

# In search of tetrafluoroborate anion: $^{19}\text{F}$ -NMR Chemical Shifts dependence of Substituents in tri-Aryl Pyrylium Cations

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## Abstract

It is known that the anion nature, in particular,  $\text{BF}_4^-$  has a significant influence on the reactivity of Pyrylium Salts. With the aim to demonstrate the presence of this anion firstly we used Mass Spectrometry but this technique proved to be useless. By using  $^{19}\text{F}$ -NMR we have obtained remarkable results. In general, coupling constants  $^1J(\text{B-F})$  and  $^{19}\text{F}$  chemical shift ( $\delta_{\text{F}}$ ) depend on the solvent, the concentration and the nature of the associated cation. Thus, we have analyzed the small but significant variations of chemical shifts from lightly and heavily modified tri-arylpnyrylium cations.

## Keywords

Tetrafluoroborate anion; Pyrylium Salts; Chemical Shifts; Fluorine; NMR.

## Introduction

The  $^{19}\text{F}$  nucleus shares many properties with  $^1\text{H}$  such as the same nuclear spin ( $I = 1/2$ ), almost the same high natural abundance and similar gyromagnetic ratio, leading to not very different receptivity, and short spin-lattice relaxation times.<sup>1</sup>  $^{19}\text{F}$ -NMR spectroscopy offers in summary a number of advantages as compared to  $^1\text{H}$  spectroscopy. For example, the range of usual chemical shifts ( $\delta$ ) is much higher for  $^{19}\text{F}$  (~ 500 ppm) than for  $^1\text{H}$  (~ 10 ppm) producing well separated signals and first order spectra and  $^{19}\text{F}$ -NMR spectra can be recorded in non-deuterated solvents offering a clean window without solvent interference.

On the other hand, pyrylium salts belong to a very important class of cationic organic molecules that have trivalent oxygen in a six membered aromatic ring.<sup>2</sup> Numerous references are available for this kind of compounds such as crystallographic and structural studies<sup>3</sup> and specially their good absorption, fluorescence, and electron

acceptor behavior. Pirylium salts have been exploited to design sensors for anions,<sup>4</sup> amines, amino acids and chameleon labels for quantifying proteins<sup>5</sup> among others.

The reactivity of pyrylium cations depends on many factors such as solvent, nature of anion and structure of salts. In this communication, we report the study of tetrafluoroborate anion by <sup>19</sup>F-NMR spectroscopy in pyrylium compound whose synthesis was previously carried out and we have studied the small but significant variations on chemical shifts from lightly to heavily modified tri-arylpyrylium cations.

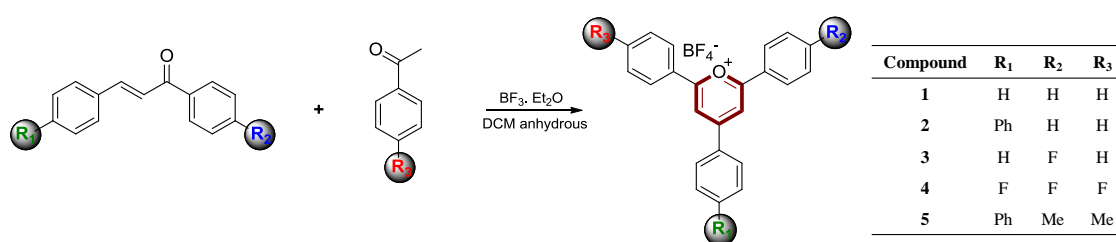
## Experimental Methods

All chemicals were purchased and used without further purification. Evaporations were conducted under reduced pressure. TLC was performed on silica gel plates (DC-Alufohlen F254, E. Merck); The syntheses of pyrylium tetrafluoroborate from chalcone was previously carried out<sup>6</sup> and detection of compounds was accomplished with UV light (254 nm) and by charring with H<sub>2</sub>SO<sub>4</sub> and characterization with NMR spectroscopy and Mass spectrometry.

<sup>19</sup>F-NMR spectra (500 MHz) were recorded with a Bruker Advance 500 spectrometer, using TMS for indirect referencing of CCl<sub>3</sub>F following the IUPAC recommendations;<sup>7</sup> chemical shifts ( $\delta$ ) are expressed in ppm from TMS; coupling constants ( $J$ ), in Hz.

