

## Comparison between Experimental and Theoretical Scales of Electrophilicity in Benzhydryl Cations

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The theoretical electrophilicity pattern of a series of benzhydryl cations as described in terms of a model based on global reactivity indexes is compared with an experimental scale recently proposed by Mayr et al. [*J. Am. Chem. Soc.* **2001**, *123*, 9500]. A good correlation between both theoretical and experimental quantities is found. The effect of chemical substitution on the electrophilic power of these charged electrophiles may also be assessed as local responses at the active site, in terms of a global contribution described by changes in global electrophilicity with reference to the dianisylcarbenium ion, and a local contribution described by the variations in electrophilic Fukui function at that site.

### 1. Introduction

The understanding of the course of organic chemical reactions was stimulated with the development of Lewis' valence electronic theory<sup>1</sup> and the general acid–base theory of Lowry and Brønsted.<sup>2</sup> On the basis of these electronic models, Ingold in the 1930s introduced the electrophile and nucleophile concepts in atoms and molecules.<sup>3</sup> These terms are associated with electron-deficient and electron-rich species, respectively. From that time, there have been several attempts to classify organic molecules within empirical (hopefully unique) scales of electrophilicity and nucleophilicity. Consider, for instance, the linear free-energy relationships (LFERs), including the well-known Hammett equation.<sup>4</sup> Similar relationships involving kinetic parameters instead of equilibrium constants have also been proposed in the literature.<sup>5–8</sup> One of the first quantitative attempts to classify *electrophilicity* and *nucleophilicity* as general

concepts was reported by Swain and Scott.<sup>9</sup> These authors defined nucleophilicity, *n*, as an intrinsic property of the nucleophile using the rates of S<sub>N</sub>2 reactions of organic compounds, according to the following expression:

$$\log(k/k_{\text{H}_2\text{O}}) = sn \quad (1)$$

where  $k_{\text{H}_2\text{O}}$  corresponds to the nucleophile rate constant of the reaction with water, and *s* represents the sensitivity (specific to each electrophile) of the rate constants to variations in the nucleophile system;<sup>9</sup> *k* is the rate constant for the reaction of the electrophiles with the reference nucleophile. In a series of papers, the first one in 1954, Edwards proposed a more general four-parameter equation, which related the rate constants with different properties of the nucleophile such as basicity, polarizability, and oxidation potential.<sup>10,11</sup> Although the model did a better job correlating an impressive amount of experimental data, Pearson preferred to use the more qualitative principle of hard and soft acids and bases (HSAB) to explain these nucleophile–electrophile interactions.<sup>12</sup>

In 1972, Ritchie proposed a model based on reactions of carbocations and diazonium ions with nucleophiles.<sup>13</sup> He found that in this type of reaction, it was possible to characterize a particular nucleophilic system by one

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constant parameter  $N_+$ , which is independent of the nature of the electrophile, namely:

$$\log(k/k_0) = N_+ \quad (2)$$

where  $k$  is the rate constant for the reaction of a cation with a given nucleophile (i.e., a given nucleophile in a given solvent), and  $k_0$  is the rate constant for the reaction of the same cation with water in water.<sup>13</sup> It was later shown that eq 2 is not strictly valid and that better correlations are obtained when different families of electrophiles are treated separately.<sup>14</sup> The comparison of eqs 1 and 2 suggests the tendency to find definitions of absolute electrophilicity and nucleophilicity scales. However, this objective is difficult to reach if one considers that a universal electrophilicity/nucleophilicity model should accommodate substrates, within the same scale, with a large diversity in electronic and binding properties, without mentioning the presence of the medium.

