A correlation Analysis Study Reinvestigation of a 13 C SCS for Some Substituted Poly Aromatic Fused Rings

Dr.Nezar . L . Shihab Aldain
College of Education
University of Basrah

Abstract : -The substituent effect on the 13C substituent chemical shift (SCS) and the additively for series namely . (1 – X – naphthalene (I) , 2 – X – naphthalene (II) , 9 – X – anthracene (III) , have been investigated by using MSP , DSP . Tafts model was the best on the DSP model due to the wide scale of resonance parameters ($^{O+}_{R}$, $^{O-}_{R}$, $^{O}_{BA}$ R , $^{OR}_{O}$) . ^{13}C chemical shift of distant carbons could be predicted reason ably well on the basis of calculated change of electron densities . The influences of electronic , steric and the conformational analysis of the fused system were discussed . The fused aromatic system have a behavior differ than the simple aromatic system due to its regularity .

In this work ^{13} C (SCS) proved to be used as a monitor in many physical calculation like qualitative and quantative studies .

This may be lead to the field effect the difference in planarity like in COMe . while OMe and OEt = 26 and CO_2H (1.1) , Cl (2) , Br (-2.2) . C_{10} have a small effect on the substituent change and in this fused system the change in chemical shift for most of the carbon atoms was small . So that it can not be evaluated or to estimate a reasonable feature about this difference . The dielectric field [12] effect have been studied intensively in this type of poly cyclic aromatic rings and a separation between л – Polarization and DEF effects a not straight – forward , DEF effects were suggested to be the reason for the high field shift of the carbon atoms . Like the high field of C – 2 in 1 – nitro – naphthalene , the electric field effect will polarize the C – H bond decrease the electron density at the proton and consequently interact at the carbon nucleus . As ^{13} C chemical shifts are much more sensitive to changes in electron density than at ^{1}H shifts , one expects the high field of the carbon resonance to be much stronger than the corresponding low field shift of the proton .

Introduction

^{13}C NMR investigation of polycyclic aromatic hetro carbons provide useful in formation about reaction parameters to give a new sight into reaction intermediates and to be informative on ionic species in general [1] . Polycyclic aromatic compounds [2,3] have a structural rigidity and large number of sites that can be probed via ^{13}C NMR .

The substiuent effect on the ^{13} C (SCS) will be in restigated by constructing (MSP) and (DSP) models also the performance of these model in reproducing the experimental chemical shift will be compared .

It seems also interesting to investigate the transmission of substituent effect through different substituent . Fused polycyclic aromatic system like (1 – X , 2 – X – naphthalene and 9 – X – anthracene) . Substituent effect are transmitted to even the furthest carbone in poly cyclic aromatic and are hence a very sensitive method of monitoring redistribution of changes in electron system .

In (1937) Hammett [4] introduced that the electronic effect (polar / mesomeric) as on component reached to the carbon atom which carried the substituent and to other distant carbon in (MSP) model then the models were modified by the (DSP) models which shows that there were a polar and mesomeric effect [5] , also other modification (LDR) (Localized , Delocalized , Resonance) (three parameters) Chartons [6] approach . , Finally the steric and conformation analysis were involved in these types of studies for poly cyclic aromatic system , ^{13}C Chemical shift of distant carbons can be predicted reasonably well on the basis of calculated change of electron densts .

(MSR) Hammett equation [4] was the oldest model to explain the treasmission of electronic effect of substituent in poly aromatic ring and it shows that there is a sum of electronic factors affecting the molecules but for many sustems this model failed in its explanation , so many modification were introduced which suggest that the effect was reached by two ways either by inductive or by mesomerism like in DSP model (Dual Substituents Parameters) .

$P^i = P_O$ …… MSP

$P^i\ P_R O_R + P_I O_I$ ……. DSP

Where P^i is the substituent in fenced properly to the hydrogen substituent like swain – Lupton , Takts , Reynolds and Yauho Tsuno models [5] then other factors were

introduced and were considered like the field and the steric hindernse . As known the other data for any compounds which seems that the steric was the main rule in affecting which the other electronic factors could be ignored here .

^{13}C chemical shift of distant carbon can be predicted reasonably well on the basis of calculated change of electron densities . In physical organic chemistry substituent effects have traditionally been divided in to two contributions , firstly the polar (Inductive / field) and secondly the mesomeric effect . The occurrence of steric as well as polar (field / inductive) effects in aliphatic system and ortho – substituted systems complicate the applications of correlation analysis . It was noted early that the Δ ^{13}C para values are proportional to the corresponding 1H para values , and Δ q л values was calculated by solely л electron methods .

