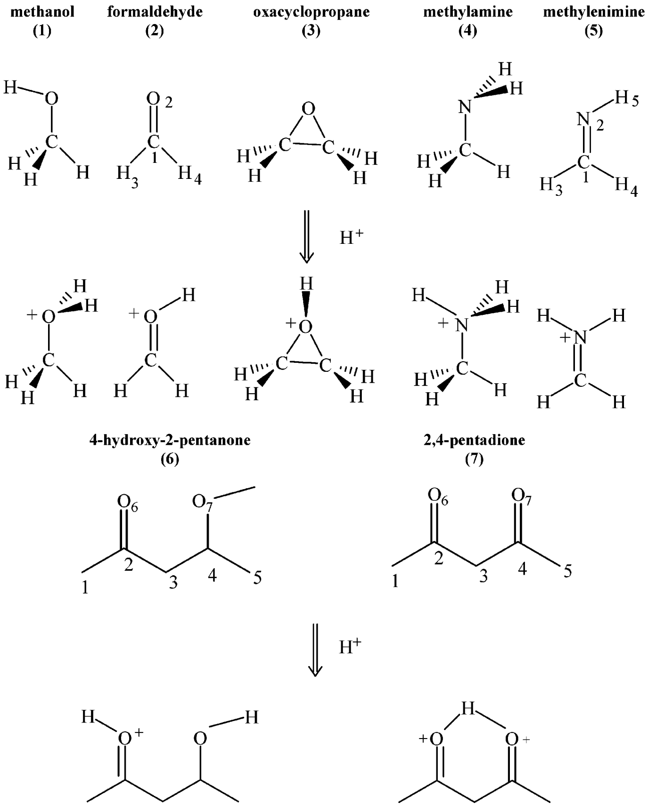

Figure 1. Structure and nomenclature of molecules **1**−**7**.

TABLE 2: Atomic Charges (*q*) of Molecules 6 and 7 and Their Variations (Δ*q*) Calculated upon Protonation[a]

	q		Δ*q*			*q*		Δ*q*	
	AIM	STOCK	AIM	STOCK		AIM	STOCK	AIM	STOCK
6					**7**				
C1	−0.042	−0.089	0.028	0.043	C1	−0.041	−0.083	0.016	0.030
C2	0.990	0.160	−0.234	0.115	C2	0.995	0.162	−0.083	0.057
C3	−0.013	−0.058	0.005	0.025	C3	−0.071	−0.066	−0.008	0.034
C4	0.518	0.062	0.029	0.018	C4	0.995	0.162	−0.129	0.080
C5	−0.005	−0.091	−0.018	0.007	C5	−0.041	−0.083	0.020	0.035
O6	−1.092	−0.226	0.004	0.227	O6	−1.090	−0.222	0.027	0.146
O7	−1.120	−0.206	−0.018	0.020	O7	−1.090	−0.222	0.015	0.186
H[b]	0.562	0.145	0.040	0.032	H[c]			0.651	0.138
H[c]			0.648	0.228					

[a] See Figure 1. Variations were calculated as protonated − unprotonated. All values are in atomic units (au). [b] Hydroxyl hydrogen. [c] Charge values for H^+.

tions during protonation that are not consistent with the resonance model.[23] Thus, cyclic systems **9**−**11** extend the *π* system of the carbonyl group over chemical environments with and without nitrogen, placed in positions that will or will not build the amide unit. We have considered only the most stable protonated forms of molecules **9** and **11**, where the protons are in a trans arrangement to the nitrogen. The symmetry of these systems allows us to perform the separation of the electron density and to calculate the *σ* and *π* atomic populations for the AIM and Hirshfeld partitionings.

Results and Discussion

Atomic Charge Redistribution in Small Molecules. Table 1 contains the atomic charges and their variations upon the protonation process for molecules **1**−**5** (Figure 1). With respect to previous findings,[10] the absolute values obtained for the atomic charges with both methodologies are significantly different, with the AIM method always providing much larger values. Nevertheless, we are interested in the trends exhibited by the atomic charges in the protonation process, not in their absolute values. The results obtained for the carbon, oxygen, and nitrogen atoms, and the final charge of the protons show trends that are significantly different when both partitionings are compared. The AIM method, as already found in previous works,[18−23] provides (i) nearly constant values for the charge on the atom to which the proton is added, X (oxygen or nitrogen in this case), and (ii) a large positive charge for the proton (∼0.7 au in the oxygen and ∼0.5 au in the nitrogen). Thus, according to the AIM results, the O- and N-protonated species would be better represented by the $X-H^+$ forms rather than by the classical X^+-H forms. On the contrary, the results of the Hirshfeld atomic partitioning indicate (i) that the charge of the X atoms is substantially affected by the protonation (Δ*q*(X) surpassing 0.2 au in all cases) and (ii) that the positive charge is more uniformly distributed over the molecule, and the charge on the proton never reaches 0.3 au.