Recent works of Mayr and co-workers<sup>15–25</sup> have strengthened this tendency. In fact, these authors have established that, in contrast to the accepted opinion about the relative character of the experimental electrophilicity/nucleophilicity scales for many reactions in organic and organometallic chemistry, it would be possible to define nucleophilicity and electrophilicity parameters that are independent of the reaction partners. Mayr et al. proposed that the rates of reactions of carbocations with uncharged nucleophiles obey the linear free-energy relationship given by:<sup>15–25</sup>

$$\log k = s(E + N) \quad (3)$$

where  $E$  and  $N$  are the electrophilicity and nucleophilicity parameters, respectively, and  $s$  is the nucleophile-specific slope parameter, which is usually close to 1, so that it may be neglected for qualitative considerations. These authors observed that in general, the solvent effects on the reaction rates with  $\pi$  nucleophiles and hydride donors were small and could, to a first approximation, be neglected.<sup>17</sup> For the determination of the strengths of electrophiles, Mayr et al. performed a correlation analysis of the reactions of the electrophiles with reference  $\pi$  nucleophiles that yielded  $E$ ,  $N$ , and  $s$  of the reagents involved.<sup>15–25</sup> On this basis, these authors have constructed experimental relative scales of electrophilicity and nucleophilicity for a wide diversity of organic and organometallic species, including diarylcarbenium ions, aryldiazonium ions, alkoxy-carbenium ions, etc.<sup>15</sup> This

scale particularly includes reactions of cationic carbon electrophiles with nucleophiles in which only one bond is formed in the rate-determining step and no  $\sigma$ -bonds in the electrophile are broken.<sup>15–25</sup>

From the theoretical point of view, the electrophilicity concept has been recently developed by several authors,<sup>26–30</sup> on the basis of global reactivity indexes defined for the ground states of atoms and molecules. By construction, these scales are absolutes, in the sense that they are independent of the nucleophile partners, mainly because they are supposed to solely depend on the electronic structure of molecules. Up to now, it has not been possible to obtain quantitative definitions of nucleophilicity models, yet some inverse empirical relationships between nucleophilicity and electrophilicity (i.e., nucleophilicity = 1/electrophilicity) have been proposed.<sup>31</sup> Recently, Parr, Szentpály, and Liu have introduced a new and useful definition of global electrophilicity,  $\omega$ , in terms of the electronic chemical potential and the chemical hardness, that provides an absolute scale for the electrophilic power of molecules.<sup>27</sup>

In this work, we compare the experimental model of electrophilicity proposed by Mayr et al.<sup>25</sup> with the definition of electrophilicity proposed by Parr et al., based on reactivity indexes for a series of benzhydryl cations. We further study the effect of chemical substitution on the electrophilicity pattern of these systems by looking at the variation in regional electrophilicity at the active site induced by electron-releasing and electron-withdrawing functional groups.

## 2. Model Equations

The global electrophilicity index  $\omega$ , which measures the stabilization in energy when the system acquires an additional electronic charge  $\Delta N$  from the environment, has been given the following simple expression:<sup>27</sup>

$$\omega = \frac{\mu^2}{2\eta} \quad (4)$$

in terms of the electronic chemical potential  $\mu$  and the chemical hardness  $\eta$ , which may be approached in terms of the one-electron energies of the frontier molecular orbital HOMO and LUMO,  $\epsilon_H$  and  $\epsilon_L$ , as  $\mu \approx \epsilon_H + \epsilon_L/2$  and  $\eta \approx \epsilon_L - \epsilon_H$ , respectively.<sup>32,33</sup> The electrophilicity index encompasses both, the propensity of the electrophile to acquire an additional electronic charge driven by  $\mu^2$  (the square of the electronegativity) and the resistance of the system to exchange electronic charge with the environment described by  $\eta$ , simultaneously. A good electrophile is, in this sense, characterized by a high value of  $\mu$  and a low value of  $\eta$ . Associated with the

