



REFLECTION

## The alkyl group is a $-I + R$ substituent

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### KEYWORDS

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**Abstract** Electronic substituent effects are usually classified as inductive (through  $\sigma$ -bonds) and resonance effects (*via*  $\pi$ -bonds). The alkyl group has been usually regarded as a  $\sigma$ -electron donor substituent (+I effect, according to the Ingold's classification). However, a  $\sigma$ -withdrawing,  $\pi$ -donor effect ( $-I + R$  pattern) allows explaining the actual electron-withdrawing behavior of alkyl groups when bound to  $sp^3$  carbon atoms as well as their well-known electron-releasing properties when attached to  $sp^2$  or  $sp$  atoms. Alkyl substitution effects on several molecular properties (dipole moments, NMR, IR, and UV spectra, reactivity in gas phase and solution) are discussed.

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### PALABRAS CLAVE

Segundo curso de grado;  
Química orgánica;  
Errores conceptuales;  
Libros de texto;  
Ácidos/bases;  
Enlace covalente;  
Espectroscopía IR;  
Espectroscopía RMN;  
Espectroscopía UV-Vis

### El grupo alquilo es un sustituyente $-I + R$

**Resumen** Los efectos electrónicos del sustituyente se clasifican habitualmente como inductivos (a través de enlaces  $\sigma$ ) o de resonancia (mediante enlaces  $\pi$ ). El grupo alquilo ha sido considerado habitualmente como un sustituyente dador de densidad electrónica  $\sigma$  (+I, según la clasificación de Ingold). Sin embargo, un patrón  $\sigma$ -aceptor  $\pi$ -dador ( $-I + R$ ) permite explicar el comportamiento real de los grupos alquilo como atractores de electrones cuando están unidos a átomos de carbono  $sp^3$ , así como sus conocidas propiedades dadoras de electrones cuando están unidos a átomos  $sp^2$  o  $sp$ . Se discuten los efectos de sustitución del grupo alquilo en varias propiedades moleculares (momentos dipolares, espectros de RMN, IR y UV, reactividad en fase gas y disolución).

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## Introduction

Substituent effects constitute a key concept for the comprehension of reactivity and spectroscopic behavior of organic compounds (Krygowski & Stępień, 2005). In a simple approach, substituent effects can be classified according to the mechanism of interaction with the reactive center as inductive (through  $\sigma$ -bonds) or resonance effects (through  $\pi$ -bonds). Nevertheless, some further terms (such as steric, field or solvent effects) would be required for a thorough description of substituent effects.

Since the Ingold's classification of electronic substituent effects (Ingold, 1953), the alkyl group has been regarded as a  $\sigma$ -donor substituent (+I, in the Ingold's nomenclature) in most Organic Chemistry textbooks (Burrows, Holman, Parsons, Pilling, & Price, 2013; Hornback, 2006; Roos & Roos, 2014; Smith, 2013; Vollhardt & Schore, 2014). Nevertheless, the Ege's criticisms to such a simplistic viewpoint should be remarked:

"In water, propanoic acid is slightly weaker than acetic acid. The nature of the inductive effect of an alkyl group is debated by chemists. Alkyl groups stabilize carbocations and in that role appear to be electron-releasing. They also increase the basicity of amines, again suggesting that they are electron-releasing. On the other hand, though *tert*-butyl alcohol ( $pK_a$  19) is a weaker acid than ethanol ( $pK_a$  17) in water, it is stronger acid in the gas phase. This experimental observation suggests that alkyl groups can stabilize anions as well as cations and that solvation plays an important role in determining relative acidities. Thus a word of caution is necessary. The relative acidities on which the generalizations presented in this chapter are based were determined in water. In the gas phase, reversals in the order of related compounds are often seen." (Ege, 1999, p. 107)

Surprisingly, the accumulation of evidences against the assumed +I feature of the alkyl group (Böhm & Exner, 2004; Laurie & Muentzer, 1966; Minot, Eisenstein, Hiberty, & Anh, 1980; Sebastian, 1971; Tasi, Mizukami, & Pálinkó, 1997) has shown very little effect on a so widespread view.

