

Substituent Effect on Mulliken Charges (q_M) of Fluorine Atom in 4-X-phenyl-G-phenyl-4'-F System

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Abstract

Mulliken charges (q_M) of F atom in eight series of 4'-X-substituted-4-fluorobiphenyl of the general structure 4-X-phenyl-G-phenyl-4'-F have been calculated by using semi-empirical molecular orbital theory at the level of AM1 and PM3. Fluorine Mulliken charges (q_M) that calculated by the two methods for each series were correlated separately vs. ^{19}F SCS. The results revealed that the AM1 method were generally better than PM3 method. Fluorine Mulliken charges (q_M) correlated with three DSP models: Reynolds, Swain and Taft. The Taft's model was statistically more accurate. The field effect and resonance were normal for fluorine (q_M), whereas for ^{19}F SCS were reverse.

Keywords: substituent effect, Mulliken charge, correlation analysis, AM1 and PM3 methods, ^{19}F NMR data

تأثير المعوض على شحن الموليكن لذرة الفلور في 4-X-phenyl-G-phenyl-4'-F

باسل عبد المهدي صالح

قسم الكيمياء، كلية العلوم، جامعة البصرة، بصرة ، عراق

الخلاصة

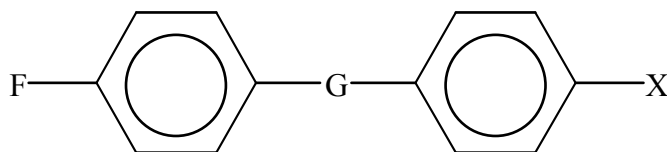
حسبت شحن الموليكن (q_M) لذرة الفلور لتسع سلاسل من 4'-X-substituted-4-fluorobiphenyl وكذلك للمركبات ذات الصيغة العامة 4-X-phenyl-G-phenyl-4'-F باستخدام نظرية الاوربتالات الجزيئية والطريقتين الشبه تجريبية AM1 و PM3. أجريت تحليل ترابطي لشحن الموليكن للفلور بوساطة الطريقتين مع ^{19}F SCS بشكل منفصل. أوضحت النتائج بان طريقة AM1

كانت بشكل عام افضل من طريقة **PM3**. كما اجري التحليل الترابطي مع الموديلات الثنائية لرينولدز وسواين وتافت. إنمذج تافت كان الافضل من بين الإنموجات الثنائية المستخدمة. تأثيري المجال والرنين كانا اعتياديا في حين كانا عكسية لـ ^{13}F SCS.

Introduction

Correlation analysis of substituent effects on the skeleton of benzene derivatives is an important methodology of physical and mechanistic organic chemistry.

The substituent effects on ^{13}C , ^{15}N , ^{19}F chemical shift (SCS) have been widely studied by using Dual Substituent Parameter (DSP) models (Johnels et al, 1983; Botto et al, 1979; Neuvonen H. and Neuvonen K., 1999; Nelson et al, 1972; Swain and Lupton, 1968; Schulman et al, 1974; Cheng et al, 2004; Neuvonen H et al, 2004; Song, 2003; Neuvonen H., 2006; Neuvonen K. et al, 2005; Valentic et al., 2003; Bromilow et al, 1980; Neuvonen K. et al, 2001; Craik et al, 1983; Wiberg et al, 2002; Neuvonen K. et al, 1994 and Neuvonen H. et al, 2002). In this study the mechanisms of field and resonance effects on fluorine Mulliken charge (q_{M}) have been studied using three DSP models: Reynolds (Zalewski, 1991; Reynolds, 1980 and Reynolds et al, 1983) Swain (Zalewski, 1991; Swain and Lupton, 1968 and Swain et al, 1983) and Taft (Zalewski, 1991; Ehrensens et al, 1973) in 4'-X-substitued-4-fluorobiphenyl (series 1) and 7 series of general structure (I), to dissect out these effects.



