

## EXTENSION OF THE METHOD OF ITERATIVE PARTIAL EQUALIZATION OF ORBITAL ELECTRONEGATIVITY TO SMALL RING SYSTEMS

MARIA DOLORES GUILLEN† and JOHANN GASTEIGER\*

Organisch-Chemisches Institut, Technische Universität München, D-8046 Garching, West Germany

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**Abstract**—By using a limited set of hybridization states the method of iterative partial equalization of orbital electronegativity has been extended to molecules containing three- and four-membered rings. The values of charges thus calculated have been successfully correlated with  $^{13}\text{C}$ - $^1\text{H}$  coupling constants, as well as with acidity constants, and can be used for the calculation of dipole moments.

Physical and chemical properties of systems with three- and four-membered rings are profoundly different from those of acyclic analogues.<sup>1,2</sup> The reasons lie in the unusual types of bonding in these molecules. Two different models for the bonding in cyclopropane have been developed<sup>3,4</sup> and it has been stated that these models can be transformed into each other.<sup>5</sup> However, this is true only if antibonding orbitals are taken into account, too.<sup>1b</sup>

We have developed the iterative partial equalization of orbital electronegativity (PEOE) method for calculating atomic partial charges.<sup>6,7</sup> In this method atomic orbitals are characterized by coefficients giving the charge dependence of their electronegativities, and allowance is made for interactions of atomic orbitals by working through the network of bonds. The wish to extend the method to small-membered rings necessitated a consideration of their special bonding. On the basis of the PEOE algorithm already implemented the valence bond model<sup>8</sup> of bonding seemed more appropriate for our purpose. In this model the (bent) bonds of three- and four-membered ring systems are considered as arising from orbitals with varying amounts of *s* and *p* character. The amount of hybridization depends on the type and number of rings involved and on whether exo- or endocyclic bonds are considered.

For the determination of hybridization states we were in the fortunate position of having developed an algorithm for the perception of the smallest set of smallest rings (SSSR).<sup>9</sup> Therefore, information concerning the individual rings which build up a ring system, and whether a bond participates in, or points out of, a ring, was directly available. With this information a list of hybridization states taken from the literature (Table 1) and contained within the program can be accessed.

An effort was made to limit the number of different hybridization states stored in the program with the result that no dependence of hybridization states on substitution patterns was considered although this

would probably give more realistic pictures.<sup>10,11</sup> Values for the orbital electronegativities of C, N, and O and the coefficients of their charge dependence for the different hybridization states have been calculated by interpolation from the values of the electronegativities of  $sp^3$ ,  $sp^2$ ,  $sp$  and  $p$  states.<sup>14</sup> With these additional parameters calculations of atomic charges by the iterative partial equalization of orbital electronegativities<sup>7</sup> were performed. As input this program only requires lists of atoms and bonds in a molecule.

### RESULTS

In order to demonstrate the significance of values obtained for atomic charges, correlations with physical or chemical data have to be derived. A physical constant reflecting rather obviously the peculiar bonding situations in systems with three- and four-membered rings is the  $^{13}\text{C}$ - $^1\text{H}$  coupling constant. Quite early on, an empirical correlation between  $^1J_{\text{C-H}}$  and the amount of *s*-character in that bond was discovered.<sup>12</sup> This relationship has been extended by several groups (e.g.)<sup>16</sup> Being interested in establishing the relevance of the computed charge values, we fitted the experimental data of Table 2 to the product of the charges on carbon,  $q_{\text{C}}$ , and hydrogen,  $q_{\text{H}}$ . The results thus obtained are given by eqn 1 ( $n = 21$ ,  $r = 0.994$ ,  $s = 3.8$ ) and listed in column 3 of Table 2.

$$^1J_{\text{C-H}} = 114.74 - 8.81 \cdot 10^3 q_{\text{C}} q_{\text{H}} \quad (1)$$

At first, in the light of correlations of  $^1J_{\text{C-H}}$  with the amount of *s*-character,<sup>12,16</sup> it might not seem too surprising that a good correlation was obtained, as some of the parameters were deduced from  $^1J_{\text{C-H}}$  data. However, several points need to be stressed.

First, eqn (1) extends over the entire range of available data, demonstrating that the charges on hydrogen and carbon are well balanced for both saturated and unsaturated compounds, as well as for the various small ring systems of quite different structure. Furthermore, the nature of our procedure,<sup>4</sup> that is, merely working through the constitution of a molecule as given by the network of bonds, seems also to be able to reproduce small trends in the coupling constants. For example, the change in  $^1J_{\text{C-H}}$

\*Present address: Departamento de Química Física, Escuela Técnica Superior de Ingenieros de Minas, Universidad de Oviedo, Spain.

