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π Charge Distribution from Molecular Topology and π Orbital Electronegativity*

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The automatic and computer-aided prediction of reactivity by means of a few basic atomic parameters is achieved. Considering that only the topology of a molecule is required for the computation it is evident that PEOE (partial equalization of orbital electronegativity) and SD-POE (sigma dependent POE) models proposed by the authors together establish a valid alternative to the presently available, time consuming quantum mechanical procedures.

Furthermore, this approach gives a new insight into the interaction between σ and π electrons which seems worthy of further investigation. In addition, we have revived the concept of orbital electronegativity, especially in the case of the π electrons for which no calculation based on POE (pi orbital electronegativity) has, up to now, ever been performed.

INTRODUCTION

The electron distribution in a molecule is one of the most important factors characterizing the compound in its chemical and physical behaviour. Up to now many experimental and theoretical methods have been developed to obtain information about the overall electron density of a molecule. For the chemist the concept of partial atomic charge is more familiar than that of electron distribution. It is often used for the qualitative interpretation of a wide number of chemical properties as acidity, basicity, polarity of bonds, reaction mechanisms, resonance effects and many others.

In the course of the development of a synthetic design program, EROS^{1,2}, we were faced with the task of assigning reactivities to the bonds of a molecule. As one of the required parameters we needed the partial atomic charges of the atoms in a given molecule. Quantum mechanical approaches did not seem suitable for our purposes because of the long computation times involved and their limited applicability to small molecules. Further, the results of a Mulliken population analysis³ for calculating partial atomic charges are heavily dependent on the level of the quantum mechanical method.

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We were forced to look for an alternative approach and, analyzing in depth the concept of orbital electronegativity⁴⁻⁶, we succeeded in constructing a model for calculating partial atomic charges in σ -bonded systems⁷⁻⁹. By regarding the effect of the electrostatic potential generated on charge separation along a σ bond only partial equalization of orbital electronegativity (PEOE) is reached in our procedure. Only partial equalization of the orbital electronegativity does, however, lead to the correct prediction of partial atomic charges in isomeric molecules or groups. For, if total equalization occurred^{10,11}, all atoms would have the same electronegativity value. This leads to the unacceptable results that the carbon atoms in ethanol would have the same charge as those in dimethylether, for example. Furthermore, atoms of the same kind in a molecule would receive the same partial charge, e.g. in ethanol all hydrogens would have the same charge. Finally, isomeric groups would have the same group electronegativity at the point of attachment. All these predictions are contrary to any chemical experience.

Before starting to introduce the main features of our new model for calculating π charge distributions a brief presentation of the PEOE model and of its merits must be given here. There is a close affinity between the formalism and the basic ideas of the two models and, as will be shown later, the π orbital electronegativities (POE) are themselves dependent on the σ charge of the molecular skeleton.

Orbital Electronegativity (OE)

Mulliken first succeeded in putting the concept of electronegativity on a theoretical basis¹². His famous formula $\chi = (I + E)/2$, where I is the ionization potential and E the electron affinity of an atom, permits, by use of valence state ionization potentials and electron affinities, an assignment to each orbital of an atom in a specific hybridization state an OE value of its own. For an orbital ν we have

$$x_{\nu} = (I_{\nu} + E_{\nu})/2 \quad (1)$$

For example, one has a single OE value for the four orbitals of an sp^3 -carbon, while two distinct OE values result for the p and the three sp^2 orbitals of an sp^2 hybridized carbon atom.

The OEs do not only depend on hybridization but also on the occupation number, or charge, of an orbital. The higher the electron density in an orbital the lower will be the OE. The highest OE is found in the cationic, the lowest in the anionic state of an orbital.

To describe the dependence of OE on charge we applied Mulliken's formula to the anionic, the neutral, and the cationic state and described the dependence of the OE on charge by a second order polynomial as shown in Figure 1.

