



REFLECTION

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



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UV-Vis spectroscopy

Abstract Electronic substituent effects are usually classified as inductive (through σ -bonds) and resonance effects (via π -bonds). The alkyl group has been usually regarded as a σ -electron donor substituent (+I effect, according to the Ingold's classification). However, a σ -withdrawing, π -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 σ) o de resonancia (mediante enlaces π). El grupo alquilo ha sido considerado habitualmente como un sustituyente dador de densidad electrónica σ (+I, según la clasificación de Ingold). Sin embargo, un patrón σ -aceptor π -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 σ -bonds) or resonance effects (through π -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 σ -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 & Muentner, 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 CH_3 and 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 CH_3X 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 $C^{\delta-}-H^{\delta+}$ 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

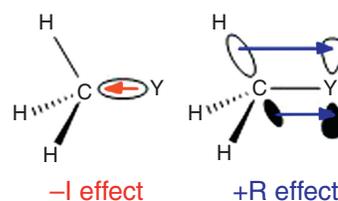


Figure 1 -I (left) and +R (right) effects of a methyl group bound to an atom Y.

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 σ electron-withdrawing group). Such a role is illustrated in Fig. 1 for the σ 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 sp^2 or sp -hybridized atoms due to electron density donation from alkyl C-H or C-C σ bonds to the empty p orbital of the contiguous atom (the simplest π -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 π -donor effect for methyl substituent (indeed, larger than that for methoxy group). However, the alkyl group should be considered as an atypical π -donor substituent due to the lack of lone electron pairs. Such a σ -bond/ π -system interaction, named as hyperconjugation (Mullins, 2012) can readily be explained by analogy with the π -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 π -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 $C_{sp^3}-H$ bond nearly perpendicular to the framework plane is slightly longer than the other $C_{sp^3}-H$ bonds (by 0.002 Å, Hameka & Jensen, 1996). The geometry dependence of hyperconjugation allows explaining the conformational analysis of methyl-substituted unsaturated

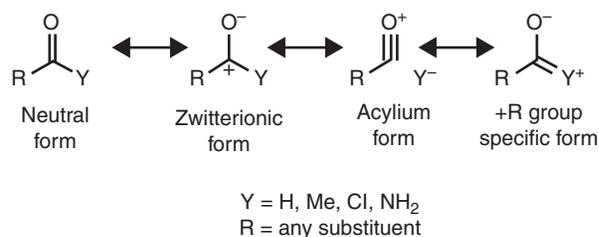


Figure 2 Neutral (left) and zwitterionic (right) resonance forms of a carbonyl compound.

compounds, such as propene (Liberles, O'Leary, Eilers, & Whitman, 1972) or acetaldehyde (Muñoz-Caro, Niño, & Moule, 1994).

As a well-known consequence of the π -donor behavior of the alkyl group, alkyl substitution yields more electron-rich alkenes and arenes (Libit & Hoffmann, 1974). The high reactivity of an alkyl-substituted arene in a S_EAr reaction can thus be attributed to the stabilization of the corresponding Wheland intermediate through π -electron donation.

The $-I+R$ behavior of the alkyl group allows explaining a number of features of alkyl-substituted compounds, such as dipole moments, spectroscopic properties and reactivity (in gas phase and solution media), as shown below.

Dipole moments

The electron-withdrawing behavior of alkyl group in aliphatic compounds is also reflected in dipole moments. Thus, the dipole moment vectors for propane and 2-methylpropane (Tasi et al., 1997), as well as some substituted bicyclo[2.2.2]octanes (Böhm & Exner, 2004) can be attributed to the withdrawing effect ($-I$) of the methyl group in comparison with hydrogen (see Fig. 3).

In contrast, the π -donor character of methyl group ($+R$) is required in order to explain the raise of dipole moments of nitrobenzene and benzonitrile through p -methyl substitution (Brown, 1959) (see Fig. 4).

Molecular dipole moments can be reliably calculated by current computational methods. Interestingly, the calculated dipole moment vectors for a set of simple hydrocarbons (Tasi et al., 1997) have allowed inferring a dual role for the methyl group: electron-withdrawing when attached to sp^3 carbon atoms, but electron-donating when bound to sp^2 or sp^3 carbons.

Such a dual behavior of the alkyl substituent is also observed for heteroatom-bearing compounds. Thus, a gradual dipole moment decrease is observed for successive

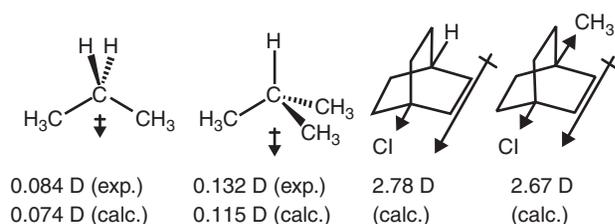


Figure 3 Dipole moments of propane and substituted bicyclo[2.2.2]octanes.