Table 1. Hybridization parameters used in the calculations. For unsaturated and polycyclic compounds only those parameters different from those of the parent monocyclic structure are given, e.g. for bond orbital 2-3 in spirocyclopentane  $sp^3$  hybridization is assumed. Note also, that bond orbital hybridization is directional whereas for bond orbital 1-2 in spirocyclopentane  $sp^3$  hybridization is taken, for bond orbital 2-1 a value of  $sp^3$  is again used




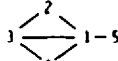

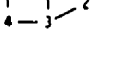
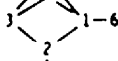

















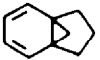

	bonds		ref.
	endocyclic	exocyclic	
	1-2 $sp^5$	1-4 $sp^2$	10
	1-2 $sp^{3.35}$	1-5 $sp^{2.84}$	11
	1-2 $sp^3$		10, 11
	1-2 $sp^3$ 1-3 $sp^9$	1-5 $sp^{1.5}$	
	1-2 $sp^{4.6}$ 1-3 $sp^{5.25}$ 1-5 $sp^{2.5}$	1-6 $sp^{1.5}$	11
	1-2 $sp^{4.72}$ 2-1 $sp^{4.45}$	1-6 $sp^{1.1}$ 2-7 $sp^{2.16}$	13
	1-2 $sp^{4.5}$	1-6 $sp^{1.29}$	13
	1-4 $sp^{3.9}$	1-9 $sp^{1.58}$	13
	1-2 $sp^3$ 1-3 $sp^3$	1-4 $sp$	5
	1-2 $sp^{2.25}$ 1-4 $sp^{2.25}$	1-5 $sp^{1.6}$	-

Table 2 Experimental and calculated (eqn 1) values of  $^{13}\text{C}$ - $^1\text{H}$  coupling constants, experimental and calculated (eqn 2) acidity constants. Values in parentheses are predicted data

	$^1J_{^{13}\text{C}-\text{H}} \text{ [Hz]}$		$\text{p}K_{\text{a}}$	
	exp.	calc.	exp.	calc.
$\text{CH}_4$	125	128.0	47	49.8
$\text{CH}_3\text{CH}_3$	125	128.4	48	49.0
$\text{CH}_3\text{CH}_2\text{CH}_3$			49	48.1
$\text{C}(\text{CH}_3)_4$	126	127.2		
	128	127.1	48	48.1
	124	127.1	49	48.1
	123	127.1		
	162	164.7	44	41.9
	160	156.1		
	2-) 156	150.9		(39.9)
	1-) 205	207.6		(37.3)
	134	130.7	47	46.0
	2-) 125	122.3		(47.0)
	1-) 146	146.0		(39.1)
	6-) 200	204.0		(37.1)
	5-) 206	204.1		
	1-) 178	180.8		
	5-) 206	202.5		
	10-) 162	156.3		
	7-) 136	130.0		
$\text{H}_2\text{C}=\text{CH}_2$	156	164.0	42	42.0
$\text{HC}\equiv\text{CH}$	249	246.9	25	25.9

in the series (tricyclo[3.1.1.0<sup>2,3</sup>] heptane, bicyclo[1.1.0]butane, spiropentane, cyclopropane (146, 156, 160, 162 respectively) is reflected by the calculated values (146.0, 150.9, 156.1, 164.7 respectively), although for each of the carbon atoms considered a hybridization of  $sp^1$  for bonds within the three-membered rings and  $sp^2$  for the two bonds exocyclic to the three-membered rings was taken.

Table 2 also gives experimental  $pK_s$  values and data calculated by eqn (2)

$$pK_s = 54.3 - 231.4 q_H \quad (2)$$

Unfortunately, some interesting  $pK_s$  values have not yet been determined experimentally, and so we were unable to test this simple relationship to its full extent. Nevertheless, we could not resist the temptation to use eqn 2 for the prediction of some unknown  $pK_s$  values (Table 2, column 5, values in parentheses).

The dipole moment is a physical property rather obviously related to the charge distribution in a molecule. However, in molecules with free electron pairs the center of electron distribution around an atom might not coincide with the nuclear center. Therefore, in calculating dipole moments by eqn (3),

$$\mu = \sum q_i r_i \quad (3)$$






















the distances  $r_i$  to these electronic centers should be used. Unfortunately, there is no simple way of estimating them. We therefore used the experimental bond distances, as approximations for  $r_i$ , in eqn (3),

knowing that for molecules with free electron pairs dipole moments which are too small might be calculated. Using atomic charges obtained by iterative partial equalization of orbital electronegativity this was confirmed for a series of simple unstrained molecules.<sup>17</sup> The calculated dipole moments were in good agreement with expectation demonstrating that not only trends in, but also the magnitudes of the atomic charges are significant. In this context it is of particular importance that in the parametrization of our method dipole moments were *not* used for calibration, in contrast to other empirical or semi-empirical approaches to estimating dipole moments.<sup>19,24</sup> Applying eqn (3) to the small ring compounds reported here gave the results collected in Table 3. Keeping in mind the approximation inherent in using bond distances in eqn (3) the calculated values are in quite good agreement with expectation. Only the values for the fluorosubstituted compounds, for oxiranes, and for cyclopropanone are slightly higher than expected. This has already been observed in a similar fashion with fluorosubstituted methanes and dimethyl ether.<sup>17</sup>

With this limitation the values of Table 3 show that the atomic charges of small ring compounds are of the correct magnitude. This gives further significance to the extension of the method of partial equalization of orbital electronegativity to small ring compounds.

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Table 3 Dipole moments (in D) calculated with eqn 3 by using bond distances. Experimental values (in parentheses) from Ref. 18

					
0.10 (0.14)	0.08 (0.14)	0.12 (0.45)	2.64 (2.32)	2.72 (2.37)	4.75 (3.89)
					
2.64 (2.98)	1.24 (1.76)	1.37 (1.58)	0.62 (1.19)	1.49 (1.46)	2.77 (2.67)
					
4.19 (4.39)	2.26 (1.88)	1.33 (1.89)	1.81 (1.84)	0.07 (0.13)	
					
1.69 (1.62)	2.69 (2.89)	1.40 (2.02)	0.50 (1.10)		

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