The coefficients a_{ν} , b_{ν} , and c_{ν} , that are characteristic for an orbital ν of an atom in a specific hybridization state can be determined by solving the system of equations for the three points of the parabola. To generate a charge of +1e on an atom A its neighbor sphere must be able to maintain an electronegativity which is at least as high as that given by eq (3). This expression is obtained by setting $q = +1$ in eq (2) (see Figure 1).

$$\chi_v^0 = \frac{1}{2} (I_v^0 + E_v^0)$$

$$\chi_v^+ = \frac{1}{2} (I_v^+ + E_v^+)$$

$$\chi_v^- = \frac{1}{2} (I_v^- + E_v^-) = \frac{1}{2} (-E_v^0 + 0)$$

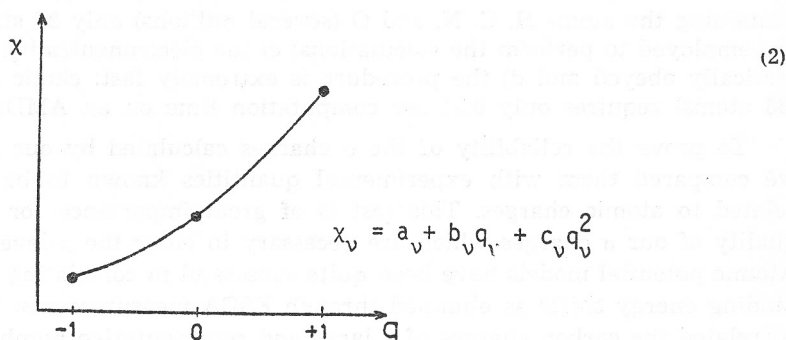


Figure 1. Dependence of orbital electronegativity on charge

$$\chi_A^+ = a_v + b_v + c_v \equiv D_v \quad (3)$$

It is necessary at this point to consider the electrostatic potential arising upon charge separation along a σ bond. The action of the electrostatic potential is opposite to that of the electronegativity and tends to diminish and dampen the charge transfer. In order to regard this important effect which is the very reason for only partial equalization of OE we developed an iterative procedure containing a geometric term representing the action of the electrostatic potential. This term provides convergence before total equalization of OE is reached. The charge shifted from an electropositive atom A to a more electronegative B in a molecule AB is given by eq (4)

$$q^{<\alpha>} = \frac{\chi_B^{<\alpha>} - \chi_A^{<\alpha>}}{D_A} \cdot \left(\frac{1}{2} \right)^\alpha \quad (4)$$

The denominator D_A scales the electronegativity difference to a charge value in electron units. In this equation α represents the actual iteration step and is the exponent for the damping factor $(1/2)^\alpha$. For molecules consisting of more than two atoms eq (4) can be expanded to eq (5). Here j are the more electronegative neighbors of atom i while k are the less electronegative ones. To compute the total charge at i after each iteration step the sum of all charges generated in the prior cycles must be added to the actual one as shown in eq (6). With the total charge new OE values can be computed by

inserting $Q_i^{<\alpha>}$ into the proper OE parabola (see Figure 1) and with these modified OE values eq (5) is re-entered.

$$q_i^{<\alpha>} = \left[\sum_j \frac{1}{D_{jv}} (\chi_{ju}^{<\alpha>} - \chi_{iv}^{<\alpha>}) + \sum_k \frac{1}{D_{k\lambda}} (\chi_{k\lambda}^{<\alpha>} - \chi_{iv}^{<\alpha>}) \right] \left(\frac{1}{2} \right)^\alpha \quad (5)$$

$$Q_i^{<\alpha>} = \sum_\alpha q_i^{<\alpha>} \quad (6)$$

The outstanding advantages of this procedure are a) only the connectivities of the atoms, i. e., the topology of a molecule, are required; b) for each orbital of an atom only three coefficients are necessary, thus for all these molecules containing the atoms H, C, N, and O (several millions) only 27 starting values are employed to perform the calculations; c) the electroneutrality rule is automatically obeyed and d) the procedure is extremely fast: cholic acid chloride (68 atoms) requires only 0.31 sec computation time on an AMDAHL 470 V6.

To prove the reliability of the σ charges calculated by our PEOE model we compared them with experimental quantities known to be intrinsically related to atomic charges. This test is of great importance for defining the quality of our σ charges which are necessary to enter the π -level calculation. Atomic potential models have been quite successful in correlating core electron binding energy shifts as obtained through ESCA measurements. We therefore correlated the carbon charges of a large and representative number of organic molecules with their C-1s-ESCA shifts as shown in Figure 2. The result is