Both AIM and Hirshfeld charges point out that the presence of a C═X group (**2** and **5**) results in an important increase of the charge on the C atom. The charge increment experienced by the C atom upon X-protonation is also substantially increased when a C═X group is present.

Effects of Two Functional Groups. We have studied two molecules containing two functional groups, **6** and **7**, one with one carbonyl and one hydroxyl group and another with two carbonyl groups. Table 2 lists the atomic charges and their variations upon protonation. The charges obtained for the C and O atoms of the hydroxyl and carbonyl groups of these molecules are very similar to those obtained, respectively, in molecules **1** and **2** with the same method. Therefore, no influences between the different groups are observed in the charges, which displays an independent behavior for each functional group.

propanone
(8)

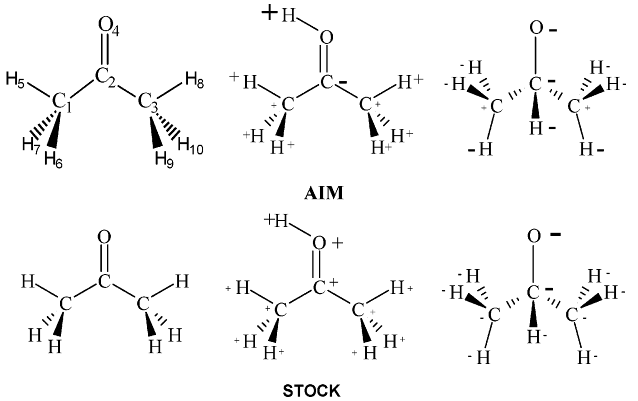

Figure 2. Structure, nomenclature, and charge redistribution upon hydride addition and protonation of propanone. The size of the sign is proportional to the charge variation.

The atomic charges of the remaining carbon atoms display different trends when AIM and Hirshfeld partitionings are employed. Thus, C1 in **6** (the carbon closest to the carbonyl group) has a more negative charge than C5 (the carbon closest to the hydroxyl group) in the AIM results. However, these values are similar in the Hirshfeld results and larger than the AIM values. The charge of C3, situated between the two groups, displays differences, too. While this atom has a charge that is lower than the charges of C1 and C5 in the AIM partitioning, the contrary happens when the Hirshfeld partitioning is employed. The hydrogen atoms transfer the electron population to the rest of the atoms according to both the AIM and Hirshfeld results.

The most stable conformer for the protonated form of **7** presents a ring critical point. In this molecule, the electron transfer to the proton is completed by the two carbonyl groups, although one of them has a stronger bond (O7). Therefore, the charge variations are different in this molecule, but they follow the trends observed for the other molecules. Δ*q* is negative for the carbonyl carbon and null for the oxygen employing AIM partitioning, whereas it is positive for the carbonyl carbon and oxygen atoms employing Hirshfeld partitioning. Another remarkable difference is found in the proton of **7**, which is significantly smaller (0.138 au) than the values found for the remaining molecules. However, the AIM charge for this atom does not show any significant difference with respect to the other molecules.

Hydride Addition on the Propanone Molecule and Comparison with the Protonation. A study of the charge redistribu-

TABLE 3: Atomic Charges of Neutral Propanone (8) and Its Ionic Forms Obtained upon Protonation (8−H$^+$) and Hydride Addition (8−H$^-$) Calculated Using the AIM Theory and the Hirshfeld Scheme (STOCK)[a]