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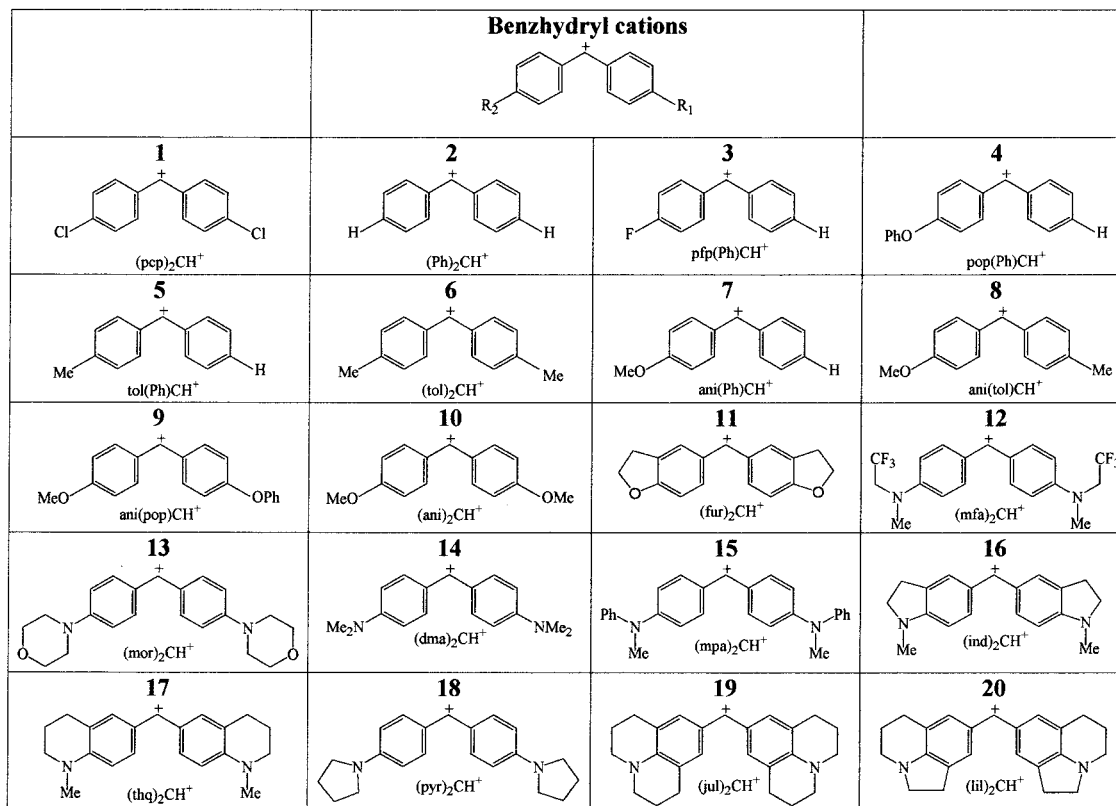
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CHART 1. Structures of Benzhydryl Cations Chosen to Determine Global and Local Parameters



definition of global electrophilicity, there is an additional and useful relationship that accounts for the maximum electronic charge  $\Delta N_{\max}$  that the electrophile may accept from the environment. Note that in the present approach, the environment may be represented by either external effects coming, for instance, from the interaction with the solvent, or more simply as *field effects* coming from the presence of substituent groups in the molecule.  $\Delta N_{\max}$  has been defined as:<sup>27</sup>

$$\Delta N_{\max} = -\frac{\mu}{\eta} \quad (5)$$

Starting from eq 4, it is possible to define a local (regional) counterpart for the  $\omega$  and  $\Delta N_{\max}$  quantities as follows: use the inverse relationship between the chemical hardness and the global softness  $S = 1/\eta$ <sup>32</sup> and the additivity rule for  $S$ , namely,  $S = \sum_k s_k^+$ <sup>32,33</sup> to rewrite eq 4. The result is the following equation:

$$\omega = \frac{\mu^2}{2\eta} = \frac{\mu^2}{2} S = \frac{\mu^2}{2} \sum_k s_k^+ = \sum_k \omega_k \quad (6)$$

from which we may define a semilocal, or regional, electrophilicity power condensed to atom  $k$ :

