Theoretical Investigation and Substituent Effect on Mulliken Charge for compounds Z- [α- (p- substituted phenyl) β- (5- substituted 2- thienyl) acrylonitrile]

Hanan A. RAdhy Al. Hazam
College of Science, University of Basrah - Iraq
Email: hananalhazam1965@yahoo.com

(NJC)

(Received on 12/3/2008) (Accepted for publication 16/7/2008)

Abstract

The structural and electronic properties of Z-[α-(p-substituted phenyl) β-(5-substituted 2-thienyl) acrylonitrile] of general formula $Y-C_2H_2S-CH=C(CN)C_6H_4X$ (where X=Me, OMe, H, Cl, NO_2, Y=H, Me, Br) have been investigated theoretically by using semi – empirical molecular orbital method at the level of PM_3 theory. The optimized structures relative binding energies, Mulliken charge, position of HOMO and LOMO, electronic energy and total energy were estimated.

Subsituent effect on Mulliken charge for C_P, $C\alpha$, Co, C_β, C_2, and C_5 have been done using dual substituent paramder DSP, Reynolds's model. It was found that these atoms gave a good correlation with Reynold's model in three series.

Key words: correlation analysis Mulliken charge Reynold's model PM_3 semi-empirical method

الخلاصه

تم دراسه الخواص الالكترونيه لثلاث سلاسل لمركبات:
Z-[α-(p-substituted phenyl) β-(5-substituted 2-thienyl) acrylonitrile]
ذو الصيغه الجزيئيه OMe, $Y-C_2H_2S-CH=C(CN)C_6H_4X$ حيث $X = NO_2$, H, Me, OMe, Cl; $Y =$
Me, H, Br لطرق الشبه التجريبيه PM_3 حيث قيست شحن موليكان وطاقة الربط وحرارة التكوين وطاقة اعلى اوربيتال مملوء (هومو) واوطا اوربيتال فارغ (لومو) والطاقة الكلية وطاقة الالكترون.
تم اجاز التحليل الترابطي لشحن موليكان لذرات C_P, $C\alpha$, Co, C_β, C_2, C_5 للسلاسل الثلاثة وباستخدام النموذج الثنائي رينولد فوجد على العموم ان هذه الذرات ترتبط ارتباط جيد مع هذا الانموذج (رينولد).

Introduction

Nitriles are considerably important in all branches of chemistry [1]. They are used in synthesis intermediates and important organic compounds and in consequence the resonance spectra have been studied since the beginning of NMR spectroscopy.

In substituted nitrile compounds, there are two effects that influence the charge density and ^{13}C chemical shifts, first, $C \equiv N$ group has isotropic and field effect [2], second, substituent effect have traditionally been divided into two contribution, firstly, the polar (inductive / field) and secondly, the mesomeric effect [3].

The effect of substituent on nmr parameters in mono substituted five mebered heterocycles is also well known due to fundamental studies carried out by Gronowitz and coworkers [4] on mono substituted thiophenes, furans, selenophenes and tellurophenes , including comparison of ^{13}C chemical shift with ^{1}H and ^{77}Se.

The influence of benzene ring substituents on side chain carbon chemical shifts has also been studied in substituted benzo nitrile [5], β- nitro styrene [6], cinnamic [7] , 2- thienyl and 2- furanyl methylene propane nitriles [8].

Saleh and et al [9] was studied the substituent effect on mulliken charg for 4-(4-X-phenyl methylene)-2-phenyl-5-oxazolone for both cis and trans isomer, the result of regression was the sigma model is the preferable for trans isomer while the Hammett $sigma^{AB}$ model is preferable for the cis isomer.

^{13}C nmr shifts for fifteen ~~Z~~-α- [(p- substituted phenyl) β- (5- substituted 2- thienyl) acrylonitrile] of general formula $Y - C_2H_2\ S\text{-}CH = C(CN)\ C_6H_4\ X$; X= Me, OMe, H, Cl, NO_2, Y= H, Me, Br in dmso-d_6 solution are reported. Substituted chemical shift (scs) consideration allows the assignment of disubstituted aromatic ring carbons. The effect of X and Y substituents on aromatic and ethylenic carbon shifts is discussed . JCCCH long range coupling constants provide evidence in favor of the Z configuration for these compounds[10].

