Substituent Electronic Effects on the Mulliken Charges of N-(4-Substituted Benzylidene)-1-Phenylmethanamine Oxide Elucidated by DFT Calculations

A. H. Essa[*]

Department of Chemistry, College of Science, University of Basrah, Basrah, Iraq

Abstract

Calculations based on density functional methods are carried out to investigate the effects of a variety of substituents (NMe$_2$, OMe, Me, F, H, Cl, CN, NO$_2$) on the Mulliken charges (Q_M) for C$_\alpha$ and N atoms of N-(4-Substituted benzylidene)-1-phenylmethanamine oxide using Hammett's MSP and Taft's DSP equations. The MSP and DSP correlations give normal substituent effect at C$_\alpha$ and N atom sites. This can be attributed to extended π-polarization, which predominates over the localized π-polarization.

Keywords: Correlation analysis; Hammett's and Taft's equations; Nitrone compounds; π-polarization; Mulliken charges; DFT calculation.

1. Introduction

The main merit of the Hammett and Taft's equations,

$$log\ K_{i,X} - \log K_i^\circ = \rho_i\sigma_X \tag{1}$$

is in its general validity within a given range for practically all substituents (subscript X), and for most well-defined reaction series (subscript *i*) [1]. Successful applications are numberless and reported failings are very scarce [2]. This broad success focused attention on the meta and *para* derivatives of benzene, particularly of benzoic acids as a reference standard. For this reason quantum chemical calculations on these compounds were also started early with different intentions. An important question was whether the linear form of equation 1 can be deduced even from low-level calculations. This was achieved [3] from the linear dependence of log $K_{i,X}$ calculated for two reaction series and for variable substituents *X* at the CNDO level; for *para* substituents even HMO was sufficient. It was suggested that empirical simplifications made in deriving equation 1 are similar in

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[*] *E-mail* : alihashemalyunis@yahoo.com

character as the simplifications involved in the low-level quantum chemical calculations. Similar conclusions was followed from earlier correlations of different quantum chemical indices in one reaction series [4].

In this paper, we focused attention on substituent effects which play a fundamental role in a variety of observed physical chemical phenomena [1] at Mulliken charge (Q_M) of N-(4-Substituted benzylidene)-1-phenylmethanamine oxide (Scheme I). Applying the density functional theory (DFT) at the B3LYP/ STO-3G level, we expected to obtain more accurate values than in previous work. This series played significant roles in organic chemistry due to their broad utility, serving both as units for many biologically active compounds and as important chiral ligands or chiral auxiliaries for asymmetric synthesis [5, 6].
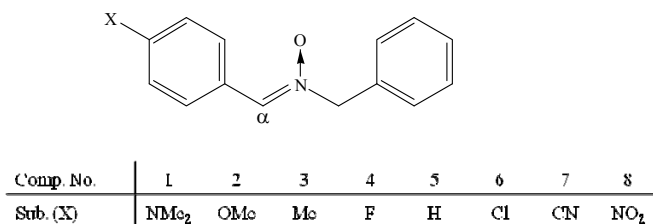

Comp. No.	1	2	3	4	5	6	7	8
Sub. (X)	NMe_2	OMe	Me	F	H	Cl	CN	NO_2

Fig. 1. The structure of *N*-(4-Substituted benzylidene)-1-phenylmethanamine oxide.

2. Method of Calculation

The calculations were carried out using the Gaussian 03 program package [7] running on a windows XP workstation with a Pentium IV PC. The Q_M for C_α and N atoms of *Para*-substituted phenyl-N-benzylnitrone were done by performing DFT method [8, 9] considering B3LYP exchange- correlation function [10, 11]. STO-3G basis set [12] has been chosen in the DFT calculations. The SCF convergency is set to 0.001 kcal/mol and the RMS gradient is set to 0.001 kcal/(Å mol) in the calculations.

Regression analysis were performed by using MINITAB data analysis software release 11.11 standard version [13]. Hammett and Taft constants were taken from the compilation done by Hansch *et al*. [14].

3. Results and Discussion

The present work examines for the first time applicability of mono substituent parameter (MSP) (Hammett's equation) and dual substituent parameter (DSP) (Taft's equation) as descriptors for substituent effects on the Mulliken charge (Q_M) for C_α and N atoms of N-(4-Substituted benzylidene)-1-phenylmethanamine oxide (Fig. 1).

3.1. *Hammett's equation*

Table 1 shows the σ constants of Hammett's and Taft's models as well as Mulliken charges (Q_M) for C_α and N atoms of the studied molecules.