$$\omega_k = \frac{\mu^2}{2} s_k^+ \quad (7)$$

Also, the following partition for  $\Delta N_{\max}$  is possible in terms of the electrophilic Fukui function  $f_k^+$ :

$$\Delta N_{\max}(\mathbf{k}) = \Delta N_{\max} f_k^+ \quad (8)$$

Note that within the present model, the maximum electrophilicity power within a molecule will be located at the softest site of the system. If we further use the exact relationship between the local softness and the electrophilic Fukui function, namely,<sup>32,33</sup> then the local electrophilicity power given in eq 7 may be also expressed as

$$\omega_k = \frac{\mu^2}{2} s_k^+ = \frac{\mu^2 S}{2} f_k^+ = \omega f_k^+ \quad (9)$$

thereby showing that the maximum electrophilicity power in a molecule will be developed at the site where the Fukui function for a nucleophilic attack  $f_k^+$  displays its maximum value, i.e., at the active site of the electrophile. Local (regional) descriptors of electrophilicity/nucleophilicity have been previously proposed in the literature.<sup>34,35</sup> The relative electrophilicity ( $s_k^+/s_k^-$ ) and relative nucleophilicity ( $s_k^-/s_k^+$ ) indexes introduced by Roy et al.<sup>34,35</sup> defined in terms of the electrophilic and nucleophilic softness apply only to those sites having comparable and higher values of  $s_k^+$  and  $s_k^-$ , and in this sense, these definitions are less universal than the one presented in eqs 7 and 9 for local electrophilicity. Another advantage of eqs 7 and 9 is that they provide normalized definitions of local electrophilicity.

### 3. Computational Details

Full geometry optimizations for different benzhydryl cations (see Chart 1) were performed at the B3LYP/6-31G(d) level of

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**TABLE 1.** HOMO and LUMO Values, Global Electrophilicity Values ( $\omega$ ), Electronic Chemical Potential ( $\mu$ ), Chemical Hardness ( $\eta$ ), Electrophilic Fukui Function at the Active Site ( $f_C^+$ ), Local Electrophilicity ( $\omega_C$ ), Experimental Electrophilicity ( $E$ ), and Maximum Electronic Charge at the Active Site ( $\delta\Delta N_{\max}(k)$ ) Values for a Series of Benzhydryl Cations<sup>a</sup>