In this study, the electronic properties of Z- [α- (p- substituted phenyl) β- (5- substituted 2- thienyl) acrylonitrile] are determined using semi – empirical molecular orbital method. The substituent effects on Mulliken charge (q_M) was also studied by using Reynold`s model.

Theoretical Study

Three series of ~~Z~~-α- [(p- substituted phenyl) β- (5- substituted 2- thienyl) acrylonitrile] [Fig. (1)] were used in the present work which were prepared by Ballistrer [10]. Theoretical study consist of two parts was conducted. The first part concerns with the determination of the electronic properties for the above series by using Hyperchem program 6.5[11]. The electronic properties include:

(a) Total energy, there are several ways to describe the energy of a molecule. The classic method which it is still very useful also for larger molecules - is to describe the energy as a sum of contribution from bond distance(E_b), bond angles(E_{ang}) , torsion angles(E_t) and non – bonded interactions(E_{nb}).

The total energy of the molecule should in this frame work be written as

$$E_{total} = \Sigma E_b + \Sigma E_{ang} + \Sigma E_t + \Sigma E_{nb}$$

where the sums are over all interaction of each type.

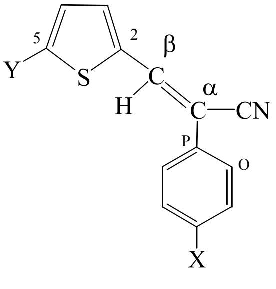


Fig. 1: The Structural of Z-[α-(p-substituted phenyl) β-(5-substituted 2-thienyl) acrylonitrile] X=Me, OMe, H, Cl, NO_2; Y=H, Me, Br

(b) Electronic energy which is presented by :

$$E_{ele} = E_{vib} + E_{rot} + E_{transl}$$

Where:-

E_{vibr} = energy of vibration of electron.
E_{rot} = energy of rotation of electron.
E_{transl} = energy of translation of electron.

(c) Binding energy which is the energy required to either separate on electron from an atom or separate the protons and neutrons of an atomic nucleus.

(d) Heat of formation, (e) HOMO& LOMO energy (f) Mulliken charge.

The second part of the work is to study the correlation analysis between Mullikan charge and Reynold's model [12] using a second program. Minitab version 11, which is used to calculate regression coefficient (R) and standard deviation (S).

Reynold's model is only used here to compare the three series.

Results and Discussion

The calculated total energy, electronic energy, binding energy and heat of formation values of the studied three series are given in Table (1). The Table shows that the smallest value of calculated binding energy is obtain for OMe substituent, while the Cl substituent has largest calculated binding energy for (series 1; y = H; series 2; y = Me and series 3; y = Br) .

The heat of the formation of molecules emerges to change with variation of donor and acceptor groups as shown in Table (1) which gives the heat of formation for three series are exothermic (positive sign) .

The highest occupied and the lowest unoccupied molecular orbital (HOMO and LOMO, respectively) energy and energy band gap (LOMO – HOMO energy difference ΔE) with the lowest and highest levels are given in Table (2). The energy band gaps are largely responsible for chemical properties [13]. ΔE for the unsubstituted molecule was larger than any other substituents. This means that substituted molecules need energy to reach the excitation state.

The Mullikan charges (q_M) for all atoms are calculated by PM_3 molecular orbital semi – empirical methods for the geometry optimized of the three series. Results are presented in Table (3).

Correlation analysis of q_M for each atom was performed using dual substituent parameters (Reynold's model) which are illustrated in Table (4).

As the table reveals q_M C_P (Mullikan charge for para carbon) gives a good response (R=0.992; series 1, 0.966; series 2, 0.968; series 3) for the substituent when the phenyl and thiophen ring are in the trans for double bond. This may be explained from the free rotation for substituted phenyl as compared with cis which has steric hindrance restrict to this free rotation as illustrated in Fig. 2.