Later workers [5] claimed that the ^{13} C shifts at all positions in mone substituted benzene followed the total electron densities at the carbon atoms , although caution has been stressed in extending this correlation to molecutes where any anisotropic field steric or hybridization change might be concerned .

The proposed dependence of ^{13}C shift on change densities and some times on the bond orders as well as thought of in terms of the paramagnetic contribution to the shift .

One of the important effect , Mesomerism is best studied in large conjugated system such as pyrene chemical shifts of distant carbons in compounds with substituent of bonth (+ M , - M) character above an alternation in both magnitude and sign in accordance with mesomeric release or with drawal of electrons . A DSP analyes of substituted naphthalenes showed clearly that the mesomeric contribution was dominant almost all positions .

Schulman et . al [7] using the Dewar three parameter (FMFM) equation that in benzene and biphenyl , the mesomeric contribution was forty times as large as the field effect contribution and this proved the fact that mesomerism always larger than polar .

Reynolds'et . al [8] and Hammett has drawn attention to the limitation of the FMFM method , second important effect was the inductive effect (I) , no general has yet been reached as to how many contributions can be limited under this general heading .

Brownlee et . al [9] have given a very comprehensive explanation of this effect and their definition will be adopted here . The л – inductive is divided into three types : -

(I) : - The $л_o$ effect (inductive of change) difference in an underlying from work may lead to the thmpen sating changes in the л – electron distribution , this effect has also been called (I_o) and inductomes – omeric effect .

(ii) : - The л – effect (The л – electron system may be polarized by a through space electrostatic interaction) or field induced л – polarization .

(iii) : - The $л_{orb}$ effect (the л – system may be distributed by repulsion interaction with highly using filled orbital of the substituent) л – inductive effect have been studied extensively as in model system .

DEF effect (Direct Electric Field effect)

The separation between л – polarization and DEF effect is not straight forward it was suggested to be reason for the high field shift in the nearly carbon atom (ipso) which carrying the substituent (C – X) in any series .

Steric effect and conformational analysis

One of the important effect in any system (Aliphatic or Aromatic) which default any electronic effect to effect . The different steric enfironment in positions (a , B or r) found in poly cyclic aromatic make these types of compounds convenient for the studies of steric effect and it will effect the chemical shifts in several ways , polarization of nearly bond , diminishing the conjugation of perturbed groups and changing bond angles .

Conformational studies are show chearly in the poly cyclic systems due to large molecules with different substituents in several positions lead to different situations of conjugation and steric hindrance like (1 – X and 2 – X – naphthalenes for example) where as he 1 – X seems to the kinetically isomers while 2 – X isomer was the rmodynamically one which dominates with the bulk group .

Experimental : -

^{13}C NMR were obtained from the literature [2] and they were sing $CDCL_3$ as a solvent for the studies series and ^{13} C NMR spectra was reported in (ppm) down field from the internal reperence (Me_4Si)

Calculations : -

Calculations were performed on Pentium (IV) pe , using standard step wise regression computer program

Results : -

The theoretical fact for the molecules that the increase in substituent electronagtivity increase ξ_q the charge and therefore lead to shifts to high frequency in the resonance increase in deshielding which observed in our work [5] .

$$O^A = O^{AA}{}_{dia} + O^{AA}{}_{para} + \sum O^{BR}{}_{inter} + O$$

Mason [10] have suggested that the diamagnetic term in lamb formula might also be important .

Where O_{dia} depeds also on the electronagativity of any substituent since an electronegative group eauses a reduction in electron density at nucleus in research and also causes a shift to a high frequency . A set of standard chemical shifts values in table (1 – 3) .

The compounds of fixed reometry was the derives of naphalene and anthracene . Other studies gave in addition to rotational barrier and the probability of finding a specific rotamer . Conformations of naphthalenes at low temperature have studies using these parameters .
Barriers to rotation were determind using live shape analysis and the free energy of activation both experimental from CNDO12 calculations and population rates were obtained .

Also substituted polycyclic aromatic are good model systems for study the conformational analysis and show how the position of substituent affected the data and this leads to many degrees of conjugation and different degrees of steric reaction like in our studies series O – X and B – X – anphthalenes .

In ^{13}C substituted chemical shift the mean factor was the additively in the aromatic system which based upon the transmission of the sum of electronic effect to the distant carbon , the attached carbon and the others depending on the nature of substituents . In many cases the attached carbon is out of explanation due to the distortion with the charge cloud of substituent and also with the direct effect of the substitiuents .

