

PHYSICAL

UNDERGRADUATE EXPERIMENT

Observing Electronegativity via NMR Spectroscopy Chemical Shifts



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INTRODUCTION

Electronegativity is one of the most fundamental concepts as it explains several phenomena in chemistry. Therefore, this chemical property is introduced early in the undergraduate curriculum. Based on a published method by Everest and Vargason^[1] the theoretical concept of electronegativity can be demonstrated by directly observing its effect on the chemical shift of signals in the ^1H NMR spectra of a series of commercially available compounds. This experiment is highly suitable for an undergraduate laboratory and can easily be implemented by teaching assistants.

BACKGROUND

Electronegativity describes the ability of an atom in a molecule to attract electrons to itself.^[2] The first electronegativity scale was introduced by Linus Pauling in 1932. Beside this commonly used scale, the Allred-Rochow (1958) and the Mulliken (1934) models (among others) were developed later by taking into account more properties like the Coulomb potential, ionization energy, and electron affinities.^[3] However, their electronegativity values only differ slightly compared to Pauling's scale and the general trend stays mostly the same. In Pauling's scale, fluorine is the most electronegative element ($\chi = 4.0$) and cesium is the least electronegative element with ($\chi = 0.7$). Within the periodic table the electronegativity generally increases from left to right across a period and decreases from top to bottom down a group (figure 1).

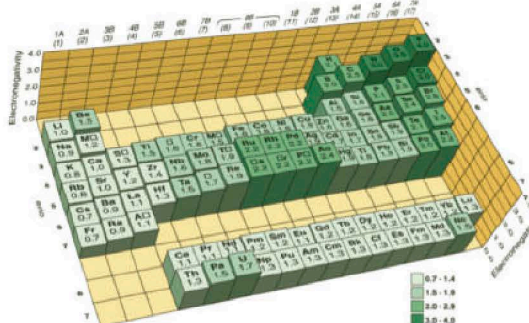


Figure 1. The Pauling electronegativity scale.^[4]

In NMR spectroscopy, changes in the distribution of electrons around an observed nucleus like ^1H affect the local magnetic field this nucleus experiences and its Larmor frequency.^[5] Electrons in the neighboring atoms will reduce the field experienced by the proton, effectively 'shielding' it from the external magnetic field and moving the signal to lower ppm (upfield). On the contrary, electronegative groups close to the nucleus of interest reduce the surrounding electron density, 'deshielding' the proton from the external magnetic field and moving the signal to higher ppm (downfield). With this knowledge, the theoretical concepts of electronegativity can be visualized by NMR spectroscopy with the experiment presented in this Application Note. We will observe the chemical shift of the $-\text{CH}_2-$ group located alpha to: (a) a group 17 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) substituent; and (b) a first row atom ($\text{E} = \text{C}, \text{N}, \text{O}, \text{F}$) and use this information to better understand electronegativity.

PROCEDURE

The samples for the experiment were prepared by combining 0.1 mL of each compound (1-fluoropentane, 1-chloropentane, 1-bromopentane, 1-iodopentane, decane, tributylamine, dibutyl ether) in 0.5 mL of CDCl_3 until homogenous. The 60 MHz ^1H NMR spectra of each sample was recorded on the NMReady-60 using the following parameters:

spectral width: 12 ppm interscan delay: 1 sec
spectral center: 4 ppm number of points: 2048
number of scans: 16 dummy scans: 0

To illustrate the effect of electronegativity going down a group, compare the ^1H NMR spectra of 1-fluoropentane, 1-chloropentane, 1-bromopentane, and 1-iodopentane. To elucidate the effect of electronegativity going from left to right across a period, compare the ^1H NMR spectra of decane, tributylamine, dibutyl ether, and 1-fluoropentane.

RESULTS & DISCUSSION

Using the reported method,^[1] trends in electronegativity can be directly observed in a series of ^1H NMR spectra of compounds varying only in the electronegativity of the chosen heteroatom X (figure 2) or E (figure 3). In figure 2 the protons (red) in the α -position to the halogen X are sequentially shielded with the decrease in electronegativity from fluorine to iodine in the alkyl halides **1a** - **1d**.