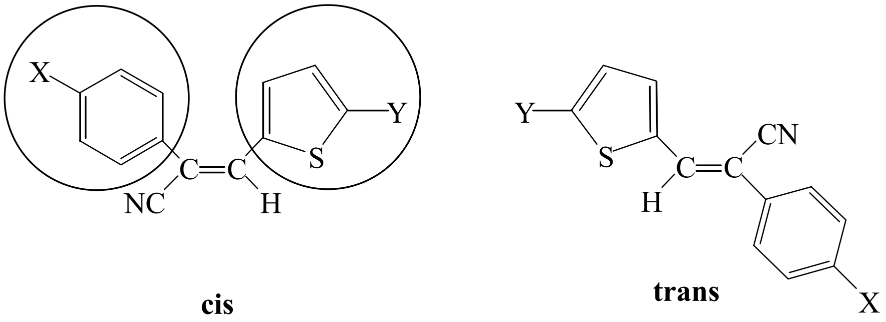


Fig. 2: Shows the free rotation for substituted phenyl and thiophene in trans as compared with cis which has steric hindrance

Reynolds' model correction of q_M C_P reveals normal substituent effect [positive sign for ρ_R(resonance parameter) and ρ_F (field parameter)]. Resonance contribution is twice than that of field effect (Table 4). This due to that the position of para carbon is affected directly by resonance effect occurring by π – bond which gives full charge to this position. However, field effect gives partial charge in this position (Fig. 3). This behavior is similar to para C^{13} substituent chemical shift (scs) in both compounds Para-disubstituted benzene[14], 3-(4-X-phenacylidene)oxindol [15] and q_M C_P for substituted 2,3- dioxindole [16].

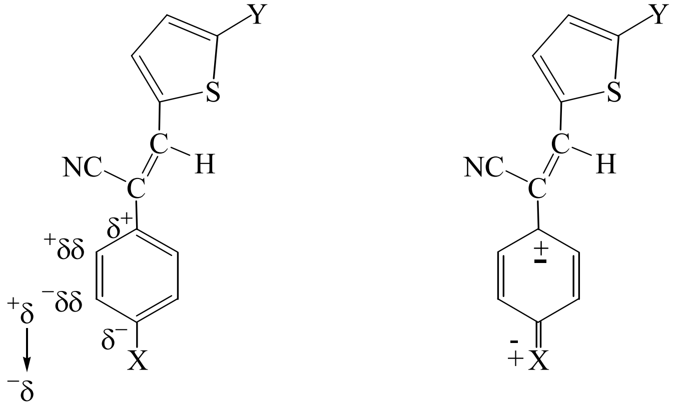


Fig. 3: Shows the field and resonance effect

q_M C_o (Mullikan charge for ortho carbon) gave excellent correlation for substituent effect (R= 0.994 for series 1 ; 1 for series 2 ; 0.999 for series 3) .

ρ_F and ρ_R have negative values indicating a reverse resonance and field respectively. Reverse field effect behavior may be attributed to extended π – polarization (Fig. 4).

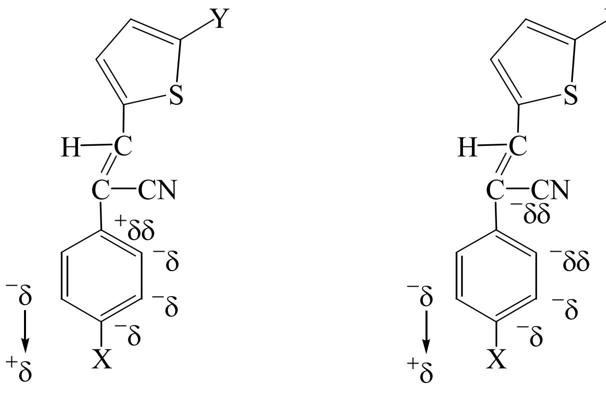
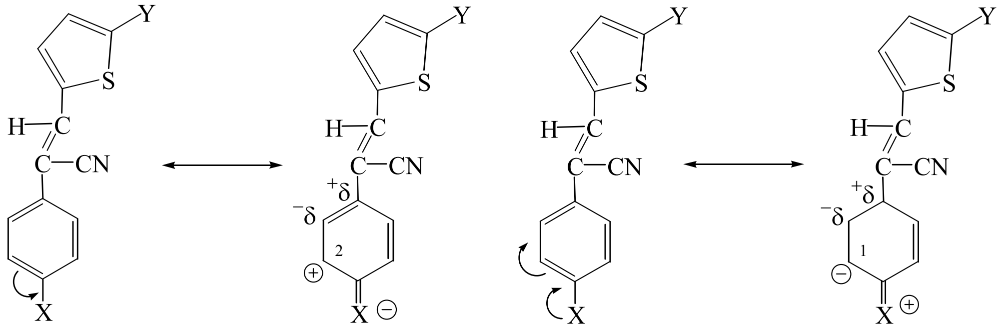