## Results and discussion

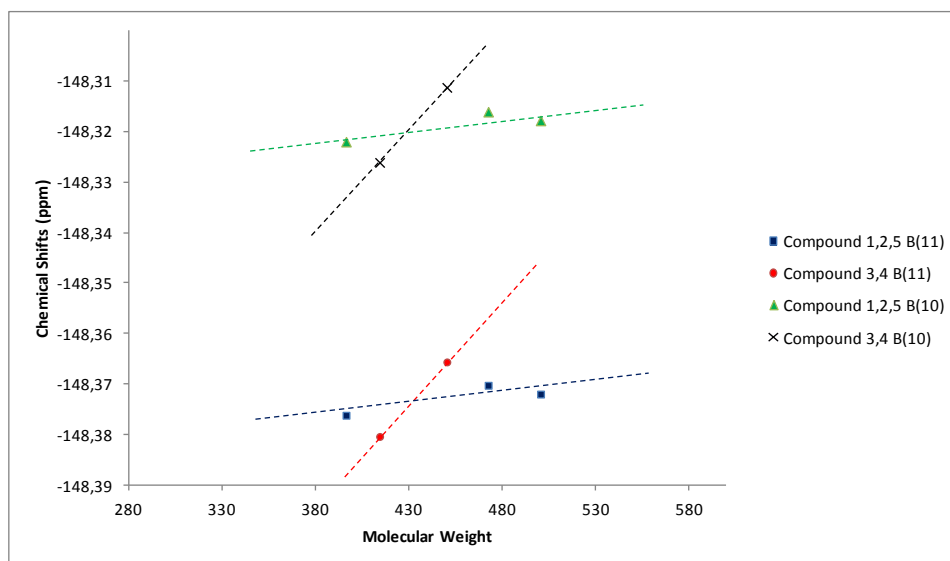
The synthesis of pyrylium salts (**1-5**) depend on the symmetry around the pyrylium cation. In particular, for unsymmetrical systems, the synthesis of chalcones from the less reactive ketone as a previous step is required (Scheme 1).



**Scheme 1.** Synthesis of Pyrylium salts tetrafluoroborates (**1-5**)

With the aim to demonstrate the presence of the anion, firstly we used Mass Spectrometry but this technique proved to be useless to determinate it in pyrylium salts. While by using  $^{19}\text{F}$ -NMR, we observed for each case two equidistant signals: a broad singlet for coupling between  $^{10}\text{B}$ -F and a quartet for coupling  $^{11}\text{B}$ -F.

Previous work<sup>8</sup> in this field shown: (i) that the value of coupling constants varies from 1.1 Hz at infinite dilution to 4.8 Hz in a saturated solution, and (ii) that in dilute solution the  $\text{BF}_4^-$  ion parameters are insensitive to the cation type.<sup>9</sup> In this study, the measures have performed in triplicate to check that the changes did not due to the electric field or other NMR parameters and the solvent ( $\text{DMSO-}d_6$ ) and concentration have been kept constant in all experiments. At the dilute concentration used of 20 mM, we observed the expected value (1.13 Hz). However, we have observed as preliminary results, that even for the diluted concentration used, small but significant variations on chemical shifts when tri-arylpyrylium cation was modified. (Figure 1) The lowest molecular weight compound, **1**, has been considered as reference compound in this study.



**Figure 1.** Plot of  $^{19}\text{F}$  chemical Shifts ( $\text{CCl}_3\text{F}$ ) against molecular weight for compound 1-5

The modification in compounds **2-5** provide if the chemical shifts would vary with molecular weight of pyrylium cations. A linear trend for compounds **1**, **2** and **5** both in  $^{11}\text{B}$  and  $^{10}\text{B}$  was observed but we did not see the same trend on compounds **3** and **4**. The difference for these compounds is the presence of fluorine, one atom for **3** and three

atoms for compound **4**. This electronegative substituent, their electronic effect and the possibility of participate in hydrogen bonding could explain the chemical shift trend, depending now not only of molecular weight contribution.

## Conclusions

Small coupling constant value in dilute solution has been observed according to the literature. On the contrary, in respect to chemical shifts we have concluded from this preliminary study that in dilute solution there is a mild variation ( $\Delta\delta$  0.004 ppm) with molecular weight that could be increase by the concentration. The presence of electronegative substituents causes a higher shift ( $\Delta\delta$  0.015 ppm).

## Acknowledgements

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