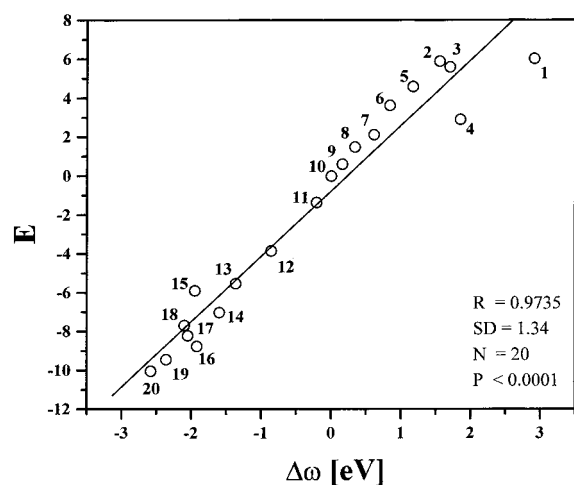
benzhydryl cation	HOMO [au]	LUMO [au]	$\mu$ [eV]	$\eta$ [eV]	$\omega$ [eV]	$f_C^+$	$\omega_C$ [eV]	$E^b$	$\delta\Delta N_{\max}(k)$
<b>1</b>	-0.39019	-0.28291	-9.16	2.92	14.36	0.3290	4.73	6.02	0.1428
<b>2</b>	-0.40519	-0.28171	-9.35	3.36	13.00	0.3550	4.61	5.90	0.0981
<b>3</b>	-0.40195	-0.28124	-9.29	3.28	13.15	0.3479	4.58	5.60	0.0952
<b>4</b>	-0.35351	-0.25793	-8.32	2.60	13.30	0.3285	4.37	2.90	0.1614
<b>5</b>	-0.39328	-0.27350	-9.07	3.26	12.62	0.3456	4.36	4.59	0.0726
<b>6</b>	-0.38248	-0.26604	-8.82	3.17	12.29	0.3376	4.15	3.63	0.0509
<b>7</b>	-0.37617	-0.26149	-8.68	3.12	12.06	0.3311	3.99	2.11	0.0311
<b>8</b>	-0.36658	-0.25512	-8.46	3.03	11.79	0.3252	3.84	1.48	0.0177
<b>9</b>	-0.34361	-0.24283	-7.98	2.74	11.61	0.3138	3.64	0.61	0.0238
<b>10</b>	-0.35229	-0.24596	-8.14	2.89	11.45	0.3161	3.62	0.00	0.0000
<b>11</b>	-0.34076	-0.23905	-7.89	2.77	11.24	0.3094	3.48	-1.36	-0.0073
<b>12</b>	-0.31987	-0.22465	-7.41	2.59	10.59	0.2903	3.07	-3.85	-0.0594
<b>13</b>	-0.30547	-0.21432	-7.07	2.48	10.08	0.2790	2.81	-5.53	-0.0939
<b>14</b>	-0.30772	-0.21382	-7.10	2.56	9.85	0.2845	2.80	-7.02	-0.0992
<b>15</b>	-0.30028	-0.20786	-6.91	2.51	9.50	0.2827	2.69	-5.89	-0.1121
<b>16</b>	-0.29575	-0.20590	-6.82	2.44	9.53	0.2778	2.65	-8.76	-0.1137
<b>17</b>	-0.29625	-0.20525	-6.82	2.48	9.40	0.2799	2.63	-8.22	-0.1179
<b>18</b>	-0.29958	-0.20641	-6.88	2.54	9.35	0.2815	2.63	-7.69	-0.1250
<b>19</b>	-0.28844	-0.19938	-6.64	2.42	9.09	0.2723	2.47	-9.45	-0.1436
<b>20</b>	-0.28629	-0.19678	-6.57	2.44	8.87	0.2688	2.38	-10.04	-0.1641

<sup>a</sup> See the text for details. <sup>b</sup> Experimental electrophilicity values were taken from reference 25.

theory using the Gaussian98 package.<sup>36</sup> Global electrophilicity ( $\omega$ ) was evaluated using eq 4. The electronic chemical potential  $\mu$  and the chemical hardness  $\eta$  were evaluated using the frontier molecular orbital model described in the Model Equations Section. Electrophilic Fukui functions  $f_C^+$  were obtained from single-point calculations at the optimized structures in their ground states, by a method described elsewhere.<sup>37–39</sup> This method evaluates the Fukui function for electrophilic and nucleophilic attack as the electron density of the molecular orbital involved in the reaction. The electrophilic Fukui function is obtained from the frontier molecular orbital coefficients and the overlap matrix. With these values at hand, the local electrophilicity ( $\omega_k$ ) is obtained from eq 9.

#### 4. Results and Discussion

Chart 1 depicts the structure of the whole database of benzhydryl cations considered in the present study with a wide combination of substituents at the para position. Table 1 summarizes the global and local quantities used to establish the relationship between the experimental and theoretical scales of electrophilicity, including the HOMO and LUMO values for the whole series. The values of electronic chemical potential ( $\mu$ ) and chemical hardness ( $\eta$ ) are included for computing the global



**FIGURE 1.** Linear correlation between the experimental electrophilicity ( $E$ ) and the theoretical relative global electrophilicity ( $\Delta\omega$ ) at the B3LYP/6-31G(d) level of theory.  $R$  is the regression coefficient, and  $SD$  is the standard deviation;  $N$  is the number of points, and  $P$  is the probability that the observed relationship between the variables was randomly obtained. Compound **10** is the reference for both scales.

electrophilicity index ( $\omega$ ) using eq 4. It may be seen that variations in global electrophilicity as described by the  $\omega$  index are not as regular as the variations in local electrophilicity described by  $\omega_C$ , which shows a monotonically decreasing pattern in a better agreement with the experimental scale (compare, for instance, compounds **2–4** and **15** and **16** in the  $\omega$  column with the experimental values in Table 1).