Fig. 4: Shows the extended π – polarization

The reverse resonance effect being larger than reverse field effect. Similar reverse resonance effect has observed for ^{13} C substituent shifts correlation at non conjugating sites aromatic compounds such as Meta position of mono substituted benzene [17].

C_{ortho} is a non – conjugated site with the substituent and presents a Meta position.

Figure (5) represents the action of donor and acceptor substituent on C_{ortho}.



X=acceptor **X=donor**

Fig. 5: Represents the action of donor and acceptor substituent on C_{ortho}.

The resonance generated sign at the mentioned position 1 and 2 of Fig. 5 which induced field of opposite sign of polarization at C_{ortho} . This called the ρ_F reverse resonance effect.

q_M C_α (Mullikan charge for alpha carbon) gave a good correlation (R=0.994 for series 1 ; 0.902 for series 2 and 0.930 for series 3) .

In general q_M C_α suffered from reverse resonance field effects. The value of ρ_F is larger than ρ_R and this may be due to the presence of the polar group C≡N that made attraction reaction between different charges (minus charge on C_α and pluse charge at the polarize group (C≡N) this effect will strength the π–polarization (Extended π–polarization) so the field is larger than resonance .

The reverse resonance effect is found to be due to the secondary resonance effect and this as shown in Fig. 6. This behavior is similar to substituted oxoazonate [18].

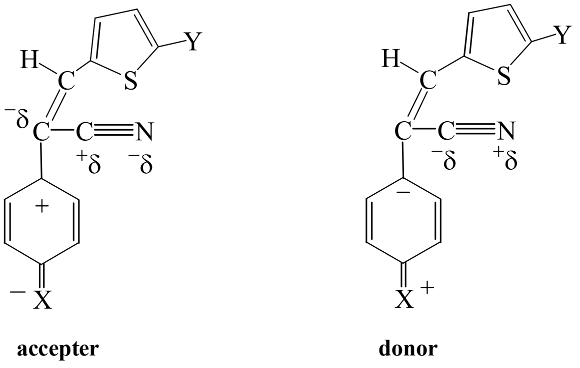


Fig. 6: Shows the secondary resonance effect

q_M C_β reveals acceptable correlation with Roynold's model (R≈0.91 for the three series) , this may be due to shielding and anisotropic effect for CN and thiophen groups which distort the sensitivity for substituent effect Fig. 7 .

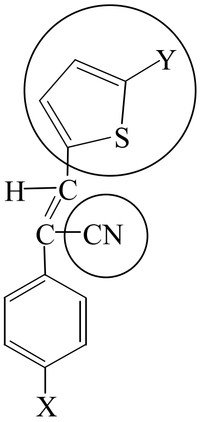


Fig.7: Represents shielding and anisotropic effect for CN and thiophen groups

q_M C_2 & C_5 (Mullikan charge for C_2 and C_5 carbon) gave somewhat acceptable correlation (R≈ 0.89 for C_2 ; R≈ 0.88 for C_5) . These values of R are because of highthe relatively long distance from the substituent.

