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Analysis of Substituent Effects on C-13 NMR Parameters of Substituted Arylacetylene Derivatives. Linear Free Energy Relationships and PM3 Semiempirical Calculations

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Abstract—The substituent-induced chemical shifts (SCS) of C(α,β) on the ^{13}C NMR spectra of arylalkynes (i.e. containing H, CH_3, Cl and Br) were studied. The correlation between SCS and Hammett constants shows that the tendency of the effect by the substituents on the phenyl ring is Br (ρ=8.15)>Cl (ρ=7.27)>CH_3 (ρ=6.79)>H (ρ=5.78). This order can be rationalized as due to the ability of the group on the alkyne to stabilize the partial positive charge on C(β) resulting from polarization with π electron transfer from C(β) to the phenyl ring. The SCS values are also well correlated with the electron densities obtained from PM3 calculations. The solvent effect on the ^{13}C chemical shifts of phenylalkynyl bromide demonstrates a strong dependence on the relative permittivity as well as the shielding character of the solvents.

Introduction

Carbon-13 NMR spectroscopy is an especially valuable tool for studying the electronic properties of aromatic systems.[1] Hammett-type correlation with the rate constant is also able to reveal the nature of the reaction center.[2] In spite of some theoretical limitations, the use of linear free energy relationships (LFER) to correlate NMR data with Hammett constants is a useful technique to determine the transmission of inductive and resonance electronic effects through benzene rings, and some reviews are available.[3,4] Good linear correlations have been found between differences in chemical shifts with σ constants or with dual substituent parameters ($\Delta\delta$ vs $\rho_I\sigma_I+\rho_R\sigma_R$) for atoms directly linked to benzene ring. There are a number of reports in which the ^{13}C NMR spectra for various *para*-substituted styrene derivatives present as the positive ρ values.[5] On the other hand, the correlation for β carbons of the substituted ethylbenzene appear as the negative ρ values (reverse effect).[6] In our previous work, we applied this concept to obtain a correlation between substituent induced chemical shifts (SCS) and Hammett constants in a series of halocyclopropylarenes,[7] which behave as ethylbenzene derivatives leading to a reverse effect.

Although the relationship between SCS and Hammett constants has been utilized to study the possible electronic properties of various aromatic systems since the first report in 1973,[5a] there is, however, still no such study for arylacetylene derivatives. In this work, we determined the ^{13}C NMR spectra of arylacetylene halides (Br (**1**) and Cl (**2**)) and compiled the spectra of arylacetylenes (**3**)[8] and propynylarenes (**4**)[9] for an analysis of the substituent effects. Nine solvents were used to study their effect on 4-methylphenylacetylene bromide (**1C**). Furthermore, semiempirical calculations were successfully applied for simulating the thermodynamic data and electron densities of atoms.[10] In this work, the correlation between the electronic parameters thus calculated from an extensive semiempirical PM3 calculation of substituted arylacetylene derivatives with ^{13}C NMR chemical shifts were also studied.

Results and Discussion

Preparation of arylacetylene halides

Arylacetylene halides have been prepared by (1) halogenation of metal acetylides or surrogates,[11] (2) oxidative halogenation of terminal alkynes,[12] and (3) dehydrohalogenation of 1,1-dihaloolefins by using strong base, such as amide, butoxide, DBU etc.[13] In this work, arylacetylene halides can be simply prepared from dehydro-halogenation of β, β-dihalostyrenes using KOH in the presence of benzyltriethylammonium chloride (Eq. (1)). Dehydrobromination and dehydrochlorination from the corresponding styrenes occur readily to form arylacetylene halides with nearly quantitative yields in CH_2Cl_2 solution within 2 h. This reaction fails for the preparation of arylacetylene fluorides

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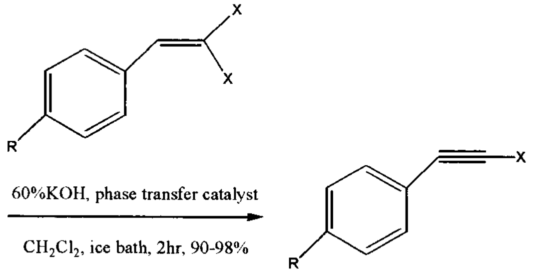
Table 1. The ^{13}C chemical shifts for arylacetylene bromides and arylacetylene chlorides in deuteriochloroform (ppm form TMS as an internal standard)

