

# Substituent effects in the $^{13}\text{C}$ NMR chemical shifts of $\alpha$ -mono-substituted acetonitriles

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## Abstract

$^{13}\text{C}$  chemical shifts empirical calculations, through a very simple additivity relationship, for the  $\alpha$ -methylene carbon of some  $\alpha$ -mono-substituted acetonitriles,  $\text{Y-CH}_2\text{-CN}$  ( $\text{Y} = \text{H, F, Cl, Br, I, OMe, OEt, SMe, SEt, NMe}_2, \text{NEt}_2, \text{Me}$  and  $\text{Et}$ ), lead to similar, or even better, results in comparison to the reported values obtained through *Quantum Mechanics* methods. The observed deviations, for some substituents, are very similar for both approaches. This divergence between experimental and calculated, either empirically or theoretically, values are smaller than for the corresponding acetones, amides, acetic acids and methyl esters, which had been named non-additivity effects (or intramolecular interaction chemical shifts, ICS) and attributed to some orbital interactions. Here, these orbital interactions do not seem to be the main reason for the non-additivity effects in the empirical calculations, which must be due solely to the magnetic anisotropy of the heavy atom present in the substituent. These deviations, which were also observed in the theoretical calculations, were attributed in that case to the non-inclusion of relativistic effects and spin-orbit coupling in the Hamiltonian. Some divergence is also observed for the cyano carbon chemical shifts, probably due to the same reasons.

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## 1. Introduction

Nitriles are versatile synthetic intermediates and are of considerable importance in all branches of chemistry. The classical description of the cyano group involves sp carbon and nitrogen atoms, making a  $\sigma$  and two  $\pi$  bonds, resulting in a linear arrangement. The large dipole moment of the cyano group has been attributed to the nitrogen electron lone pair directed along the CN axis, which has been also considered as an sp hybrid orbital [1].

Despite their importance,  $^{13}\text{C}$  NMR data of nitriles are scarcely found in the literature. Bailey and Cioffi reported data for 26 nitriles, but just as reference data [2]. Data for unsubstituted aliphatic nitriles have also been recently published [3].  $^{13}\text{C}$  and  $^{14}\text{N}$  NMR experimental data and theoretical calculated values for four aliphatic nitriles showed that the occurrence of autoassociation decreases with the volume of the substituent and with dilution in aprotic solvents [4]. A comprehensive investiga-

tion on electron field and  $\pi$ -electron effects of the cyano group on NMR chemical shifts was also reported, but just on  $^1\text{H}$  chemical shifts values [5].

Analysis on chemical shifts values have relied on empirical rules and recently on theoretical calculations. Unquestionably, the most important observation in the field of  $^{13}\text{C}$  NMR spectroscopy is the existence of simple additivity relationships based on empirical rules which, with remarkable precision, correlate the shieldings within specific families of compounds with a limited number of structural parameters [6,7]. Several examples of application of additivity relationships were published since 1964 and were reviewed by Martin et al. [8] and by one of us [9], and were also incorporated into a book by Breitmaier and Voelter [10]. For the empirical calculation of the  $^{13}\text{C}$  NMR chemical shift ( $\delta_{\text{calc}}$ ) of a disubstituted methylene carbon ( $\text{X-CH}_2\text{-Y}$ ), the  $\alpha$ -effect of X ( $\alpha_{\text{X}}$ ) and of Y ( $\alpha_{\text{Y}}$ ) are added to the methane carbon chemical shift ( $-2.3$ ), according to Eq. (1):

$$\delta_{\text{calc}} = -2.3 + \alpha_{\text{X}} + \alpha_{\text{Y}} \quad (1)$$

However, further work on  $^{13}\text{C}$  NMR chemical shifts of a disubstituted methylene or methine carbon have shown that they may deviate from additivity, and that this non-additivity is a

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powerful and sensitive tool to detect any kind of intramolecular interaction, due to the simultaneous presence of both substituents at the same carbon atom [11,12]. This non-additivity has been defined according to Eq. (2), and named as *Intramolecular Interaction Chemical Shift* (ICS) [11] by analogy to the well-established *Substituent Induced Chemical Shifts* (SCS):

$$\text{ICS} = \delta_{\text{exp}} - \delta_{\text{calc}} \quad (2)$$

Although, ICS are observable for a large number of aliphatic and alicyclic systems, it is relevant that the deviations from additivity vary from one system to another and within a specific family of compounds. In order to elucidate the reasons for the apparently random changes in the ICS values, a systematic work with aliphatic and alicyclic systems has been undertaken. Thus, studies with 2-hetero-substituted acetones [13], *N,N*-diethylacetamides [14], methyl acetates [15], *N*-acetyl-2,2-dimethyl-aziridines [16], 2-methylpropenes [17] and cyclohexanones [18] have been reported. For all series, significant ICS values were observed for all substituents and were qualitatively attributed to intramolecular interactions between the  $\alpha$ -heteroatom and the carbonyl or olefin group.