Structure I

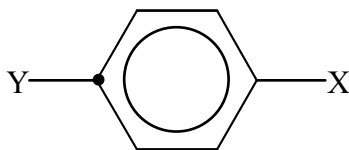
Here, X is the substituent (H , NH_2 , NMe_2 , OCH_3 , CH_3 , F , Cl , Br , I , CF_3 , CN and NO_2) and the linking groups G are varied to encompass a wide range of electronic properties: CHPh (series 2), CH=N (series 3), N=CH (series 4), CH=CH (series 5), N=N (series 6), $-\text{O}-$ (series 7), $-\text{S}-$ (series 8).

In DSP models, the substituent – influenced property P^i is linearly related to a field effect ($\rho_F \sigma_F$) and resonance effect ($\rho_R \sigma_R$) by:

$$P^i = \rho_F \sigma_F + \rho_R \sigma_R \quad \dots (1)$$

In this study the property P^i is a fluorine Mulliken charge (q_M) or ^{19}F SCS. The coefficients ρ_F and ρ_R represent the sensitivity of the probe under investigation to field and resonance effects respectively, and σ_F and σ_R represent the substituent constants (Zalewski, 1991; Reynolds, 1980; Reynolds et al, 1983; Swain and Lupton, 1968; Swain et al, 1983 and Ehrensens et al, 1973). The three DSP models (Reynolds, Swain and Taft) only differ in the method of derivation of the values of the substituent constants (σ_F and σ_R). The Taft model includes four different type scale σ_R (σ_R^{BA} , σ_R^0 , σ_R^+ and σ_R^-). Therefore the Taft model has more flexibility than other models.

The work has been stimulated by results of a recent study of substituent effects on the Mulliken charge (q_M) of para carbon atom in a series of benzene derivatives, structure II (Al-Magmoy, 2005), where, X was the substituent and Y was varied side chains.



Structure II

Reynolds' DSP model equation (1) was used for the correlation analysis while the semi-empirical method PM3 was used for calculating the Mulliken charges of para carbon atom. That study revealed a significant relationship between Mulliken charges of para carbon atom and ^{13}C SCS for most of the molecules in the series. These aspects and other interpretations were discussed in this study.

The aims of this study are firstly to study of the nature of transmission of substituent electronic effects on fluorine Mulliken charge (q_M) which are computed by the semi-empirical methods with the help of the three selected DSP models, secondly to compare the quality of two semi-empirical MO methods: AM1 (Dewar and Dieter, 1985; Dewar et al, 1986 and Stewart, 1990) and PM3 (Stewart, 1989 and Stewart, 1989), thirdly to compare which of three DSP models is the most suitable for this study.

Theoretical Approach

The semi-empirical MO methods AM1 and PM3 have been chosen to calculate the Mulliken charges (q_M) of F atom for all compounds with the HyperChem 6.0 program (Dewar and Dieter, 1985; Dewar et al, 1986; Stewart, 1990; Stewart, 1989 and Stewart, 1989). The geometries have been fully optimized. The ^{19}F SCS data in CCl_4 for eight series were taken from literature (Dayal and Taft, 1982). The correlations for each DSP model, by means of equation (1) were performed by using a MINITAB program for Windows release 11.11. The softwares were run on a Windows XP workstation in a Pentium IV PC.

The factors F-Snedecor (F-Fisher) (Shorter, 1982) and multiple regression coefficient (R) (Shorter, 1982) were used to assess the quality of the models and correlation coefficients factor (r) used to qualify of linear relationship graphs.

Results

The AM1 and PM3 fluorine Mulliken charges (q_M) are given in Table (1) and Table (2) respectively.

Table (3) shows the correlation coefficients (r) for relationship between ^{19}F SCS and Mulliken charges (q_M) for each series. Table (4) shows the statistical factors F-Snedecor (F-Fisher) test and correlation coefficient (R) of Mulliken charges (q_M) of F atom by using three DSP (Reynolds, Swain and Taft) models for the series of this study.