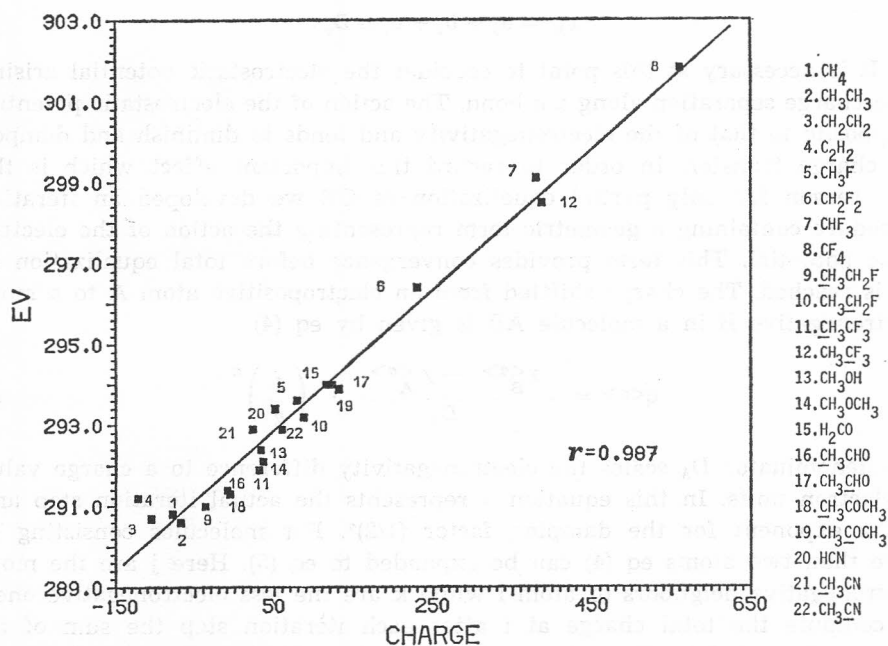


Figure 2. Correlation of PEOE charges at carbon with ESCA shifts. Charges given in millielectron units.

excellent as evident from the correlation coefficient of 0.987. In comparison, for the same compounds, the ab initio charges calculated on a STO-3G basis set show a much poorer agreement with the carbon ESCA shifts (see Figure 3). The correlation coefficient drops to 0.938, showing that the ab initio charges used here do not have predictive value for ESCA shifts.

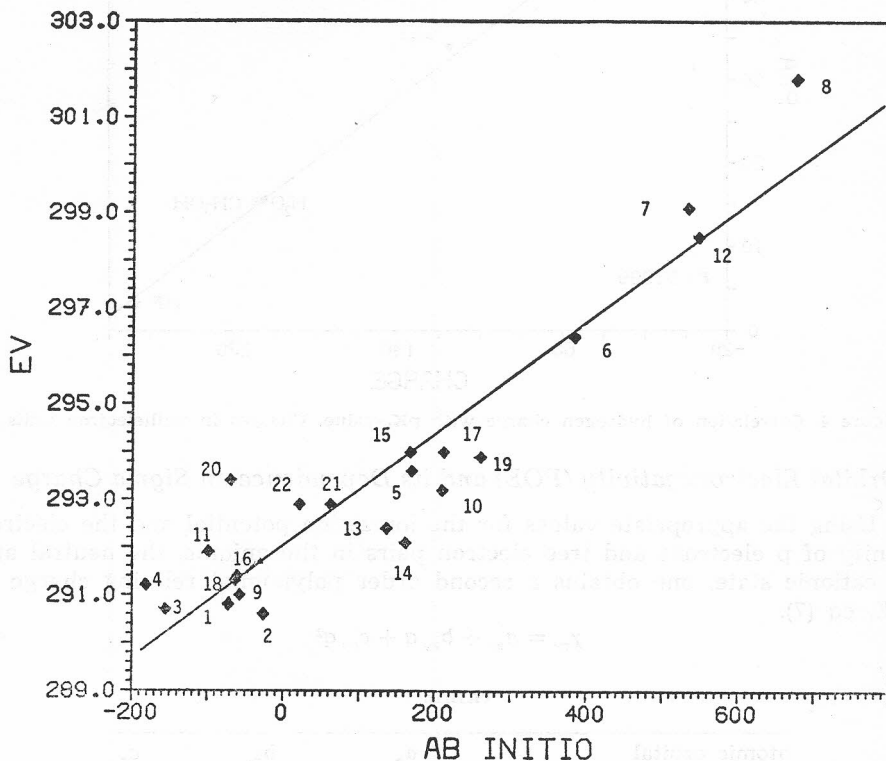


Figure 3. Ab initio charge correlation with ESCA shifts of the compounds given in Figure 2. Charges in millielectron units.