Empirical calculations of simple functional groups having an  $\text{sp}^2$  (excluding aromatic and heteroaromatic systems) or  $\text{sp}$  carbon are not usual. It has been reported by Brouwer and Stothers a method for olefinic carbon shifts [19], by Hörbold et al. for alkynes [20] and by Tanaka for carbonyl compounds [21]. However, no method has been described for the cyano carbon chemical shifts.

Moreover, the increasing facilities for performing almost any kind of theoretical calculations at a reasonable level of accuracy lead one of us to the study the  $^{13}\text{C}$  NMR chemical shifts of a series of  $\alpha$ -substituted acetonitriles, to check if they would reproduce the experimental values, but the obtained results showed also large deviations for some substituents, despite the basis sets and methods used (GIAO or CSGT) [22].

## Y-CH<sub>2</sub>-CN

Y = H **1**, F **2**, Cl **3**, Br **4**, I **5**, OMe **6**, OEt **7**, SMe **8**, SEt **9**,  
NMe<sub>2</sub> **10**, NEt<sub>2</sub> **11**, Me **12** and Et **13**

Scheme 1.

Therefore, it was of interest to perform empirical calculations of the  $^{13}\text{C}$  chemical shifts of the  $\alpha$ -methylene and cyano carbon atoms, for a comparison with the experimental and theoretically calculated values and also for a comparison with the results of other series of  $\alpha$ -substituted compounds. The  $\alpha$ -mono-substituted nitriles chosen for this work are presented in Scheme 1.

## 2. Experimental

Experimental and theoretically calculated  $^{13}\text{C}$  NMR chemical shifts were taken from a recent publication [22]. Empirical calculations of chemical shifts and of ICS values are trivial and were performed through the equations presented in the text.

## 3. Results and discussion

### 3.1. $\alpha$ -Methylene carbon chemical shifts

The  $\alpha$ -methylene carbon chemical shift is dependent on the effect of Y substituent and on the deshielding effect of the cyano groups. Therefore, a simple prediction can be made by summing up both effects through the application of Eq. (3):

$$\delta_{\text{CH}_2} = -2.3 + \alpha_Y + \alpha_{\text{CN}} \quad (3)$$

where  $\alpha_Y$  (Table 1) and  $\alpha_{\text{CN}}$  are the  $\alpha$ -effects of the Y substituent and cyano group in mono-substituted alkanes [9], and  $-2.3$  is the chemical shift for the methane carbon atom. The

Table 1  
Experimental ( $\delta_{\text{exp}}$ ) and empirically calculated  $\alpha$ -methylene carbon chemical shifts, and ICS values for  $\alpha$ -substituted acetonitriles (**1–12**) and for the corresponding carbonyl compounds [Y-CH<sub>2</sub>-C(O)-Z]. The substituent  $\alpha$ -effect ( $\alpha_Y$ ) is also listed

Compound	Y	Acetonitriles				Carbonyl compounds, ICS <sup>a</sup>		
		$\alpha_Y^b$	$\delta_{\text{exp}}$	$\delta_{\text{calc}}^c$	ICS <sup>d</sup>	Z=Me	Z=OMe	Z=NEt <sub>2</sub>
<b>1</b>	F	70.2	70.7	71.7	-1.0	-13.4	-13.4	-11.3
<b>2</b>	Cl	31.3	24.5	32.8	-8.3	-11.4	-11.2	-11.4
<b>3</b>	Br	18.9	5.1	21.3	-16.2	-13.7	-14.9	-14.9
<b>4</b>	I	-7.1	-32.0	-5.6	-26.4	-15.0	-19.1	-17.4
<b>5</b>	OMe	59.2	58.7	60.7	-2.0	-9.5	-10.2	-7.9
<b>6</b>	OEt	57.1	56.0	58.6	-2.6	-9.4	-	-
<b>7</b>	SMe	21.0	18.8	22.5	-3.7	-6.0	-6.3	-7.6
<b>8</b>	SEt	18.2	16.4	19.7	-3.3	-5.4	-	-
<b>9</b>	NMe <sub>2</sub>	46.1	48.6	47.6	1.0	-4.8	-7.1	-4.5
<b>10</b>	NEt <sub>2</sub>	39.5	40.1	41.0	-0.9	-3.7	-	-
<b>11</b>	Me	9.2	10.7	10.7	0.0	-1.1	-2.4	-4.3
<b>12</b>	Et	18.5	18.8	20.0	-1.2	-1.4	-3.0	-4.5

<sup>a</sup> From Refs. [13–15], respectively.

<sup>b</sup> From Ref. [9].

<sup>c</sup> Calculated by Eq. (3);  $\alpha_{\text{CN}} = 3.8$  ppm, obtained from CH<sub>3</sub>CN ( $\delta_{\text{CH}_3} = 1.5$  ppm).

<sup>d</sup> Calculated by Eq. (2).

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