Table 1. Hammett's and Taft's scales and Mulliken charges values for N-(4-Substituted benzylidene)-1-phenylmethanamine oxide

Comp.	Sub.	Hammett			Taft			Mulliken charges	
		$\sigma_p{}^{BA}$	$\sigma_p{}^+$		σ_I	$\sigma_R{}^{BA}$	$\sigma_R{}^+$	C_α	N
1	H	0.00	0.00		0.00	0.00	0.00	-0.019	-0.046
2	NMe$_2$	-0.83	-1.75		0.06	-0.83	-1.75	-0.020	-0.056
3	OMe	-0.27	-0.74		0.27	-0.61	-1.02	-0.020	-0.051
4	Me	-0.17	-0.31		-0.04	-0.11	-0.25	-0.019	-0.048
5	F	0.06	-0.07		0.50	-0.45	-0.57	-0.019	-0.049
6	Cl	0.23	0.11		0.46	-0.23	-0.36	-0.019	-0.044
7	CN	0.66	0.66		0.56	0.13	0.13	-0.018	-0.041
8	NO$_2$	0.78	0.78		0.65	0.15	0.15	-0.018	-0.042

MSP analysis (Hammett's model) of the Q_M values for both atom sites (C_α and N atoms) of N-(4-Substituted benzylidene)-1-phenylmethanamine oxide are shown in equations 1 and 2.

$$Q_{M\,(C\alpha)} = -0.0191 + 0.0014\ \sigma_P{}^{BA} \tag{2}$$
$$n = 8 \qquad r = 0.930 \qquad\qquad s = 0.205 \qquad\qquad F = 38.43$$
$$Q_{M\,(N)} = -0.0461 + 0.00598\ \sigma_P{}^+ \tag{3}$$
$$n = 8 \qquad r = 0.970 \qquad\qquad s = 0.214 \qquad\qquad F = 93.44$$

where n is the number of compounds, r is the correlation coefficient, s is the standard deviation and F is the Fisher ratio.

The empirical Hammett σ constants, as expected, exhibited a moderate correlation with the Mulliken charges (Q_M) values. The regression is illustrated in Fig. 2. The N atom ($r = 0.970$) showed a correlation that was only much better than the C_α atom ($r = 0.930$).
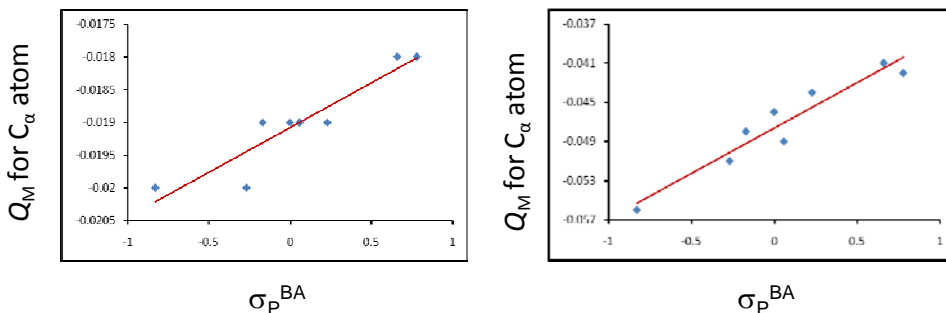

Fig. 2. Correlation between $\sigma_P{}^{BA}$ Hammett constants and Mulliken charges (Q_M) for C_α and N atoms.

The C_α and N atoms give the same charge, in opposite to the charge sign which alternate in charge sign, similarly to their corresponding σ_I and σ_R values. σ_I and σ_R are being negative for C_α and indicate a reverse resonance and field effects.

Eqs. 2 and 3 demonstrate the need for a dual parameter correlation in the studied molecules. These equations do not show the ratios of resonance to polar effects at the two investigated atoms.

3.2. Taft's equation

The systematic studies of this series by Essa and co-workers in 2009 [15] revealed that the Q_M of N atom are more affected by the substituent than those of C_α. This can be attributed to the greater influence of resonance effects at the N atom, evidenced, for example, by the through conjugation shown in structure 1.
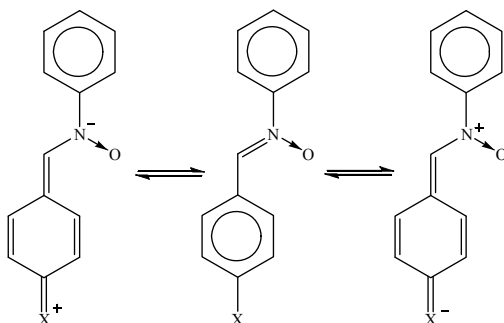
Structure 1

In these canonical structures the C_α site remains relatively unperturbed by resonance effects of X, whereas N atom obtains excess electron density when X is a donor, and becomes deficient when X is an acceptor.