Another interesting and convincing test about the quality of the PEOE charges is provided by a correlation of the hydrogen charges of first row hydrides and related compounds with their pK_a -values. Here the acidity of the hydrogen atom is shown to be directly dependent on its atomic charge. The correlation is excellent with $r = 0.999$, and once again the PEOE charges show their applicability to chemical problems. The plot (Figure 4) shows that even small differences in the pK_a between water and methanol are correctly predicted.

These results encouraged us to attempt an extension of the model to π electron systems. By analogy with the σ -bonded systems we used the Mulliken equation and the values of the OE of p electrons and free electron pairs found in the literature¹³.

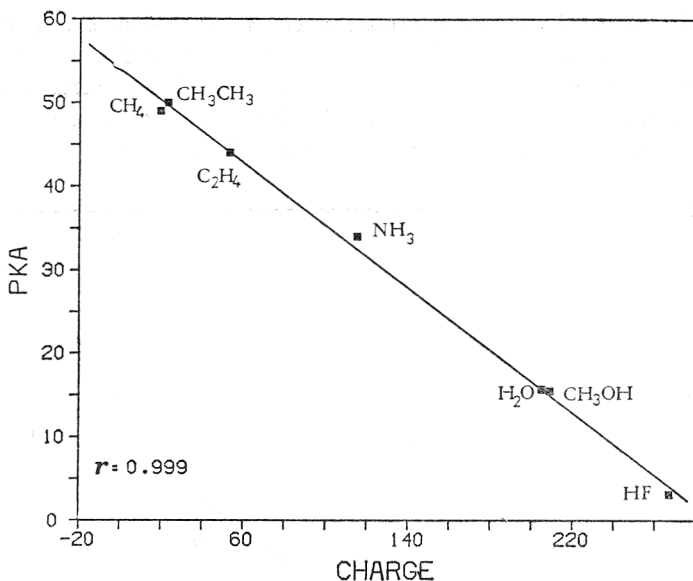


Figure 4. Correlation of hydrogen charge with pK_a -value. Charges in millielectron units.

π -Orbital Electronegativity (POE) and its Dependence on Sigma Charge

Using the appropriate values for the ionization potential and the electron affinity of p electrons and free electron pairs in the anionic, the neutral and the cationic state, one obtains a second order polynomial relating charge to POE, eq (7).

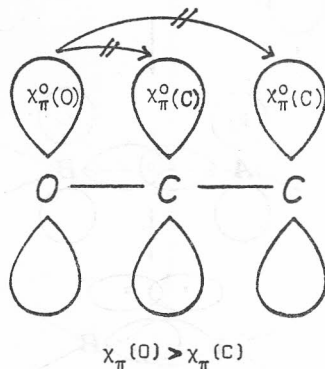
$$\chi_{\pi\nu} = a_{\pi\nu} + b_{\pi\nu} q + c_{\pi\nu} q^2 \quad (7)$$

TABLE I

atomic orbital	a_{π}	b_{π}	c_{π}
O-sp ² (p _z)	10.09	11.73	2.87
O-sp ³ (electron pair)	7.91	14.76	6.85
S-sp ² (p _z)	7.73	8.16	1.81
S-sp ³ (electron pair)	6.60	10.32	3.72
N-sp ² (p _z)	7.95	9.73	2.67
N-sp ³ (electron pair)	4.54	11.86	7.32
C-sp ² (p _z)	5.60	8.93	2.94
F (electron pair)	7.34	13.86	9.64
Cl (electron pair)	6.50	9.69	5.49
Br (electron pair)	5.20	9.68	4.48
J (electron pair)	4.95	8.81	3.86

A serious problem seemed at this point to make a π -level calculation based on POE impossible. If one were going to calculate the charge transferred from a free electron pair to a vicinal double bond using the POE values of the neutral state, no transfer from the heteroatom to the double bond would be possible. This is due to the higher POE of the free electron pair compared with that of the carbon p electron. So, for example, in fluoroethylene or hydro-

xyethylene no charge transfer to the double bond results, being $\chi_{\pi}^0(\text{F})$ or $\chi_{\pi}^0(\text{O})$ larger than $\chi_{\pi}^0(\text{C})$ as shown in Figure 5. Generally, whenever a +M effect is expected none can be predicted if the neutral state POE values are used.



FOR NEUTRAL STATE PI-ELECTRONEGATIVITIES

($Q_{\pi}=0$) NO DONOR CHARGE $\text{O} \rightarrow \text{C}$ POSSIBLE

Figure 5. For neutral state POE values no charge transfer $\text{O} \rightarrow \text{C}$ is possible.