^1H NMR

(60 MHz, CDCl_3):

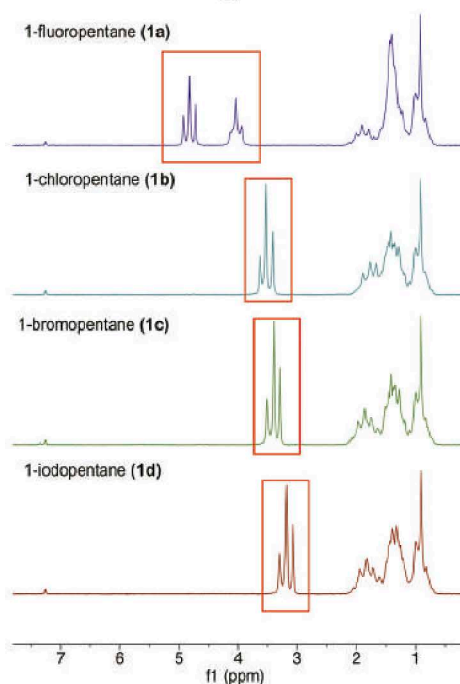
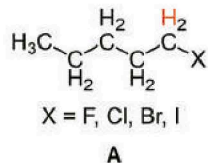


Figure 2. Stacked ^1H NMR spectra of the compounds **1a**–**1d** recorded 60 MHz in CDCl_3 .

For 1-fluoropentane (**1a**) the FCH_2 group signal appears as a distorted doublet of triplets centered at 4.4 ppm due to coupling with the fluorine center ($^3J_{\text{FH}} = 6 \text{ Hz}$). The signal of interest in the other alkyl halides **1b**–**1d** is observed as a triplet with varying chemical shift: $\delta [\text{ppm}] = 3.53$ (ClCH_2 , **1b**), 3.40 (BrCH_2 , **1c**) and 3.18 (ICH_2 , **1d**).

The effect of the increase in electronegativity for the elements across the period from carbon to fluorine can be visualized in the spectra depicted in figure 3. Here, as we move across from carbon to fluorine, the protons in red are deshielded due to the increase in electronegativity. Although, the molecules being compared differ slightly in their structures, the effect on the magnetic field experienced by the CH_2 group is dominated by the identity of E. For decane (**2a**) all CH_2 signals overlap in one signal at 1.27 ppm. The NCH_2 groups of amine **2b** show a downfield shifted signal at 2.36 (t) ppm. For ether, **2c** the $\alpha\text{-CH}_2$ signal is observed with an even more downfield shifted triplet ($\delta = 3.36 \text{ ppm}$). Again, the alkyl fluoride **1a** shows the most downfield shifted signal at 4.4 ppm.

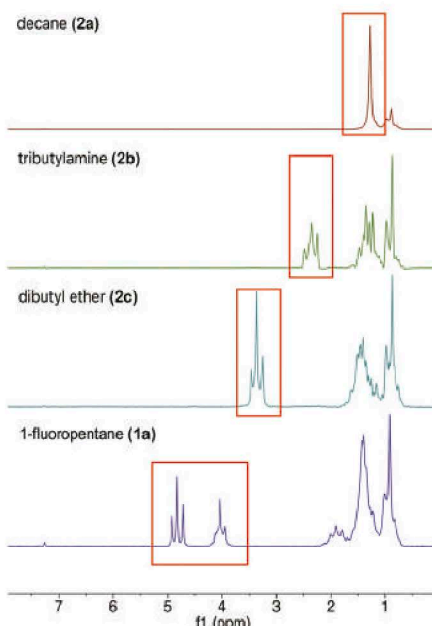
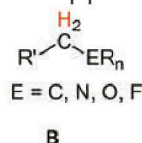


Figure 3. Stacked ^1H NMR spectra of the compounds **1a**, **2a**–**2c** recorded 60 MHz in CDCl_3 .

Naturally, at 60 MHz the dispersion of chemical shifts is lower relative to a high-field instrument. However, the resulting spectra are more than suitable to observe changes in chemical shifts, consistent with the concept of electronegativity.

CONCLUSIONS

In summary, the effect of electronegativity was visualized by recording a series of ^1H NMR spectra using the NMReady-60. This experiment is simple to perform and implement in undergraduate laboratories and can be used to emphasize the concepts of electronegativity to undergraduates.

REFERENCES

- [1] M. A. Everest, J. M. Vargason, *J. Chem. Edu.* **2013**, 90, 926.
- [2] E. V. Anslyn, D. A. Dougherty, *Modern Physical Organic Chemistry*, University Science Books, **2007**.
- [3] A. F. Hollemann, N. Wiberg, *Lehrbuch der Anorganischen Chemie*, 102. Auflage, De Gruyter, Berlin, **2007**.
- [4] Carr, D. (**2016**, January 26). Periodicity Ionisation energy and electronegativity of the elements. Retrieved from <https://derekcarrsavvy-chemist.blogspot.ca/2016/01/periodicity-1-ionisation-energy-and.html> (accessed January 2019).
- [5] J. Clayden, N. Greeves, S. Warren & P. Wothers, *Organic Chemistry*, 2nd edition, Oxford University Press Inc., New York, **2012**.

DATA ACCESSIBILITY

The data can be processed directly on the NMReady-60 and printed and/or exported directly to a USB or networked file where it can be worked up using third party NMR processing software.

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