Table 1: Total energy, Binding electron energy and Heat of formation

Series 1 : Y=H

No.	Substituent (X)	Total energy(K J Mole^{-1})	Binding energy(K J Mole^{-1})	Electronic energy(K J Mole^{-1})	Heat of formation(K J Mole^{-1})
1	H	-46685.2	-2760.6	-271224.1	109.3
2	OCH_3	-56898.75	-3133.58	-344073.3	70.95
3	Cl	-53635.8	-2743.9	-305337.0	102.7
4	CH_3	-50137.8	-3045.2	-304412.1	99.74
5	NO_2	-63551.5	-2948.5	-374220.4	101.3

Series 2 : Y=Me

No.	Substituent (X)	Total energy	Binding energy	Electronic energy	Heat of formation
1	H	-50135.9	-3043.3	-303599.1	101.6
2	OCH_3	-60349.3	-3416.1	-378487.1	63.46
3	Cl	-57086.6	-3026.7	-338672.7	95.1
4	CH_3	-53588.6	-3327.9	-337733.6	92.1
5	NO_2	-67002.4	-3231.4	-409133.2	93.6

Series 3 : Y=Br

No.	Substituent (X)	Total energy	Binding energy	Electronic energy	Heat of formation
1	H	-5447.6	-2721.6	-304261.2	122.9
2	OCH_3	-64688.1	-3094.5	-379114.2	84.7
3	Cl	-61425.2	-2704.9	-339312.2	116.5
4	CH_3	-57927.3	-3006.2	-338391.3	113.3
5	NO_2	-71340.7	-2909.3	-409706.8	115.2

Table 2: The value of HOMO & LUMO energy and energy band gap (ΔE)

No.	Substituent (X)	HOMO	LUMO	$\Delta E(KJMole^{-1})$
Series 1 : Y=H				
1	H	-8.986	-1.395	7.591
2	OCH_3	-8.742	-1.34	7.402
3	Cl	-8.962	-1.50	7.462
4	CH_3	-8.88	-1.37	7.510
5	NO_2	-9.516	-2.01	7.506
Series 2 : Y=Me				
No.	**Substituent (X)**	**HOMO**	**LUMO**	$\Delta E(KJMole^{-1})$
1	H	-8.877	-1.37	7.507
2	OCH_3	-8.669	-1.321	7.348
3	Cl	-8.871	-1.475	7.396
4	CH_3	-8.785	-1.345	7.440
5	NO_2	-9.369	-1.981	7.382
Series 3 : Y=Br				
No.	**Substituent (X)**	**HOMO**	**LUMO**	$\Delta E(KJMole^{-1})$
1	H	-9.051	-1.537	7.514
2	OCH_3	-8.816	-1.486	7.330
3	Cl	-9.025	-1.634	7.391
4	CH_3	-.8948	-1.512	7.436
5	NO_2	-9.558	-2.113	7.445

Table 3: Mulliken charge of series 1 ; Y=H , series 2 ; Y=Me , series 3 ; Y=Br

Series 1 : Y=H

No.	Substituent (X)	Mulliken Charges					
		Para	**Ortho**	**Alpha**	**Beta**	**2**	**5**
1	H	0.046	0.088	0.053	0.021	0.247	0.283
2	OCH_3	0.088	0.047	0.064	0.030	0.242	0.284
3	Cl	0.045	0.076	0.049	0.015	0.250	0.281
4	CH_3	0.054	0.082	0.057	0.024	0.245	0.284
5	NO_2	0.026	0.119	0.019	0.020	0.271	0.273

Series 2 : Y=Me

No.	Substituent (X)	Mulliken Charges					
		Para	**Ortho**	**Alpha**	**Beta**	**2**	**5**
1	H	0.044	0.089	0.049	0.017	0.250	0.241
2	OCH_3	0.086	0.053	0.061	0.028	0.245	0.243
3	Cl	0.043	0.077	0.045	0.011	0.254	0.239
4	CH_3	0.053	0.083	0.052	0.020	0.248	0.242
5	NO_2	0.028	0.120	0.014	0.024	0.275	0.229

Series 3 : Y=Br

No.	Substituent (X)	Mulliken Charges					
		Para	**Ortho**	**Alpha**	**Beta**	**2**	**5**
1	H	0.044	0.089	0.049	0.017	0.250	0.241
2	OCH_3	0.086	0.053	0.061	0.028	0.245	0.243
3	Cl	0.043	0.077	0.045	0.011	0.254	0.239
4	CH_3	0.053	0.083	0.052	0.020	0.248	0.242
5	NO_2	0.028	0.120	0.014	0.024	0.275	0.229