The multiple regression results of Taft's model of Mulliken charges of F atom were summarized in. Table (6) shows the recalculation of multiple regression results of Taft model of ^{19}F SCS by introducing all four types of scale $\square_{\text{R}}$.

Discussion

A recent study showed that there is a significant correlation between the Mulliken charges (q_{M}) of para carbon atom and an experimental property influenced by the substituent effect of ^{13}C SCS for structure II (Al-Magmoy, 2005). The similar trend was obtained for the study of the present series with respect to the relationships between Mulliken charges of F atom vs. ^{19}F SCS. In this study the fluorine Mulliken charges (q_{M}) that calculated by the two semi-empirical methods AM1 and PM3 for each series were correlated separately against ^{19}F SCS. A comparison of accuracy between the two methods becomes possible by comparing the correlation coefficient (r) of the relationship between fluorine Mulliken charges (q_{M}) computed by both methods and ^{19}F SCS for each series individually as shown in table (3). The correlation coefficients (r) revealed that the AM1 method (0.909-0.993) are generally better than PM3 method (0.850 – 0.978). Therefore the AM1 method will be preferred to study the substituent effect on fluorine Mulliken charge for the series of interest.

Fluorine Mulliken charges (q_{M}) correlated with three DSP models: Reynolds, Swain and Taft as shown in Table (4). The values of the statistical factors (correlation coefficients (R) and F-Snedecor) revealed that the Taft model is statistically more accurate [$R = (0.975-0.999)$, F-Snedecor = (28.45 – 658.02)] than Reynolds [$R = (0.917 – 0.991)$, F-Snedecor = (11.9 – 142.8)] and Swain [$R = (0.915 – 0.998)$, F-Snedecor = (12.8 – 506.6)] models, therefore this model will be recommended to study the substituent effect in this research.

The field and resonance substituent effects ($\square_{\text{F}}$ and $\square_{\text{R}}$) for fluorine Mulliken charge were normal (positive slope) for all series under investigation, i.e. the donator substituents increase the fluorine Mulliken

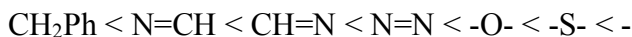
charge (q_M) and the withdrawing substituents decrease it. In ^{19}F SCS were reverse (negative slope) for both effects. Whereas the mentioned effects were normal in both ^{13}C SCS and Mulliken charges of para carbon atom in structure II (Al-Magmoy, 2005).

σ_F Analysis

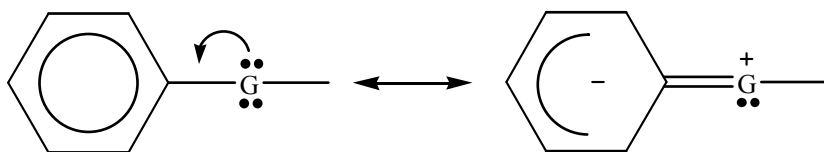
The noticeable observation we found here is that the σ_F of fluorine Mulliken charges (q_M) are consistent with the σ_F of ^{19}F SCS for each series except series (1), which gave essentially fair correlation with ^{19}F SCS fig. (1).

In other words, the linearity of the plots confirms that the nature of substituent field effect on Mulliken charges (q_M) could be related to that of ^{19}F SCS for a given series.

It is found that the field effect increases in the following sequence :



From Table (5) it could be seen that the F-X distance is not the predominant variable determining σ_F . Instead, σ_F increases with increasing conjugation between the two phenyl rings. In series (1) the two benzene rings are attached directly, so, the σ -polarization will transfer to F atom larger than other series, the high value of σ_F reflect this fact. The saturated hydrocarbon linking group (series 2) [$\text{G} = \text{CHPh}$] acts to decrease the lowest σ_F value (0.439) while atomic centers with polarizable lone-pair electrons ($\text{G} = -\text{O}-$ and $-\text{S}-$) give rise to the largest values (0.671 and 0.710) respectively. This because the lone – pair electron of ($\text{G} = -\text{O}-$ and $-\text{S}-$) atoms interact with ring enhancing the field effect which transfer by space as shown in structure III.