	C_1	$C_{2,6}$	$C_{3,5}$	C_4	C_α	C_β	Others
1a	122.62	131.91	128.25	128.59	80.05	49.78	
1b	114.55	133.31	113.80	159.69	79.85	47.86	55.10
1c	119.54	131.81	129.04	138.83	80.08	48.75	21.48
1d	121.02	133.11	128.60	134.68	78.92	51.06	
1e	129.45	132.81	123.60	147.25	78.37	56.40	
2a	122.15	131.95	128.56	128.44	69.39	67.99	
2b	113.62	133.19	113.77	159.64	69.27	66.16	54.90
2c	119.04	131.82	129.10	138.75	69.64	67.16	21.50
2d	120.59	133.15	128.69	134.68	68.34	69.12	
2e	128.97	132.77	123.59	147.27	67.74	73.88	

from difluorostyrenes. All pure compounds for NMR studies were obtained from column chromatographic separation.



(1)

1, 2

1a X=Br;R=H; **1b** X=Br;R=OMe; **1c** X=Br;R=Me; **1d** X=Br;R=Cl; **1e** X=Br;R=NO_2

2a X=Cl;R=H; **2b** X=Cl;R=OMe; **2c** X=Cl;R=Me; **2d** X=Cl;R=Cl; **2e** X=Cl;R= NO_2

Carbon-13 NMR spectra of arylacetylene halides

The ^{13}C chemical shifts of arylacetylene bromides and arylacetylene chlorides are summarized in Table 1. The C(β) chemical shifts of compounds **1** appear much further upfield than those of compounds **2**,**3**, and **4** due to the heavy atom factor.[14] In general, SCS(β) values are shifted downfield when the substituents on the aromatic rings are electron-donating groups, and the SCS(α) work in the other way (Table 2 and Fig. 1). The linear regressions of compounds **3**, **4** are also compiled from the literature for comparison.[8,9] There appears to be an inflection in the correlation line which corresponds to the slope of 8.15 (r^2=0.9847), 7.27 (r^2=0.984), 6.79 (r^2=0.925), 4.47 (r^2=0.907), and −1.73 (r^2=0.845), −1.73 (r^2=0.886), −1.91 (r^2=0.894) for C(β) of compounds **1**, **2**, **3**, and **4**, and C(α) of compounds **1**, **2**, and **3**, respectively. Very poor correlation was obtained for C(α) of compounds **4**.

Table 2. SCS (in ppm) of arylacetylene bromides and arylacetylene chlorides in deuteriochloroform solution (positive values represent downfield shifts)

Compounds	σ	C_α	C_β
1b	−0.27	−0.20	−1.92
1c	−0.17	0.03	−1.03
1a	0	80.05(0)	49.78(0)
1d	0.23	−1.13	1.28
1e	0.76	−1.68	6.62
2b	−0.27	−0.12	−1.83
2c	−0.17	0.07	−0.83
2a	0	69.39(0)	67.99(0)
2d	0.23	−1	1.13
2e	0.76	−1.64	5.88

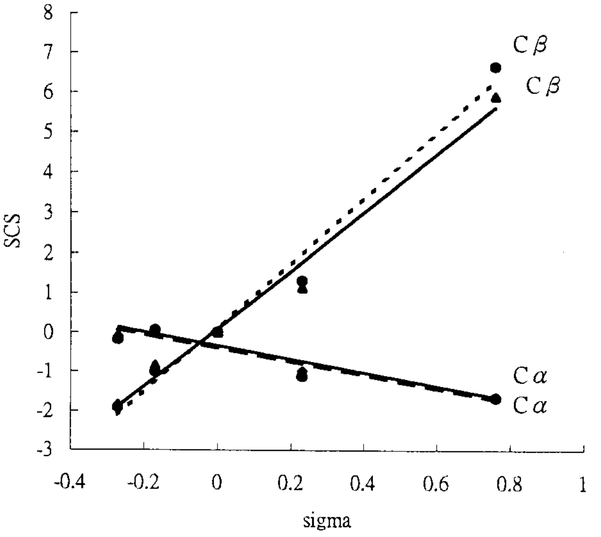


Figure 1. Carbon-13 SCS(α,β) values in ppm for arylacetylene bromide (●, dotted line) and arylacetylene chloride (▲, solid line) vs Hammett substituent constants (σ).