The data of the additivity of each substitent was shown and the effect on the ^{13}C chemical shift was introduced and compound with (X = H) to sho additivity

for the donor group (OMe , OH , Me , ….) and the drawer groups (Br , NO2 , CHO , COR) for naphthalene and anthracene series . The charge in the chemical shift of carbon No . 2 in methoxy naphthalene compound with 1 – hydroxyl naphthalene was caused by the r – effect of the methyl group . This effect could be thus be based to show rhat the methoxy group adopted a conformal with the methyl group from H_8 in good a agreement exceptions . A similar a agreement applied to a preferred orientation which was less readily explained .

One was of achieving the useful separation of inductive and mesomeric was the Taft DSP for ^{13}C (ScS) of substituted aromatic compounds . The analysis showed that C_5 and C_6 experience very feeble polar and resonance effect . The shielding parameters for C_6 and C_7 of 2 – X – naphthalenes were well correlated and these two naphthalenes disposition can be emply for estimating $\S_1$ and $\S_R$ for other substiuents .

Only for nuclei at large distances from the subsituent like poly aromatic cyclic rings . The high field of C8 in substituted naphthalene (a and B is due so called (y – gauche) effect , in the case of alkyl substituents has been attributed to the polarization of the CH bond caused by steric tinteraction .

It should be noted that this polarization may also be produced by a direct electric field (DFF) effect . The direct electric field effect have been studied intensively in this type of poly cyclic aromatic rings and a separation between π – polarization and (DEF) effects were suggested to be the reason for the high field shift of the carbon atoms like the high field of C – 2 – in nitro – naphthalene . The electric field effect will polarize the C – H bond decrease the

electron density at the proton and consequently interaction at the carbon nucleus .

As ^{13}C chemical shift are much more sensitive to changes in electron density than at 1H shift . One expects the high field of the carbon resonance to be much stronger than the corresponding low field shift of the proton resonance . In anthracites Adcock et . al [11] reflected the proposal that the meso disposition was a model for detection of inductomesomeric (π_s) effect for the substituent directly attached to the electron distribution at the proximate carbon atom , so (π_f) inductive have been demonstrate to contribute significating to ^{13}C SCS .

Additivity of Substituent : -

In 1 – X – naphthalene , all the substituent have a significant effect in the (C_1) ipso chemical shift carbon atom either shielding like in halogens while all other substituent ave deshielding in the ipso atom . While C_2 gave shielding in (OMe , NH_2 , OH , Me) and this include drawer and donor groups , which means unreasonable and abnormal . The sum varies to be bigger in C_1 , C_4 , C_5 C_8 (y – positions) while it will smaller in C_2 , C_3 , C_6 , C_7 (B – isomers) . This may be caused to the stability of (a – position) , in the 2 – x – naphthalenes also the same manner for (C_2) ipso chemical shift carbon atom either shilded (CN , Br , COMe , and CHO) and deshielded for (Me , OMe , OH and NH_2) . This was due to the resonance effect of these substituent also C_1 , C_3 and affected by substituents in the same manner with different factors because of the fused poly aromatic systems C_1 (a) differ than C_3 (B) while in C_3 only (Br , CHO , CN and COMe) are deshielded while in C_3 only (Br , Me , CN) are deshilding while (COMe) was caused shielding , this may be pointed to its bulkiness (- CO – Me) As we mentioned to resonance have

a great role than the polar effect as proved in DSP models for may physical data .

In 9 – X – anthracene , the ipso C additivity change from Me (3.7) , Et (0.8) while for a large molecule like isopropyl and – butyl was about 14 .

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دراسة التحليل الترابطي لأعادة تشخيص الإزاحة الكيماوية التعويضية لذرة الكاربون – 13 لسلاسل في مشتقات بعض المركبات الاروماتية متعددة الحلقات

د. نزار لطيف شهاب الدين
كلية التربية – جامعة البصرة

الخلاصة : –تم أعادة تشخيص الإزاحة الكيمياوية التعويضية لذرة الكاربون – 13 لمشتقات النفثالين (المعوضة في ذرة كاربون 1 و 2) والانثراسين (المعوض في ذرة كاربون 9) باستخدام انموذجين رئيسين أحادي المعامل وثنائي المعامل وكان أفضل نموذج ثنائي هوتافت بسبب كونه المعامل الرنيني ذا مدى واسع ($^{O+}_{R}$, $^{O-}_{R}$, $^{O}_{R}{}^{BA}$, $^{OR\ O}$) .

كما درست الإضافة للمعوضات المختلفة على الإزاحة الكيميائية لذرات الكاربون القريبة والبعيدة عن المعوض بينت الاختلافات الاروماتية الملتحمة عن غيرها وبرهن على استخدام تقنية الكاربون – 13 لدراسات كمية ونوعية .