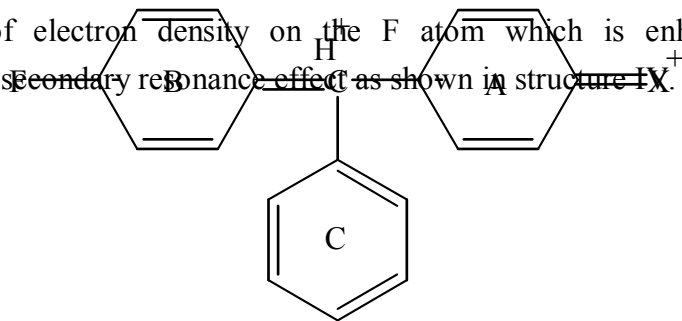
Structure III

σ_R Analysis

Fluorine Mulliken charge (q_M) of series (2 and 8) [$G = \text{CHPh}$ and $-\text{S}-$] correlated with σ^-_R , while, series (1, 3, 4, and 6) [$G = -, \text{CH}=\text{N}, \text{N}=\text{CH}$, and $\text{N}=\text{N}$] correlate with σ^0_R and series (5 and 7) [$G = \text{CH}=\text{CH}$ and $-\text{O}-$] correlate with σ^{BA}_R . Such behavior of σ_R in the correlation can be attributed to the variety of linking groups (G) which play a different role in electron delocalization (resonance) in each series.

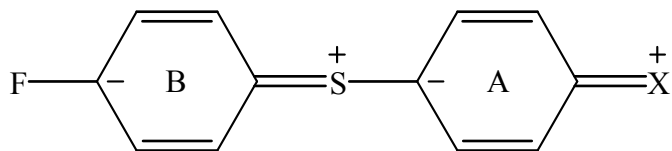
The matching of fluorine Mulliken charges (q_M) with one of four scales σ_R (i.e., σ^{BA}_R , σ^0_R , σ^-_R and σ^+_R) of Taft model was identical to other given series of ^{19}F SCS except that for series (5, 6 and 7) [$G = \text{CH}=\text{CH}$, $\text{N}=\text{N}$ and $-\text{O}-$] as shown in Table (5 and 6). However, this is not dramatic different, because the values of statistical factors (correlation coefficients (R) and F-Snedecor) for both σ^0_R and σ^{BA}_R were approximate in these series.

The correlation of series (2) [$G = -\text{CHPh}$] with σ^-_R may be attributed to the effect of hyperconjugation with ring (B). Such effect shows an extra donating of electron density on the F atom which is enhancing the substituent secondary resonance effect as shown in structure IX.



Structure IV

Whereas the correlation of series (8) [$G = -S-$], with $\square_R^-$ could be attributed to the interaction between the lone-pair of S atom with ring (B), again here this resonance will increase the $\square$ -electron on the F atom which is enhancing by substituent secondary resonance effect as shown in structure (V)



Structure (V)

The resonance effect is small in series (7) [$G = -O-$], because oxygen is more electronegative than sulfur, thus the delocalization of the lone-pair of oxygen on ring (B) will be less than for series (8) [$G = -S-$]. Therefore series (7) [$G = -O-$] correlated with $\square_{BA}^R$.

Correlations of series (1, 3, 4 and 6) [$G = -, -CH=N-, -N=CH-,$ and $-N=N-$] with $\square_R^0$ revealed that the sense of fluorine Mulliken charges to the substituent resonance effect is less than other series. Correlations of series (5 and 7) [$G = CH=CH$ and $-O-$] with $\square_{BA}^R$ reveal that the fluorine Mulliken charge in these series is more sensitive to the substituent resonance effect than the above series.