Figure 1 displays the observed correlation between the experimental electrophilicity scale of Mayr et al. ( $E$ ), and the theoretical global electrophilicity index described by  $\Delta\omega = \omega(\text{cation}) - \omega(\text{reference})$ , where the dianisylcarbenium ion ( $R_1 = R_2 = \text{OMe}$ , compound **10**, or  $(\text{ani})_2\text{CH}^+$ ) is taken as a reference in both scales. The electrophilicity value of the reference in Mayr's scale is  $E = 0.0$ .<sup>15,25</sup> It

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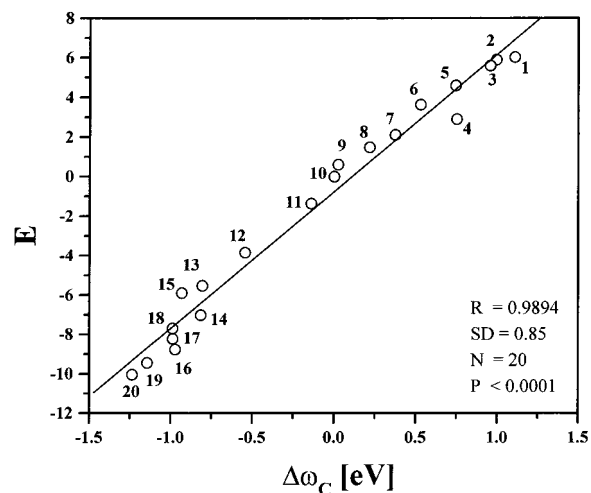


may be seen that in general, a good correlation is obtained between both scales. Compounds that lie below the reference in the experimental axis and correspondingly at the left-hand side of the zero of the  $\Delta\omega$  scale display a deactivating electrophilic pattern induced by the para substitution with groups that seem to act as electron-releasing groups when compared to the reference compound **10**. Compounds with electrophilicity values over the reference in the experimental axis and correspondingly at the right-hand of the zero of the theoretical scale show electrophilic activation by chemical substitution with groups that seems to act as electron-withdrawing substituents when compared to the reference compound **10**. To quantitatively establish the inductive effect at the active site that explains the observed electrophilic activation and deactivation shown in Figure 1, we propose to analyze this effect within a simplified model of electrostatic inductive effects. This model is based on eq 8 describing the responses in the maximum electronic charge that the active site may accept from the environment. If we define

$$\delta\Delta N_{\max}(\mathbf{k}) = \Delta N_{\max}(\mathbf{k}, \text{cation}) - \Delta N_{\max}(\mathbf{k}, \text{reference}) \quad (10)$$

where  $\mathbf{k}$  is the active site, then eq 10 describes the change in the maximum charge that this site may accept from the chemical environment upon substitution with reference to the dianisylcarbenium ion, the zero in both the experimental and theoretical scales of electrophilicity. The values of  $\delta\Delta N_{\max}(\mathbf{k})$  are quoted in the last column of Table 1. It may be seen that the whole subseries of compounds that deactivates the electrophilic pattern in the carbenium electrophiles (i.e., those lying below the reference dianisylcarbenium ion in Figure 1) consistently shows negative values of  $\delta\Delta N_{\max}(\mathbf{k})$ , whereas those compounds lying above the reference compound show positive values of  $\delta\Delta N_{\max}(\mathbf{k})$ . Therefore, the chemicals belonging to the first subseries (compounds **11–20** in Chart 1) promote electrophilic deactivation due to chemical substitution by groups that act as electron-releasing groups, thereby lowering the maximum charge capacity at the active site ( $\delta\Delta N_{\max}(\mathbf{k}) < 0$ ). On the other hand, the chemicals belonging to the second subseries (compounds **1–9** in Chart 1) promote electrophilic activation due to chemical substitution by groups acting as electron-withdrawing functionalities, thereby enhancing the maximum charge capacity at the active center of the charged electrophiles ( $\delta\Delta N_{\max}(\mathbf{k}) > 0$ ).