These correlations resemble those obtained from styrene derivatives and contrast with those of arylcyclopropanes and ethylbenzene derivatives.[6,7] For the acetylene halides, the slopes of the Hammett-plot are larger than that for styrenes (Table 3). ^{13}C NMR provides information which shows that the interaction of the substituent on C(β) through phenyl rings should be accentuated by the field-induced polarization of the arylacetylene π electron system.

The soft bromine atom is able to stabilize the partial charge on C(β) leading to a greater shift difference for C(α) and C(β) and higher slope. The incremental shifts of the aromatic carbon atoms of compounds **1**, **2**, and **3** along with phenylacetylene appear in Table 4. It shows that the incremental shifts for all the carbon atoms are similar to the corresponding phenylacetylene.[15] The incremental shifts for C-1 are −5.7, −6.3, and −5.8 ppm for compounds **1**, **2**, and **3**, respectively, due to the shielding character of the triple bond. On the other hand, these values for C-2 are +3.5, +3.5, and +3.8 ppm in the same series of compounds. This implies that the higher electronegativity of the sp-hybrid carbon reduces the electron density on the C-2 atom. The presence of halogen on the acetylene group

Table 3. Slopes for Cβ of styrenes and arylacetylenes obtained from the plots of SCS vs Hammett constants

X	$R{-}C_6H_4{-}C{\equiv}CX$	$R{-}C_6H_4{-}CH{=}CX_2$
Br	8.15	5.94
Cl	7.27	5.76
F	~	1.20[19]
Me	6.79[9]	6.26[5g]
H	4.47[8]	6.50[20]

Table 4. The incremental shifts of the aromatic carbon atoms of monosubstituted benzene (ppm from benzene at 128.5 ppm, + to the left, − to the right)

$R–C_6H_4–C≡CX$	C_1	C_2	C_3	C_4
1 (Br)	−5.7	3.5	−0.3	0.5
2 (Cl)	−6.3	3.5	0	0.1
4 (H) 15	−6.1	3.8	0.4	−0.2

does not alter those incremental shifts from the unsubstituted compound.

Correlation between SCS and charge densities of carbon atoms

An optimization of the electronic structure and geometry of arylacetylene derivatives by PM3 semiempirical molecular orbital calculations has been carried out. Molecular characteristics of the arylacetylenes described below corresponding to the energy minima obtained by a geometry optimization and a full all degrees of freedom analysis were investigated using the gradient optimization routine in the programs. The correlation between the net atomic densities and the ^{13}C NMR chemical shifts is well established in the literature.[3,4] The most significant molecular parameters to be related with NMR chemical shifts are the net atomic densities on C(α) and C(β). The correlation between the net atomic densities and the ^{13}C NMR chemical shifts are summarized in Tables 5 and 6 and shown in Figs. 2 and 3. Fig. 2 shows good regression lines both for compounds **1** (ρ=179.22, R^2=0.9931) and compounds **2** (ρ=174.47, R^2=0.9921). The correlations of $\delta_{C(\beta)}$ vs. $q_{C(\beta)}$ are more sensitive than that of C(α), is agreement with the experimental resultants.

Chemical shifts in various solvents

For the interaction field of a polar molecule in a medium of relative permittivity, ϵr, the ^{13}C screening constants in substituted methanes should depend linearly on the function, $(\epsilon r-1)/(2+2n)$, where n is the refractive index of the solvent molecule.[16] Also, the difference between the methane shift in a given solvent is found in the linear relationship with ΔHr. This indicates that the van der Waals interaction between analyte and solvent plays an important role.[14,17] The variation of the chemical shifts resulting from different solvents can reveal structural information in the solution phase.

Table 5. Calculated net atomic charge densities of C(β) and SCS(β) for $R–C_6H_4–C≡C–X$

R	**1**-C_β (SCS)	**1**-C_β charge	**2**-C_β (SCS)	**2**-C_β charge
4-OMe	−1.92	−0.2843	−1.83	−0.3073
4-Me	−1.03	−0.2798	−0.83	−0.3031
H	0	−0.2767	0	−0.3004
4-Cl	1.28	−0.2698	1.13	−0.2938
4-NO_2	6.62	−0.2375	5.88	−0.2644

Table 6. Calculated net atomic charge densities of C(α) and SCS(α) for $R–C_6H_4–C≡C–X$