The values of $\square_R$ of fluorine Mulliken charge (q_M) were plotted vs. the values of $\square_R$ of ^{19}F SCS for eight series under investigation as shown in fig. (2). The relationship shows that the substituent resonance effect on fluorine Mulliken charges (q_M) was not equal with that for the ^{19}F SCS.

Conclusions

- 1- There are linear relationships between Mulliken charges (q_M) and ^{19}F SCS for series under investigation.
- 3- Taft's DSP model is statistically more efficient than other DSP models.

- 4- In general the fluorine Mulliken charges (q_M) and ^{19}F SCS behave similarly toward field and resonance effects.

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Table (1) : Fluorine Mulliken charges (q_M) calculated by (AM1)

Substituent	G							
	- *	CHPh	CH=N	N=CH	CH=C H	N=N	-O-	-S-
H	-0.105	-0.107	-0.103	-0.104	-0.105	-0.102	-0.105	-0.106
NH ₂	-0.108	*	*	*	*	*	-0.108	*
NMe ₂	*	-0.108	-0.105	-0.106	-0.108	*	*	*
OCH ₃	*	-0.108	-0.104	-0.105	-0.106	-0.102	-0.106	*
CH ₃	*	-0.107	-0.103	-0.104	-0.106	-0.102	-0.106	-0.105
F	-0.103	-0.106	-0.102	-0.103	-0.104	-0.100	*	-0.103
Cl	*	-0.106	-0.102	-0.103	-0.104	-0.100	*	-0.103
Br	-0.103	*	*	*	*	-0.100	*	*
I	-0.103	*	*	*	*	-0.100	*	*
CF ₃	*	-0.104	-0.100	*	*	-0.098	-0.102	-0.101
CN	-0.101	*	-0.100	-0.101	-0.103	*	*	*
NO ₂	-0.098	-0.102	-0.098	-0.099	-0.101	*	-0.100	-0.099

* - means 4'-substitued-4-fluorobiphenyl

Table (2) : Fluorine Mulliken charges (q_M) calculated by (PM3)

Substituent	G							
	-*	CHPh	CH=N	N=CH	CH=CH	N=N	-O-	-S-
H	-0.092	-0.093	-0.091	-0.091	-0.092	-0.090	-0.092	-0.090
NH ₂	-0.095	*	*	*	*	*	-0.093	*
NMe ₂	*	-0.093	-0.092	-0.093	-0.094	*	*	*
OCH ₃	*	-0.093	-0.092	-0.092	-0.093	-0.091	-0.092	*
CH ₃	*	-0.093	-0.092	-0.091	-0.093	-0.091	-0.092	-0.090
F	-0.091	-0.092	-0.091	-0.090	-0.092	-0.089	*	-0.089
Cl	*	-0.092	-0.091	-0.091	-0.092	-0.090	*	-0.089
Br	-0.091	*	*	*	*	-0.089	*	*
I	-0.091	*	*	*	*	-0.090	*	*
CF ₃	*	-0.091	-0.089	*	*	-0.088	-0.089	-0.088
CN	-0.089	*	-0.090	-0.089	-0.090	*	*	*
NO ₂	-0.087	-0.090	-0.089	-0.088	-0.089	*	-0.088	-0.086

* - means 4'-substituted-4-fluorobiphenyl

Table (3) : Correlation coefficient (r) of relationship between Mulliken charge (q_M) and ^{19}F SCS for two methods

Series No.	G	AM1	PM3	n*
		r	r	
1	-	0.964	0.975	7
2	CHPh	0.975	0.970	8
3	CH=N	0.977	0.903	9
4	N=CH	0.975	0.960	8
5	CH=CH	0.965	0.983	8
6	N=N	0.921	0.850	8
7	-O-	0.993	0.978	6
8	-S-	0.909	0.943	6