It is well recognized, however, that the change in electrophilicity induced by chemical substitution manifests itself as a local response at the active site (i.e., at the carbocation site in this case).<sup>40–42</sup> This argument is reinforced by the result discussed above, showing that the enhancement/lowering in the electrophilic pattern of carbenium ions induced by chemical substitution may be explained on the basis of a localized inductive effect at the active site. With this argument in mind, we performed an additional comparison between the experimental electrophilicity scale,  $E$ , and the local index  $\Delta\omega_{\mathbf{k}}$



**FIGURE 2.** Linear correlation between the experimental electrophilicity ( $E$ ) and the theoretical relative local electrophilicity ( $\Delta\omega_{\mathbf{C}}$ ) at the B3LYP/6-31G(d) level of theory.  $R$  is the regression coefficient, and  $SD$  is the standard deviation;  $N$  is the number of points, and  $P$  is the probability that the observed relationship between the variables was randomly obtained. Compound **10** is the reference for both scales.

$= \omega_{\mathbf{k}}(\text{cation}) - \omega_{\mathbf{k}}^0(\text{reference})$ , where  $\mathbf{k}$  is the carbocation site. The results are depicted in Figure 2. It may be seen that a slightly better correlation ( $R = 0.9894$ ) is obtained with respect to the comparison between the experimental electrophilicity scale and the global index  $\Delta\omega$  ( $R = 0.9735$ ). Note also the effect in the standard deviation in both correlations ( $SD = 0.85$  for  $\Delta\omega_{\mathbf{C}}$  and  $SD = 1.34$  for  $\Delta\omega$ ). The local picture may be used again to analyze the electrophilic site activation induced by chemical substitution, the response at the active site being now represented by variations in local electrophilicity rather than changes in charge capacity at the active site. We will show that both criteria of site activation consistently complement each other. A simple electrophilic site activation model may be set up as follows: start by defining a relative regional electrophilicity

$$\Delta\omega_{\mathbf{k}} = \omega_{\mathbf{k}}(\text{cation}) - \omega_{\mathbf{k}}^0(\text{reference}) \quad (11)$$

where  $\omega_{\mathbf{k}}^0(\text{reference})$  is the local (regional) electrophilicity at the active site in the dianisylcarbenium ion, the reference compound for both scales. Adding and subtracting the quantity  $\omega f_{\mathbf{k}}^{0,+}$  in the right-hand side of eq 11, we obtain

$$\Delta\omega_{\mathbf{k}} = \omega\Delta f_{\mathbf{k}}^{+} + f_{\mathbf{k}}^{0,+}\Delta\omega \quad (12)$$

where  $\omega$  corresponds to the global electrophilicity value of the cation under study, and  $\Delta f_{\mathbf{k}}^{+}$  represents the variation in the electrophilic Fukui function in the substituted carbenium ion at the carbon site ( $\mathbf{k} = \text{C}$ ) with reference to the corresponding value in the electrophilic Fukui function in the dianisylcarbenium ion ( $f_{\text{C}}^{0,+}$ );  $\Delta\omega$  is the change in global electrophilicity with reference to the dianisylcarbenium ion. Equation 12 is a convenient partition to discuss electrophilic site activation induced by chemical substitution: while the first term in eq 12 describes local activation (deactivation), the second term