A closer and more critical scrutiny of the bond formation steps lead us to the solution of this inadequacy. Figure 6 schematically shows two atoms forming a σ and a π bond. Because of the geometric arrangement of the orbital lobes the σ orbitals of the sp^2 hybridized atoms A and B will interact first. At this distance (stage 2 in Figure 6) there is no significant interaction between the two p_z orbitals. When the π interaction begins (stage 3 in Figure 3) a considerable amount of overlap in the σ bond has been formed with a consequent charge separation. This charge at the σ level causes a change in the nuclear screening which in turn affects the POE of the p_z electrons. If atom A becomes positively charged at the σ level, the diminished core shielding will enlarge the ionization potential and consequently the POE of the $p_z(\text{A})$ orbital. At atom B, on the contrary, the excess negative charge will cause an additional screening of the $p_z(\text{B})$ orbital which thereby lowers the POE of this orbital.

This reasoning clearly shows that the parabola describing the POE must contain as independent variable not only the π charge, which must be zero at the beginning of the π level computation, but also the σ charge. The sum of σ and π charge is the quantity on which the POE is dependent. After the σ level computation the σ charges of the atoms involved in a π level calculation are inserted into their specific POE parabolas (7) and from them the starting POE values are obtained. After this treatment all +M effects become correctly predictable because the POE of the free electron pairs has now become smaller than that of the vicinal carbon p_z orbital. In our calculation the amount of π charge shifted along a π bond consisting of the orbitals $p_z(\text{k})$ and $p_z(\text{j})$ is given by eq (8)

$$Q_{\pi}(\text{j}, \text{k}) = \chi_{\pi}(\text{k}) - \chi_{\pi}(\text{j})/D_{\text{j}} \quad \text{where} \quad \chi_{\pi}(\text{j}) < \chi_{\pi}(\text{k}) \quad (8)$$

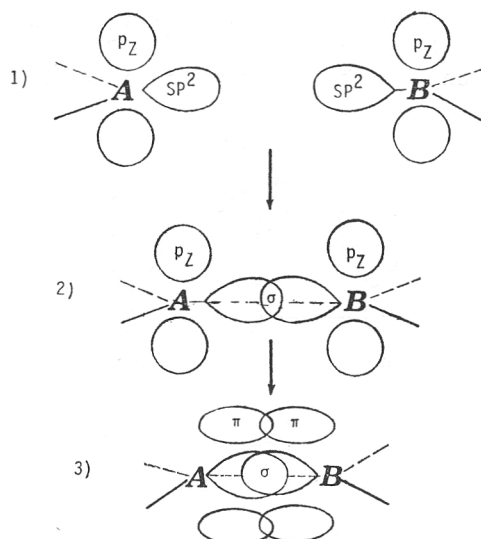


Figure 6. Two atoms A and B upon bond formation at the σ and π level.

The indices j and k in $Q_\pi(j, k)$ represent the atoms to which the orbitals involved in the calculation belong. D_j is defined by eq (3).

With eq (8) all types of $+M$ and $-M$ effects can be adequately treated by inserting the appropriate pairs of interacting orbitals (see below) generating a π charge as illustrated in Figure 7.

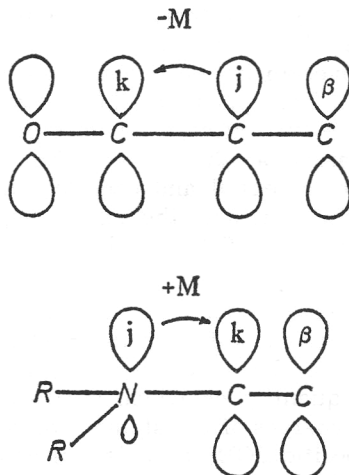
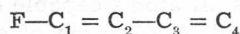


Figure 7. Schematic representation of $+M$ and $-M$ effects and the orbitals involved in the π charge generation.

When a $-M$ group, say CO, interacts with a double bond (see Figure 7) the orbitals considered in the computation of π charge are always the p_z orbital of the atom in the $-M$ group nearest to the double bond (k in Figure 7) and

the p_z orbital of the double bond atom directly connected with the $-M$ group (j in Figure 7). For $+M$ groups the free electron pair in an appropriate hybridization state interacts with the vicinal carbon p_z orbital (see Figure 7). According to the symmetry of the highest occupied MO (HOMO) and in line with the classical resonance theory the charge generated by the interacting orbitals j and k is then transmitted to the atom in position β to the respective conjugating group M (see Figure 7). Thus, for example, in aminoethylene the donor charge $Q_\pi(j, k)$ generated by interaction of the free electron pair in nitrogen and the p_z orbital of the carbon in α position is shifted onto the β carbon atom. A charge of the same magnitude but of opposite sign is found at the nitrogen atom.