* number of substituents

Table (4) : Statistical factors for regression between Mulliken charge (q_M) of F atom with Reynolds, Swain and Taft Models

Sr. No	G	Reynolds		Swain		Taft	
		F- Snedec or	R	F- Snedec or	R	F- Snedec or	R
1	—	41.7	0.977	35.26	0.979	30.57	0.976
2	CHPh	13.23	0.917	12.86	0.915	91.89	0.987
3	CH=N	20.58	0.934	28.17	0.951	71.84	0.980
4	N=CH	54.05	0.977	21.80	0.947	53.71	0.977
5	CH=CH	44.31	0.973	47.46	0.975	52.07	0.977
6	N=N	142.8	0.991	17.62	0.948	47.17	0.979
7	-O-	11.95	0.942	506.62	0.998	658.02	0.999
8	-S-	17.97	0.961	15.41	0.954	28.45	0.975

Table (5) : DSP analysis of Mulliken charges (q_M) in F atom on using Tafts' Model

Sr. No.	G	$\square_F \times 100$	$\square_R \times 100$	F-Snedecor	R	Scale
1	-	0.852	0.677	39.39	0.976	$\square_R^0$
2	CHPh	0.439	0.428	91.89	0.987	$\square_R^-$
3	CH=N	0.472	0.543	71.84	0.980	$\square_R^0$
4	N=CH	0.471	0.539	53.71	0.977	$\square_R^0$
5	CH=CH	0.497	0.334	52.07	0.977	$\square_{R}^{BA}$
6	N=N	0.630	0.497	59.27	0.980	$\square_R^0$
7	-O-	0.671	0.443	658.02	0.999	$\square_{R}^{BA}$
8	-S-	0.710	0.337	28.45	0.975	$\square_R^-$

Table (6) : DSP analysis of ^{19}F SCS using Tafts' Model

Sr. No.	G	σ_{F}	σ_{R}	F-Snedecor	R	Scale
1	-	-3.94	-4.85	565.65	0.999	$\sigma_{\text{R}}^{\circ}$
2	CHPh	-1.72	-1.23	142.63	0.991	σ_{R}^{-}
3	CH=N	-2.39	-2.97	671.45	0.998	$\sigma_{\text{R}}^{\circ}$
4	N=CH	-2.51	-3.16	649.96	0.998	$\sigma_{\text{R}}^{\circ}$
5	CH=CH	-2.76	-3.41	1861.99	0.999	$\sigma_{\text{R}}^{\circ}$
6	N=N	-3.34	-3.23	1817.24	0.999	$\sigma_{\text{R}}^{\text{BA}}$
7	-O-	-3.80	-5.11	5037.5	1.000	$\sigma_{\text{R}}^{\circ}$
8	-S-	-4.93	-5.83	1367.5	0.999	σ_{R}^{-}

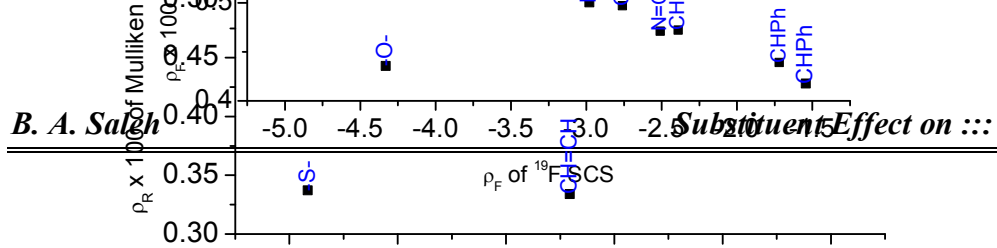


Figure (1) : Relationship between ρ_F of Mulliken charge (q_M) and ρ_F of ^{19}F SCS for given series

Figure (2) : Relationship between ρ_R of Mulliken charge and ρ_R of ^{19}F SCS for the various series