R	**1**-C_α (SCS)	**1**-C_α charge	**2**-C_α (SCS)	**2**-C_α charge
4-OMe	−0.204	−0.0581	−0.12	−0.0918
4-Me	0.034	−0.063	0.07	−0.0967
H	0	−0.0661	0	−0.0998
4-Cl	−1.134	−0.0724	−1	−0.1062
4-NO_2	−1.681	−0.1017	−1.64	−0.1368

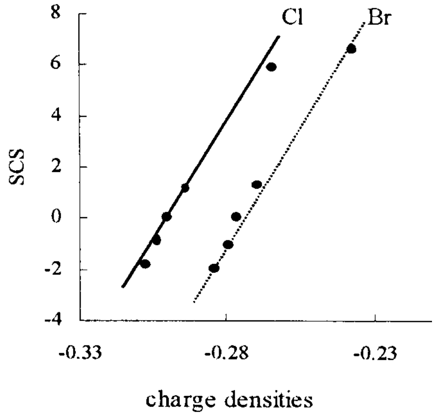


Figure 2. Correlation of calculated net atomic charge densities of C(β) and their SCS(β).

The chemical shifts of 4-methylphenylacetylene bromide in nine solvents are listed in Table 7 and shown in Fig. 4. From Fig. 4 we found that the dish-shaped molecules[16] (C_6D_6, $[^2H_5]$pyridine, and $[^2H_3]$nitromethane) and polyhalomethanes (i.e. $CDCl_3$) form a group, while the oxygen-containing solvents ($[^2H_8]$dioxane, CD_3OD, $[CD_3]_2SO$, and $[^2H_6]$acetone) and rod-like molecule[16] ($[^2H]$acetonitrile) are belonging in another group. In general, the carbon-13 chemical shifts of the whole molecule move upfield in polar solvents. We conclude from Fig. 4 that the chemical shifts are mainly affected by two factors, i.e. the shielding ability and relative permittivity of solvents. The dish-shaped molecules and polyhalomethanes are possess as a deshielding nature. It is surprising to observe the reverse influence for the arylalkyne series in this work. The difference in solvent-induced shift for C(β) is 4.6 ppm for nitromethane (deshielding solvent) and dimethylsulfoxide (more polar). This suggests that the polar solvent will stabilize the polarization of this alkyne and result in more positive character of C(β). This value is comparable to that of ethyl iodide, for which the solvent-induced shift is

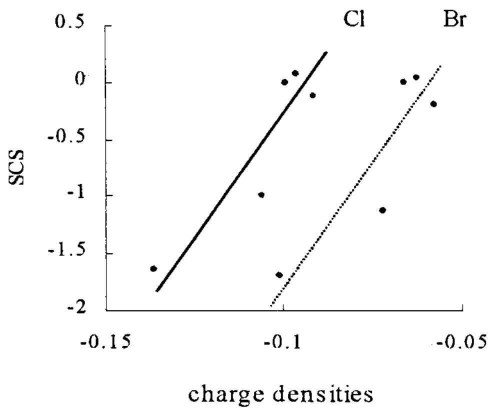


Figure 3. Correlation of calculated net atomic charge densities of C(α) and their SCS(α).

Table 7. Solvent dependence of the ^{13}C chemical shifts (in ppm) of 4-methylphenylacetylene bromide

Solvent	μ(D)	C_1	$C_{2,6}$	$C_{3,5}$	C_4	C_α	C_β	Me
$CDCl_3$	1.01	119.539	131.812	129.044	138.826	80.084	48.751	21.477
CD_3COCD_3	2.88	120.241	132.519	130.033	139.928	80.720	50.062	21.370
CD_3OD	1.7	120.899	132.791	130.154	140.204	80.890	49.831	21.486
C_6D_6	0	120.083	132.172	129.315	138.856	80.836	49.532	21.227
C_5D_5N	2.2	119.389	131.585	128.996	138.658	80.068	51.069	20.631
CD_3SOCD_3	3.96	119.591	132.517	130.283	140.02	80.853	52.094	21.881
CD_3NO_2	3.46	118.320	130.829	128.32	138.801	79.088	47.513	19.351
$C_4D_8O_2$	0.45	121.111	133.306	130.595	140.399	81.574	50.933	22.136
CD_3CN	3.92	120.123	132.655	130.189	140.387	80.759	50.086	21.469