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**TABLE 2. Contributions to Changes in Local Electrophilicity at the Active Site ( $\Delta\omega_C$ ) as Predicted by Equation 12 for a Series of Benzhydryl Cations<sup>a</sup>**

benzhydryl cation	$\Delta\omega_C$ [eV]	$\omega \Delta f_C^+$ [eV]	$f_C^{0,+} \Delta\omega$ [eV]
<b>1</b>	1.11	0.19	0.92
<b>2</b>	0.99	0.51	0.48
<b>3</b>	0.96	0.42	0.54
<b>4</b>	0.75	0.16	0.59
<b>5</b>	0.74	0.37	0.37
<b>6</b>	0.53	0.26	0.27
<b>7</b>	0.37	0.18	0.19
<b>8</b>	0.22	0.11	0.11
<b>9</b>	0.02	-0.03	0.05
<b>10</b>	0.00	0.00	0.00
<b>11</b>	-0.14	-0.07	-0.07
<b>12</b>	-0.55	-0.27	-0.28
<b>13</b>	-0.81	-0.37	-0.44
<b>14</b>	-0.82	-0.31	-0.51
<b>15</b>	-0.93	-0.32	-0.61
<b>16</b>	-0.97	-0.36	-0.61
<b>17</b>	-0.99	-0.34	-0.65
<b>18</b>	-0.99	-0.33	-0.66
<b>19</b>	-1.14	-0.40	-0.74
<b>20</b>	-1.24	-0.42	-0.82

<sup>a</sup> See the text for details.

describes the global contribution to  $\Delta\omega_K$ . The results are summarized in Table 2. For instance, inspection of Table 2 shows that the  $\Delta\omega_C$  values almost parallel the experimental scale of electrophilicity for the subseries of benzhydryl cations that show electrophilic activation (see Table 1, compounds **1–9**). Consider for instance, compound **1**, which is the species that shows the highest electrophilic activation in both theoretical ( $\Delta\omega_C > 0$ ) and experimental scales. Our model predicts that this result is mainly driven by a global electrophilic activation contribution at the carbocation site (second term in eq 12). Compound **9**, on the other hand, is correctly predicted as the benzhydryl cation showing the lowest electrophilic activation induced by chemical substitution. Here again, the global electrophilic activation term seems to account for the marginal electrophilicity enhancement at the carbocation site. Note, however, that there are some cases (compounds **2**, **3**, and **5–8**), where the local electrophilic activation described by the first term in eq 12 becomes comparable to the global activation contribution.

Within the subseries of benzhydryl cations for which the electrophilicity power is diminished (compounds **11–20**), the correspondence between the theoretical ( $\Delta\omega_C <$

0) and the experimental scales is also meaningful. Note also that those compounds that strongly deactivate by chemical substitution (e.g., compounds **15–20**) are predicted to diminish their local electrophilicity power mainly due to a strong global deactivating effect driven by the second contribution in eq 12.

## 5. Concluding Remarks

In summary, our model based on the global electrophilicity index defined by Parr et al. correctly accounts for the experimental electrophilicity scale of Mayr and co-workers for a series of benzhydryl cations. Good correlations between the experimental electrophilicity scale with the global electrophilicity index and its local counterpart defined at the carbocation site have been found. The model correctly assesses the observed electrophilic activation and deactivation with reference to the dianilylcarbenium ion, on the basis of an electrostatic inductive effect that manifests itself as the enhancement (activation) and lowering (deactivation) of the charge capacity at the carbocation site. It has been shown that the electrophilic activation and deactivation may be also assessed by looking at the changes in the local electrophilicity at the active site. Electrophilic activation appears as a local response at the carbocation site mainly induced by a global electrophilicity activation. A similar result is found for those compounds that diminishes their electrophilicity pattern (electrophilic deactivation) induced by chemical substitution. The present approach offers an interesting and useful method for evaluating the electronic properties of electrophiles in the form of a reactivity index. It provides a quantitative scale that condenses into a single number the information embodied in the FMO theory and population analysis. The theoretical scale seems to correctly describe the experimental electrophilicity pattern in these systems.

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**Supporting Information Available:** Optimized geometries of the whole series of benzhydryl cations in the Z-matrix format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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