	8		**8**−H$^+$		**8**−H$^-$	
	AIM	STOCK	AIM	STOCK	AIM	STOCK
C1	−0.042	−0.086	0.012	0.047	0.021	−0.044
C2	1.000	0.160	−0.235	0.128	−0.208	−0.171
C3	−0.042	−0.086	0.031	0.048	0.021	−0.044
O4	−1.091	−0.232	0.002	0.241	−0.190	−0.348
H5	0.042	0.040	0.043	0.037	−0.086	−0.053
H6	0.023	0.041	0.113	0.058	−0.105	−0.062
H7	0.023	0.041	0.103	0.052	−0.066	−0.053
H8	0.042	0.040	0.079	0.044	−0.081	−0.051
H9	0.023	0.041	0.108	0.057	−0.105	−0.062
H10	0.023	0.041	0.089	0.046	−0.061	−0.052
H[b]			0.656	0.243	−0.133	−0.061

[a] See Figure 2. Charge values of **8**−H$^+$ and **8**−H$^-$ are presented as differences with regard to the neutral form. All values are in atomic units (au). [b] Atomic charge variation of the H$^-$ and charge value for the H$^+$ upon hydride addition and protonation, respectively.

TABLE 4: Variations in σ, π, and Total Electron Population after the Protonation of 2 and 5 Calculated Using the AIM Theory and the Hirshfeld Scheme (STOCK)[a]

	ΔN^{σ}		ΔN^{π}		ΔN	
	STOCK	AIM	STOCK	AIM	STOCK	AIM
2						
C1	−0.028	0.269	−0.261	−0.172	−0.289	0.097
O2	−0.420	−0.189	0.220	0.191	−0.200	0.002
H3	−0.090	−0.186	−0.022	−0.010	−0.112	−0.196
H4	−0.097	−0.207	−0.020	−0.010	−0.117	−0.217
H[a]	0.635	0.313	0.083	0.001	0.718	0.314
5						
C1	−0.038	0.139	−0.160	−0.209	−0.198	−0.070
N2	−0.405	−0.124	0.120	0.219	−0.285	0.095
H3	−0.077	−0.165	−0.016	−0.013	−0.093	−0.178
H4	−0.069	−0.146	−0.018	−0.013	−0.087	−0.159
H5	−0.120	−0.171	−0.001	−0.006	−0.121	−0.177
H[b]	0.709	0.467	0.075	0.022	0.784	0.489

[a] Variations were calculated as protonated − unprotonated. All values are in atomic units (au). [b] σ, π, and total electron population for H$^+$.

TABLE 5: σ and π Atomic Populations of Molecules 9−11[a] (see Figure 3) and Their Variations after the Protonation Calculated Using the AIM Theory and the Hirshfeld Scheme (STOCK)[b]

	N^{σ}		ΔN^{σ}		N^{π}		ΔN^{π}	
	STOCK	AIM	STOCK	AIM	STOCK	AIM	STOCK	AIM
9[a]								
C1	4.983	4.342	−0.046	0.237	0.903	0.653	0.023	0.099
C2	5.092	4.997	−0.009	−0.045	1.007	1.083	−0.029	−0.043
C3	4.946	4.663	0.030	−0.011	0.996	0.865	−0.097	−0.144
O6	6.924	7.568	−0.416	−0.289	1.332	1.560	0.258	0.279
N7	5.663	6.437	0.044	0.112	1.447	1.794	−0.114	−0.132
H8	0.883	0.919	−0.032	−0.068	0.075	0.032	−0.007	−0.007
H13	0.753	0.560	−0.023	−0.047	0.119	0.024	−0.021	−0.008
H14	0.756	0.559	−0.024	−0.044	0.121	0.025	−0.022	−0.008
H[c]			0.624	0.356			0.108	0.011
10								
C1	4.996	4.375	−0.028	0.273	0.865	0.624	−0.077	−0.044
C2	5.130	5.090	−0.041	−0.097	0.925	0.979	−0.002	0.013
C3	5.126	5.106	0.006	0.042	0.894	0.933	−0.095	−0.111
C4	5.126	5.106	0.011	0.054	0.894	0.933	−0.109	−0.132
C5	5.130	5.090	−0.042	−0.088	0.925	0.979	0.011	0.038
O6	6.965	7.593	−0.427	−0.231	1.233	1.445	0.201	0.272
H7	0.878	0.897	−0.039	−0.078	0.069	0.029	−0.001	−0.006
H8	0.885	0.917	−0.035	−0.083	0.064	0.027	−0.009	−0.008
H9	0.885	0.917	−0.035	−0.082	0.064	0.027	−0.010	−0.009
H10	0.878	0.897	−0.033	−0.060	0.069	0.029	0.001	−0.004
H[c]			0.662	0.328			0.092	0.008
11								
N1	5.666	6.550	−0.001	0.082	1.358	1.668	−0.065	−0.063
C2	4.871	3.953	−0.085	0.104	1.003	0.689	0.032	0.106
C3	5.111	5.064	−0.030	−0.048	0.936	0.981	−0.013	−0.024
C4	5.108	5.067	0.000	0.020	0.918	0.942	−0.068	−0.076
C5	5.082	4.988	0.014	0.056	0.985	1.024	−0.095	−0.108
C6	4.997	4.651	−0.004	0.028	0.987	0.914	−0.061	−0.054
O7	6.885	7.511	−0.412	−0.280	1.432	1.643	0.213	0.250
H8	0.874	0.909	−0.031	−0.073	0.070	0.028	−0.008	−0.006
H9	0.881	0.904	−0.029	−0.044	0.069	0.028	−0.006	−0.004
H10	0.887	0.929	−0.031	−0.070	0.066	0.028	−0.010	−0.007
H11	0.879	0.918	−0.029	−0.068	0.076	0.033	−0.015	−0.011
H12	0.760	0.550	−0.038	−0.057	0.102	0.019	−0.014	−0.006
H[c]			0.675	0.346			0.109	0.011