Some alkyl substitution effects have been often explained in textbooks in contradictory or enigmatic ways. Thus, chemical shift differences between  $\text{CH}_3$  and  $\text{CH}_2$  groups are attributed in the Hornback's book to the fact that "carbon is slightly more electronegative than hydrogen" (Hornback, 2006, p. 549) despite the alkyl group has been previously classified as a weak inductive electron-donating substituent (Hornback, 2006, p. 117). In the Vollhardt's textbook, the relationship between methyl group chemical shifts for a number of  $\text{CH}_3\text{X}$  compounds and the X electronegativity is illustrated by a table lacking an entry for X = methyl (Vollhardt & Schore, 2014, p. 389), thus avoiding the inconvenient carbon issue.

I show here that the alkyl group behaves as a -I+R substituent. Although some factors (such as field, steric or solvent effects) are implicitly ignored in this approach, a lot of currently available theoretical and experimental evidences can thus be described in an easy way.

A  $\text{C}^{\delta-}-\text{H}^{\delta+}$  bond polarization has been experimentally observed for methane (Lazzeretti, Zanasi, & Raynes, 1987), consistently with the larger electronegativity of carbon relative to hydrogen, 2.55 vs. 2.20 in the Pauling scale (Allred, 1961). Such a polarization pattern allows predicting the

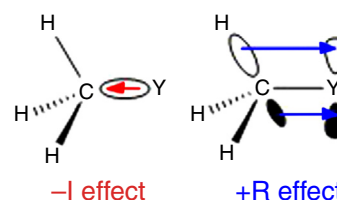


Figure 1 -I (left) and +R (right) effects of a methyl group bound to an atom Y.

dipole moment direction of simple hydrocarbons through additive models, though quantitative agreement is usually modest (2-methylpropane: 0.3 D estimated vs. 0.132 D experimental) (Dean, 1999).

Since hydrogen is used as the standard in the Ingold's classification of substituents (Krygowski & Stępień, 2005), the alkyl group should be classified as a -I substituent (hence a  $\sigma$  electron-withdrawing group). Such a role is illustrated in Fig. 1 for the  $\sigma$  bond polarization from whatever atom Y to a methyl group, though the reverse bond polarization is expected when Y is a more electronegative than carbon (e.g., chlorine).

A different behavior is found for alkyl groups when attached to  $\text{sp}^2$  or  $\text{sp}$ -hybridized atoms due to electron density donation from alkyl C-H or C-C  $\sigma$  bonds to the empty  $p$  orbital of the contiguous atom (the simplest  $\pi$ -system), as shown in Fig. 1. Thus, the decrease of gas phase acidity for phenol and benzoic acid through  $p$ -methyl substitution (McMahon & Kebarle, 1977) can only be attributed to a significant  $\pi$ -donor effect for methyl substituent (indeed, larger than that for methoxy group). However, the alkyl group should be considered as an atypical  $\pi$ -donor substituent due to the lack of lone electron pairs. Such a  $\sigma$ -bond/ $\pi$ -system interaction, named as hyperconjugation (Mullins, 2012) can readily be explained by analogy with the  $\pi$ -donor behavior of a lone pair-bearing atom (e.g., chlorine) to an empty  $p$  orbital, though C-C or C-H bonds (rather than electron lone pairs) of the alkyl group are involved as electron-releasing units in hyperconjugative interactions. Interestingly,  $\pi \rightarrow \sigma^*$  interactions (negative hyperconjugation) are usually negligible for alkyl groups lacking electronegative atoms (Bocca, Pontes, & Basso, 2004).

Some molecular structural features can be rationalized on the basis of the alkyl group properties. For example, the larger C=O bond lengths found in methyl ketones (acetone: exp. 1.210 Å, calc. 1.193 Å) in comparison with the related aldehydes (acetaldehyde: exp. 1.209 Å, calc. 1.188 Å) (Berry, Waltman, Pacansky, & Hagler, 1995) can be attributed to the stabilization of the zwitterionic resonance form (see Fig. 2) through alkyl group  $\pi$ -donation to the carbonylic carbon atom, thus weakening the double-bond feature of the carbonyl group.

Hyperconjugative interactions are dependent on the arrangement of C-H (or C-C) bonds relative to the  $p$  orbital of the contiguous atom Y, the most effective interaction corresponding to a nearly parallel arrangement. For example, the toluene  $\text{C}_{\text{sp}^3}\text{-H}$  bond nearly perpendicular to the framework plane is slightly longer than the other  $\text{C}_{\text{sp}^3}\text{-H}$  bonds (by 0.002 Å, Hameka & Jensen, 1996). The geometry dependence of hyperconjugation allows explaining the conformational analysis of methyl-substituted unsaturated

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