In the case of longer non-aromatic π systems such as 1-fluorobutadiene one must be aware of the presence of a single bond between C_2 and C_3 . This single bond prevents the full transmission of the π charge created by conjugation of the fluorine electron pair with the vicinal π system to the second double bond.



In fact, there is no complete delocalization of the π electrons as found in benzene. The consequence is that the π charge at C_2 must surmount a sort of potential barrier represented by the single bond C_2C_3 to arrive at C_4 . The π charge at C_4 will then be smaller than that calculated for C_2 . The situation in fluorobenzene is completely different from that encountered in 1-fluorobutadiene. Here we have complete delocalization of the π electrons. Once the donor charge is released from the halogen into the aromatic ring it can be attributed to the conjugating centers ortho and para without there being any additional potential barrier between these centers. We now generalize our discussion to any conjugating group R and consider the charge $Q_\pi(R, C_1)$ as being injected into the aromatic ring.

How will this charge be distributed over the ortho and para positions? Because of the different σ charge, the ortho and para atoms have a different POE value for their p_z orbital. In the case of $+M$ groups the higher the POE, the higher will be the probability of finding the π charge at this specific position in the aromatic ring. On the other hand, if R represents a $-M$ group, the higher the POE, the lower will be the probability of finding the π charge at a certain atom of the aromatic system. The π charge that goes to a resonating atom i is proportional to a statistical factor W_i , defined by eq (9a) and (9b).

$$(9a) \quad +M : W_i = \frac{\chi_{\pi i}}{\sum_r \chi_{\pi r}} ; \quad (9b) \quad -M : W_i = \frac{(\chi_{\pi i})^{-1}}{\sum_r (\chi_{\pi r})^{-1}}$$

The sum goes over all conjugating atoms in the aromatic compound.

The charge fraction resulting at atom i is the given by eq (10)

$$Q_i = W_i Q_\pi(R, C_1) \quad (10)$$

The sum of the π charges at the centers i is the total π charge of the conjugating substituent R .

We have developed a computer program in PL/1 language that performs the π -level calculation using the σ charges of the system processed. These σ

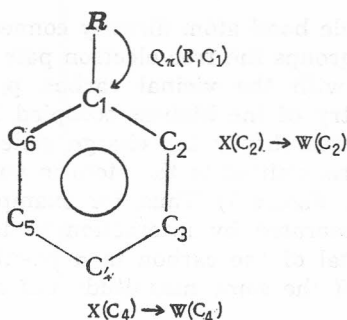


Figure 8. Schematic representation of charge generation and distribution over the conjugating atoms in an aromatic compound.

charges automatically enter the π calculation part of the program and by means of recursive procedures all atoms capable of conjugation with a specific $+M$ or $-M$ group are detected. Application of eqs (9) and (10) together with (8) allows the computation of π charges.

This simple formalism allows the calculation of the π charge distribution of any linear or cyclic conjugated system in an extremely short time. For aniline 0.16 sec are required on an AMDAHL 470 V6 for the σ and the π level computation.

The Performance of the Model: Correlation of π Charges with Experimental Quantities

To test the performance of our approach based on sigma dependent POE (SD-POE) we were looking for experimental quantities related to the π charges in order to correlate them with our ground state SD-POE charges. It is well known that π electrons have a high polarizability and show a marked sensitivity towards steric and electronic changes in the surroundings of the π system. The consequence of this is that whenever a specific measurement of a physical or chemical type is done to gain direct or indirect information about the structure of the π system in question one has to be aware of the interference of excited states with the ground state of the π system. The excited state is often generated by the measurement itself thus changing the π charge distribution pattern. It is therefore very difficult to find a quantity directly and unambiguously connected to the charge distribution in the ground state. Nevertheless, we attempted a correlation of our ground state charges for the para carbon atoms of monosubstituted benzenes with their C-13-NMR shifts. In these compounds a rigid geometry and a constant neighbor sphere interaction is expected at the C_4 in the benzene ring. This should provide similar conditions for all compounds analyzed. Figure 9 shows a very good agreement of our total charges at C_4 with the experimental shifts. Both $-M$ and $+M$ substituents fall on the same line. Even an extreme compound as the phenolate anion (see plot) is correctly predicted by our charges.