[a] The data shown for molecule **9** correspond only to a part of the molecule. [b] Variations were calculated as protonated − unprotonated. All values are in atomic units (au). [c] σ and π electron populations for H$^+$.

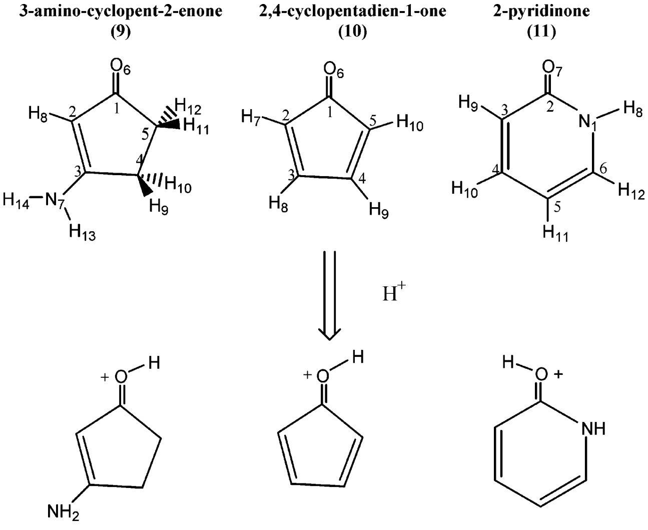

Figure 3. Structure and nomenclature of the aromatic molecules **9**−**11** studied in this work.

tion upon the hydride addition has been performed for the propanone molecule (Figure 2). The results are shown in Table 3, which also includes the charge variations experienced by this molecule upon the protonation process. The most important difference between the AIM and Hirshfeld results is found at C2. AIM partitioning shows its charge decreasing in both processes, with similar values of −0.235 au upon protonation and −0.208 au upon hydride addition. The decrease observed in the protonation is mainly due to the electron transfer from the hydrogens of the methyl groups. On the contrary, the Hirshfeld partitioning shows a decreased C2 charge after the hydride addition (similar to the AIM value) but an increased charge after the protonation.

With respect to the oxygen atoms, the charge variations are negative upon the nucleophilic addition, as expected, but the Hirshfeld value is almost twice the AIM value. We also observe that an important part of the negative charge is concentrated on the hydrogen atoms in the AIM partition, as it is with the positive charge in the protonation.

Study of the σ and π Electron Population. Because of the important differences found in the atomic charges discussed previously, we performed a σ/π analysis in order to determine which of these contributions presents larger differences between the partitionings. The variations experienced by the σ and π populations (denoted, respectively, as N^{σ} and N^{π}) in the formaldehyde and methylenimine upon the protonation of the oxygen atom and nitrogen atom, respectively, are shown in Table 4. It can be observed that the differences correspond to the σ redistribution and not to the π redistribution. Both