DSP analysis (Taft's Model) of the Mulliken charges (Q_M) of the series of compounds (1-8) for C_α and N atoms show the following results:

$$Q_{M\ (C\alpha)} = -0.0189 + 0.000952\ \sigma_I + 0.00168\ \sigma_R^{BA}$$
$$n = 8 \quad r = 0.966 \quad\quad s = 0.00023 \quad\quad F = 34.84 \quad\quad \lambda = 1.765$$
$$Q_{M\ (N)} = -0.0458 + 0.00522\ \sigma_I + 0.00629\ \sigma_R^{+}$$
$$n = 8 \quad r = 0.972 \quad\quad s = 0.00139 \quad\quad F = 42.49 \quad\quad \lambda = 1.205$$

Generally the Taft's equation gave statistically more significant results than the Hammett's equation for Q_M of C_α and N correlations. Almost identical correlation was found for the C_α and N atoms.

The resonance effects are the largest at the N atom site. The preferred resonance scale is σ_R^{+}, reflecting the electron demand placed on this site by adjacent phenyl group. The ρ_I

value at N atom has a positive sign and a magnitude roughly quintuple that of the ρ_I value at Cα. It is interesting to note that a DSP analysis of ^{13}CNMR substituted chemical shifts (SCS) for the styrene derivatives dose show a differing polar effect [16]. Because of the ability of the nitron group to conjugate with adjacent systems, the electron distribution of the aromatic and nitron systems are closely interrelated and it is therefore reasonable to ask why a positive ρ_I value, indicative of polarization as in structure **2a**, is consistently observed for the C_α site, when it might be expected that the whole conjugated π system should be polarized as a unit, as in structures **2b** or **2c**

(2a)   (2b)   (2c)
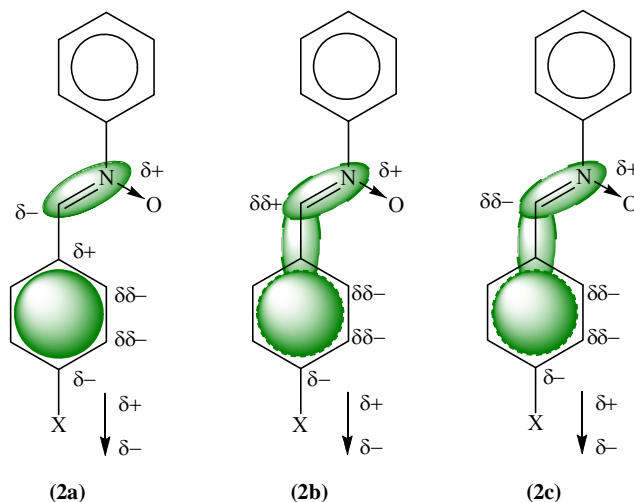
Structure 2

The type of polarization, shown in structure **2b** is called extended polarization and results in charge density at C_α having a similar sign to those at the nitrogen atom but of a smaller magnitude. (i.e. small positive ρ_I values would be expected). This type of polarization dose indeed occur, but that it does very little to perturb the charge density at C_α site. Most of the charge density change at this site are in fact due to extended polarization structures of the localized N-O bond.

It is clear that the C_α and N atoms are subject to similar substituent effects, the positive sign in ρ_I in both atoms are indicative of a normal substituent effect. It indicates that donors induce more charge and acceptors induce less charge. This effect has been noted in a number of side chain systems [17].

The blending constant λ ($\lambda = \rho_R / \rho_I$) can categorically classify atoms into two classes. The first class, in which the λ is less than one, this means that the substituent resonance effects do not affect the atoms directly. The second class in which the λ is more than one, this means that the substituent resonance effects directly affect these atoms. The larger resonance effect in the C_α and N atom in some systems [18] confirms that some type of secondary resonance effect operates at these sites. It is most likely arises from polarization

of the side chain π system by the diffuse dipole set up in the benzene ring as a result of resonance delocalization by the substituent X. There is no secondary resonance in the studied molecules since it is normal to have beta atom in this case nitrogen has positive large σ_R and the alpha in this case has positive σ_R but much smaller than the nitrogen. So, there is normal resonance effect.

4. Conclusions

In this work, we have investigated the substituent electronic effect on Mulliken charge (Q_M) of C_α and N atoms of N-(4-Substituted benzylidene)-1-phenylmethanamine oxide by using Hammett's MSP and Taft's DSP equations, and demonstrate several important points: First, We have shown that the density functional method can be used to calculate quite accurately the substituent effect on the Mulliken charge (Q_M). Second, it is now documented that single parameter treatment can not adequately describe the trend of substituent electronic effect in C_α and N atoms especially when we need to know the quantities of inductive and resonance effects. Single parameter treatment contains only one blend of these effects and hence can not, in general, cope with the many cases in which polar and resonance effects are transmitted to different relative extent. Third, the DSP correlations on the Mulliken charge (Q_M) gave significant improvement over MSP correlations.

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