It is interesting to note that the meta carbon atoms which show very little difference in the magnitude of their total charge all correctly fall on the charges with the reactivity constants σ_R .

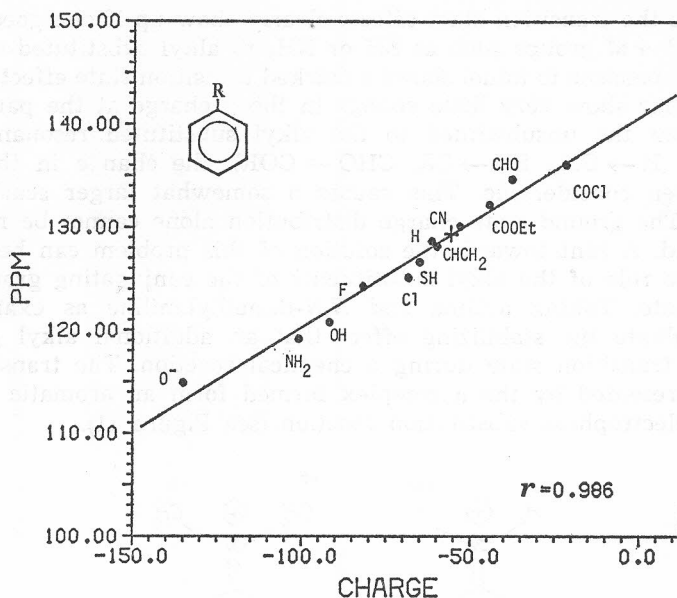


Figure 9. Correlation of total charges at para and meta atoms of monosubstituted benzenes with C-13-NMR shifts. Charges in millielectron units. The cross at about -60 me represents the cluster of meta carbons of the compounds shown.

Another interesting test is the correlation of the calculated SD-POE charges with the reactivity constants σ_R .

Our π charges at the para carbon atom show a very good agreement with the reactivity constant for all of the most important $+M$ and $-M$ groups as can be seen in Figure 10.

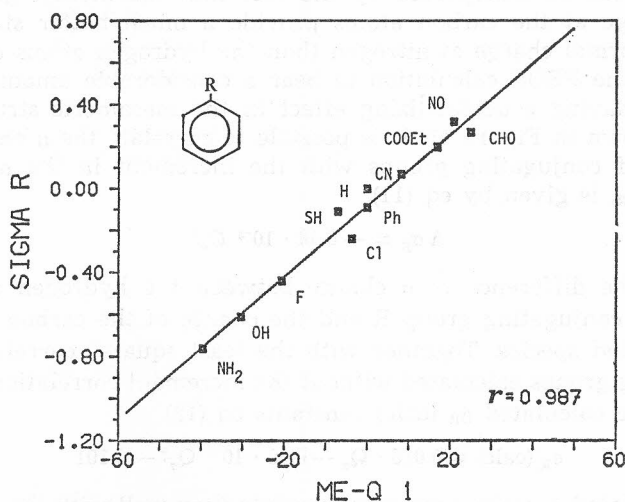


Figure 10. Correlation of π charges at the para position with σ_R constants. Charges given in millielectron units. Correlation line by least squares analysis.

But here the transition state effects clearly show up if one goes from the unsubstituted +M groups such as SH or NH₂ to alkyl substituted ones. Even the step from benzene to toluol shows a marked transition state effect. Although the calculations show very little change in the π charge at the para position in going from the unsubstituted to the alkyl substituted resonance groups (NH₂ \rightarrow NR₂, H \rightarrow CH₃, SH \rightarrow SR, CHO \rightarrow COR), the change in the σ_R constants is often considerable. This causes a somewhat larger scatter in the correlation. The ground state charge distribution alone cannot be responsible for this trend. A hint towards the solution of this problem can be found on analyzing the role of the alkyl substituents of the conjugating groups in the transition state. Taking aniline and *N,N*-dimethylaniline as examples, we want to evaluate the stabilizing effect that an additional alkyl group can have in the transition state during a chemical reaction. The transition state shall be represented by the σ complex formed from an aromatic compound during the electrophilic substitution reaction (see Figure 11).