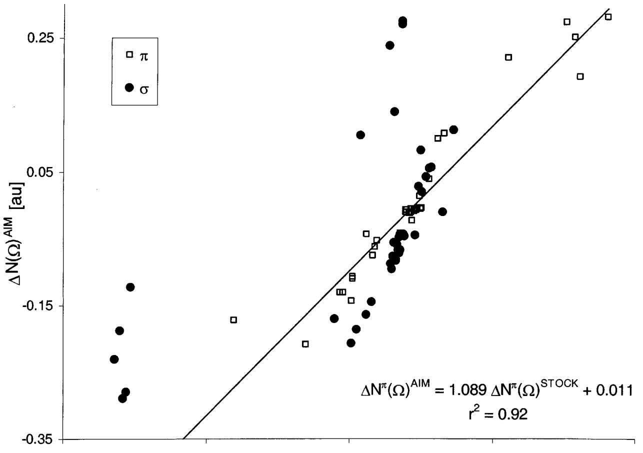

Figure 4. Plot of $\Delta N^{\sigma}(\Omega)$ and $\Delta N^{\pi}(\Omega)$ values calculated with the AIM theory vs their counterparts calculated with the Hirshfeld partitioning for all of the atoms of molecules **2**, **5**, and **9**−**11**.

partitionings provide similar variations in the π populations but large differences in the variations of the σ populations for the oxygen, carbon, and hydrogen atoms. It is a conclusion of the AIM results that the decrease of the carbon charge is originated by a σ electron donation from the hydrogen atoms. Part of this electronic population remains in the carbon atom, and another part is transferred to the oxygen atom. The oxygen atom transfers all of its charge to the proton as a σ charge, but it compensates for the part of the electron population that is lost with the π electron population that is gained from the carbon atom. Similar conclusions are obtained for the methylenimine molecule; the proton approximately gains the σ population that is lost by the hydrogens. At this point, if one observes the charge redistributions in methanol, oxacyclopropane, and methylamine (Table 1), where σ/π separation cannot be completed, it can be seen that the electronic population gained by the proton is similar to what the hydrogen atoms lost in the AIM partitioning. This is not true for the Hirshfeld partitioning. Although the hydrogen atoms transfer part of their electron population, this population loss is lower (approximately one-half of the AIM values) and not comparable to the electron population on the proton (approximately double the AIM population).

Protonation of π Electron Delocalized System and Resonance Forms. The study of the σ and π contributions to the atomic population was extended to molecules with π electron delocalization. This allows us to discuss the reliability of resonance forms for explaining the protonation process. The σ and π electronic populations calculated with both partitionings and the variations displayed after the protonation, ΔN^{σ} and ΔN^{π}, are shown in Table 5 (see Figure 3 for atom numbering). Both the absolute σ and π populations display large differences in the three molecules, as is the case for the total atomic charges. The most important differences are always found in the carbonyl group, although the nitrogen in **9** also shows large differences.

New and interesting conclusions can be obtained from the ΔN^{σ} and ΔN^{π} values. Large differences between the two partitionings are displayed for ΔN^{σ}. However, ΔN^{π} displays similar trends and almost similar values for every atom. In fact, ΔN^{π} values calculated for the same atom with the AIM and Hirshfeld partitioning display a fairly good linear relationship, whereas high scattering is observed for ΔN^{σ} (Figure 4).

The principal differences in ΔN^{σ} are found in the carbonyl group, and they are similar to those found in formaldehyde, that is, a large and positive value for the AIM charge at the carbon; on the other hand, the corresponding Hirshfeld values are small and negative. It can be observed that the presence of a nitrogen bound to the carbonyl carbon in **11** makes the AIM ΔN^{σ}(C2) value less positive than the ΔN^{σ}(C1) values in **9**, **10**, and **2**. The corresponding Hirshfeld ΔN^{σ}(C2) value is the most negative. Large and negative ΔN^{σ} values are obtained with both methods for the oxygen, but in this case, the largest values are found by employing the Hirshfeld partitioning. Similar trends between the two partitionings are obtained for the other atoms. A special case is, again, the carbon atom bonded to nitrogen in **11**. Its positive ΔN^{σ} value stays in line with the trend followed in the AIM studies by the atoms bonded to more electronegative atoms. The nitrogen atom presents positive ΔN^{σ} values that are significant in the AIM partitioning but negligible when the Hirshfeld partitioning is employed. The trends displayed by the hydrogen atoms are similar to those found in formaldehyde.