Table 4: Results of correlation analysis according to Minitab program

Series 1 : Y=H				
Position	**Reynolds**			
	F	**R`**	**R**	**S**
Para	0.0638	0.154	0.992	0.007363
Ortho	-0.0139	-0.115	0.994	0.004991
Alpha	-0.0555	-0.0542	0.994	0.003371
Beta	0.0434	0.0573	0.914	0.004899
2	-0.0253	-0.0333	0.890	0.003176
5	0.0116	0.0114	0.883	0.001217
Series 2 : Y=Me				
Position	**Reynolds**			
	F	**R`**	**R**	**S**
Para	0.0491	0.162	0.966	0.01498
Ortho	-0.0248	-0.101	1.00	0.0007474
Alpha	-0.0988	-0.003	0.902	0.05143
Beta	-0.0287	0.0687	0.915	0.01151
2	-0.0176	-0.0390	0.896	0.007514
5	0.00848	0.0180	0.885	0.003757
Series 3 : Y=Br				
Position	**Reynolds**			
	F	**R`**	**R**	**S**
Para	0.0501	0.160	0.968	0.01470
Ortho	-0.242	-0.0992	0.999	0.001034
Alpha	-0.0724	-0.0648	0.930	0.009254
Beta	0.0269	0.0705	0.913	0.01169
2	-0.0176	-0.0390	0.896	0.007514
5	0.00282	0.00689	0.887	0.001355

F = Field effect , R`= Resonance effect in Reynold`s model , R = Regression coefficient , S = standard deviation

References

1. J. McMurry, Organic Chemistry, 5 th. Edition, R. R. Donnelly & Sons Willard, Ohio, (2000).
2. J. R. Dyer, Application of Absorption Spectroscopy of Organic Compound; Prentice – Hall, Inc. (1965).
3. S. Eherenson; R. T. C. Browniee and R. W. Taft. ***Prog. Phys. Org. Chem.***, 1973, **10**, 1.
4. S. Gronowitz ; I. Fohnson and A. Harnfeldt . ***Chemica Scripta***, 1975, **7**, 76.
5. O. Exner and M. Budesinky, ***J. Mag. Res***., 1989, **27**. 27.
6. D. A. R. Happer. ***J. Chem.***, 1976, **29**, 2607.
7. D. A. R. Happer; S. M. Mckerrow and A. Wilkinson, ***J. Chem***., 1977, **30**, 1715 .
8. G. Musumarra and F. P. Ballistrer, ***J. Chemica scripta*** , 1981, **18**, 209 .
9. B. Saleh, H. Alhazam and A. Kreem, ***J of Nesan for Academic Studies***, 2008, **6**, 107.
10. F. P. Ballistrer; G. Musmarra and G. Scartalat, ***J. Chemica Scripta***, 1981, **18**, 214.
11. Hyperchem 6.5 Demo Releas for Windows, Hypercub Inc.USA (2002).
12. W. F. Reynolds, ***J. Chem. Soc.,*** 1980**,** PerkinTrans. **2**, 985.
13. P. W. Atkins, physical Chemistry, Oxford University press. Oxford (2001).
14. S. Al-shawi, Ph. D. Thesis, University of Basrah, Basrah, Iraq (1998).
15. H. A. Radhy, G. F. Fadhil, A. Perjessy, E. Kolehmainen, w. Fabian, M. Samalikova, K. Laihia and Z. Sustekova, ***University of Sharjah Journal***, 2008, **4**, 19.
16. H. A. Radhy, G. F. Fadhil, A. Perjessy, E. Kolehmainen, w. Fabian, M. Samalikova, K. Laihia and Z. Sustekova, ***Molecules***, 2002, **7**, 833.
17. H. Al-Amoode, M. Sc. Thesis, University of Basrah, Basrah, Iraq (1999).
18. B. Salah, M. Sc. Thesis, University of Basrah, Basrah, Iraq (1999).