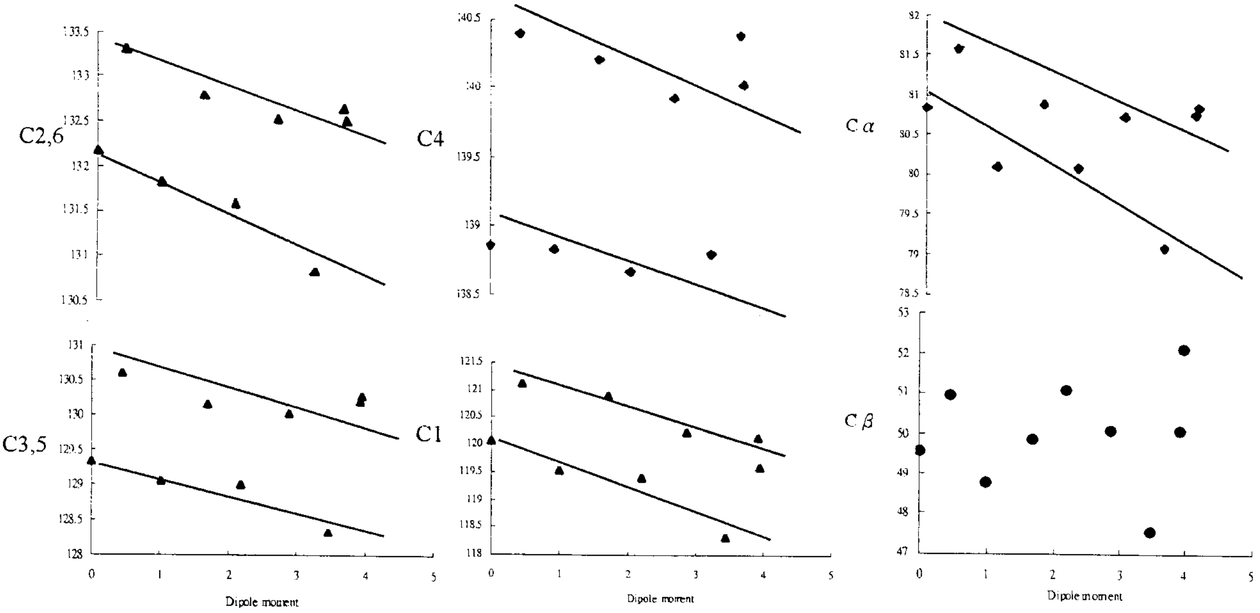


Figure 4. Correlation between the 4-methylphenylacetylene bromide with dipole moment of solvents.

5.2 ppm for cyclohexane and nitromethane.[18] The lack of a correlation between the difference in solvent-induced shifts for C(β) and the nature of the solvent might be due to the combination of the nature of solvent and the polarizability of C(β)-bromine bond.

Experimental

^{13}C (or C-13) measurements

The NMR data of 15 (w/v)% of analyte in $CDCl_3$ (or other specified solvent) were recorded on a Bruker AC-250 spectrometer at 62.9 MHz; 64 K data points were collected within a range of 15 kHz. All chemical shifts were measured relative to TMS in proton noise decoupled spectra. The digital resolution was generally 0.02 ppm. In general, 500 scans were accumulated for each compound in this study.

Preparation of arylacetylene halides—typical procedure

A mixture of dichlorostyrene (0.1 g, 5.78×10^{-4} mol) and benzyltriethylammonium chloride (0.1 g) in 2.0 mL CH_2Cl_2 and aqueous KOH (60%, 1.0 mL) in a round-bottomed flask was stirred on an ice-bath for 2 h. The resultant mixture was extracted with CH_2Cl_2 (3×10 mL) and then dried over $MgSO_4$. After filtrating and removing solvent, the residue was purified by column chromatography (silica gel) with *n*-hexane as an eluent to give 0.076 g of **2a** (yield 96%).

All of the arylacetylene bromides (and chlorides) used in this work are known compounds and were prepared using this method to give nearly quantitative yields. All compounds for NMR studies were purified by column chromatography and purity was further verified by GC-MS analysis.[21]

The calculations were carried out with the spin-unrestricted version of the PM3 method available in the MOPAC program system implanted in Alchemy 2000 software (Windows version). Geometry optimization of compounds was performed through the eigenvector following (EF) routine incorporated into the PM3 program. To obtain the minimization, the gradient convergence was set to 0.01, gradient_min_Type to NLLSQ, and minimize_type to BFGS.

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