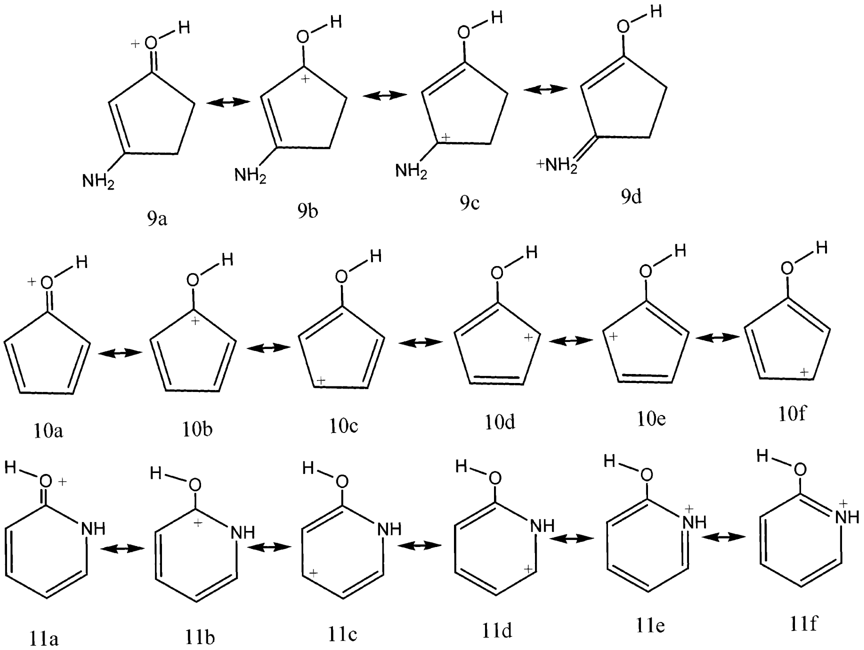

Figure 5. Resonance forms for molecules **9**−**11**.

Variations obtained with both partitionings are always negative, but those provided by AIM are approximately double those obtained with Hirshfeld.

On the contrary, similar values were obtained with both partitionings for ΔN^{π}. The carbonyl carbon is, again, the one that presents the largest discrepancies in every molecule that never reaches 0.1 au.

Figure 5 shows the possible resonance forms that can be drawn for molecules **9**−**11**. According to these forms, the O-protonation experienced by **9** should be accompanied by a decrease of the π electron population at O6, C1, C3, and N7. We can observe that both the AIM and Hirshfeld partitions show the π electron population of O6 and C1 increase (even very significantly for O6). For molecule **10**, the resonance forms predict that the π electron population should decrease in the oxygen and in all of the carbon atoms after the protonation. On the contrary, both methods employed here indicate that N^{π} increases significantly for the oxygen and slightly for C5. Finally, the resonance model predicts that the O-protonation of **11** should decrease the N^{π} value in O, N, C2, C4, and C6, whereas this quantity should remain constant for C3 and C5. Once more, both partitions reveal that the π electron charge does not follow these predictions. Thus, it results in increases at O and C2 and experiences its largest depletion at C5. Therefore, despite the fact that the applicability of the resonance model for explaining the structure and reactivity of organic compounds has been generally accepted,[30,31] and that it has been proven as a very useful tool in chemistry, this work contributes further evidence (now obtained with two different atomic partitioning schemes) of the unreliability of the resonance model for explaining the electronic charge redistribution in molecules with electronic delocalization.

Conclusions

The absolute values of the atomic charges obtained with the AIM theory are generally larger than those provided with the Hirshfeld scheme, particularly for electronegative atoms and the atoms bonded to them. With regard to the evolution of the charges, the main differences are found in the C−X−H groups. Thus, while the AIM partitioning provides large values for the charge of the proton and negligible variations for the charge of the X atom, the Hirshfeld partitioning results in a small charge for the proton and large variations for the oxygen/nitrogen charge. The carbonyl carbon displays negative and positive variations in its charge when AIM and Hirshfeld partitionings are used, respectively. The classical forms displaying the positive charge over the oxygen or nitrogen ($X^{+}-H$) in protonated forms are not supported by the AIM results, which point to $X-H^{+}$ representations.

A study of σ and π contributions to the charge variations shows that the differences between the two partitionings are concentrated in the σ contributions, with the π contributions being very similar in both methods. Thus, in this study, the unreliability of the resonance model for describing the electron charge redistribution that takes place upon protonation, proposed in previous work[23] on the basis of AIM results, is confirmed using charges based in the Hirshfeld partitioning.

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