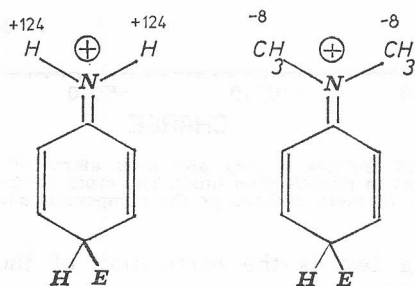


Figure 11. Stabilizing effect of alkyl groups compared to hydrogen atoms. Charges at the σ level for the neutral aromatic compound given in millielectron units.

The large negative value of σ_R in *N,N*-dimethylaniline compared to that of aniline itself can be interpreted by the fact that the methyl groups with a negative charge at the carbon atoms provide a much better stabilization of the positive formal charge at nitrogen than the hydrogen atoms do. These are predicted by the PEOE calculation to bear a considerable amount of positive charge, thus having a destabilizing effect in the mesomeric structure of the σ complex shown in Figure 11. It is possible to correlate the σ charge of alkyl substituents of conjugating groups with the increment in the σ_R value. The increment, $\Delta\sigma_R$, is given by eq (11).

$$\Delta\sigma_R = -0.48 \cdot 10^{-3} Q_{\sigma}^{\dagger} \quad (11)$$

Here Q_{σ}^{\dagger} is the difference in σ charge between the hydrogen atoms of the unsubstituted conjugating group R and the charge of the carbon atoms in the alkyl substituted species. Together with the least squares correlation line for all conjugating groups calculated without the increment correlations one finally obtains for the calculated σ_R (calc) constants eq (12)

$$\sigma_R \text{ (calc)} = 0.018 \cdot Q_{\pi} - 0.48 \cdot 10^{-3} Q_{\sigma}^{\dagger} - 0.101 \quad (12)$$

The calculated σ_R (calc) constants correlate very well with the experimental values, the correlation coefficient being $r = 0.990$. (See Figure 12)

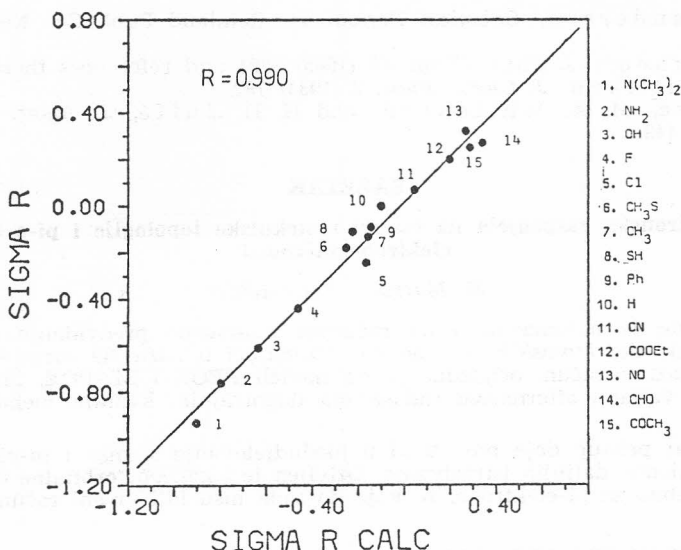


Figure 12. Correlation of calculated and experimental σ_R constants of the electrophilic aromatic substitution.

CONCLUSIONS

This encouraging result leads us close to our principal goal, the automatic and computer-aided prediction of reactivity by means of a few basic atomic parameters. Considering that only the topology of a molecule is required for the computation it is evident that our PEOE and SD-POE models together establish a valid alternative to the presently available, time consuming quantum mechanical procedures.

Furthermore, this approach gives new insight into the interaction between the σ and the π electrons which seems worthy of further investigation. In addition, we have revived the concept of orbital electronegativity, especially in the case of the π electrons for which no calculation based on POE has, up to now, ever been performed.

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SAŽETAK

Pi-elektronska raspodjela na osnovi molekulske topologije i pi-orbitalne elektronegativnosti

M. Marsili i J. Gasteiger

Postignuto je automatsko i na računalu zasnovano predviđanje reaktivnosti s pomoću nekoliko atomskih parametara. Uzimajući u obzir da samo molekularna topologija ulazi u račun, očigledno je da modeli PEOE i SD-POE, predloženi od autora, čine valjanu alternativu sadašnjima dugotrajnim kvantno-mehaničkim postupcima.

Uz to taj pristup daje novi uvid u međudjelovanje sigma- i pi-elektrona što može biti vrijedno daljnjih istraživanja. Oživljen je i koncept orbitalne elektronegativnosti, posebno za pi-elektrone, za koje do sada nisu bili vršeni računi zasnovani na POE.

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