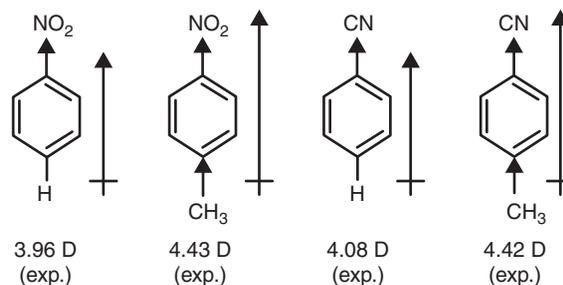


Figure 4 Dipole moments of benzene derivatives.

methyl substitution on ammonia (NH_3 , 1.47 D; $MeNH_2$, 1.31 D; Me_2NH , 1.01 D; Me_3N , 0.61 D) (Le Fèvre & Russell, 1947), in agreement with the progressive diminution of the nitrogen electron density (Hehre & Pople, 1970). In contrast, a dipole moment enhancement (from 1.53 D to 1.68 D) (Nelson, Lide, & Maryott, 1967) is found for N,N -dimethyl substitution on aniline (Targema, Obi-Egbedi, & Adeoye, 2013), consistently with the raise of the π -donor character for the amino group (Hincliffe & Kidd, 1980) due to $+R$ contributions of methyl substituents.

Spectroscopic properties

Spectroscopic properties of many organic compounds can be easily rationalized by assuming a $-I+R$ behavior for the alkyl group as a general feature. Thus, the NMR chemical shift of an atom can be regarded as an experimental measure of the electron density at the corresponding nucleus position though other effects – such as anisotropic magnetic fields – can also be involved. Downfield shifts induced by a methyl substituent on sp^3 carbon atoms (+9.6 ppm in ^{13}C NMR) or the corresponding bound hydrogen atoms (+0.63 ppm in 1H NMR) (Pretsch, Bühlmann, & Badertscher, 2009) are consistent with the behavior of typical $-I$ groups (such as halogen atoms).

Alkyl substitution effects on NMR chemical shifts of alkenes show an electron density decrease in α position (+12.9 ppm for ^{13}C NMR; +0.45 ppm for 1H NMR), as well as a density raise in β position (–7.4 ppm for ^{13}C ; –0.31/–0.40 ppm for 1H), consistently with a $-I+R$ effect, though anisotropic effects (such as ring currents) may also play a role. Such a $-I+R$ behavior is also found for alkynes, according to ^{13}C NMR spectroscopy (+8.5 ppm for α position, –3.6 ppm for β position).

A $-I+R$ effect is also found for carbonyl compounds. Thus, NMR data on methyl substitution show an electron density decrease on the carbon atom (^{13}C NMR effects: formaldehyde, +3.5 ppm; acetaldehyde, +6.2 ppm; formic acid, +10.6 ppm; methyl formate, +10.7 ppm; N,N -dimethylformamide, +7.4 ppm; 1H NMR effect on formaldehyde, +0.2 ppm) (Pretsch et al., 2009), as well as a density raise on the oxygen (^{17}O NMR effect for acetaldehyde: –33 ppm) (Gerothanassis, 2010).

The dichotomous behavior of alkyl substituents on π -systems (electron density raise for α atom, electron density decrease for β atom) cannot be explained on the basis of a simple behavior (such as a $+I$ effect).

A -I + R behavior (Meier, 2007) is observed through ^{15}N NMR spectroscopy for alkyl substitution on amines and amides depending on the nitrogen hybridization (downfield shifts for aliphatic amines, upfield shifts for N_{sp^2} -bearing compounds – such as anilines and amides).

NMR coupling constants are also dependent on substituent electronic properties (as well as some geometrical features). Thus, a significant decrease is found for ^1H - ^1H coupling constants through methyl substitution (*trans*, -2.3 Hz; *cis*, -1.6 Hz; *gem*, -0.4 Hz), in qualitative agreement with data from typical electron-withdrawing groups, such as the fluorine atom (*trans*, -6.3 Hz; *cis*, -6.9 Hz; *gem*, -5.7 Hz). The positive contribution for methyl-substitution on ^{13}C - ^1H coupling constants of aliphatic compounds (+1.0 Hz), is also qualitatively consistent with those from other -I groups (fluorine, +24 Hz).

Infrared spectroscopy is also sensitive to substituent properties, as illustrated by the C=O stretching frequency of carbonyl compounds as a function of the corresponding substituent Y, which can be rationalized in terms of resonance forms (Fig. 2). By taking an aliphatic aldehyde (ca. 1725 cm^{-1}) as a reference, the redshift (wavenumber decrease) induced by a +I substituent (acetyltrimethylsilane, 1645 cm^{-1} ; Soderquist & Hsu, 1982) can be attributed to the stabilization of the zwitterionic form. Instead, the blueshift provoked by a -I substituent (acyl chlorides, $>1800\text{ cm}^{-1}$; Pretsch et al., 2009) can be explained by means of two alternative or concurrent mechanisms (destabilization of the zwitterionic form and/or contribution of an acylium ion-bearing form). Finally, the redshifts provoked by +R substituents (amides, ca. 1680 cm^{-1} ; Pretsch et al., 2009) can be attributed to the contribution of a specific resonance form. The slight redshift induced by alkyl group (methyl ketones, ca. 1715 cm^{-1}) shows a net electron-donating effect (hence, a predominance of the +R effect over -I properties). The net donor effect of the carbonyl-bound alkyl group is consistent with the larger dipole moment of acetone (2.88 D) relative to formaldehyde (2.33 D) (Nelson et al., 1967).

The alkyl group influence on UV-Vis spectra of many compounds can also be explained in terms of electronic effects. Thus, bathochromic shifts induced by alkyl groups on UV absorption bands of α,β -unsaturated compounds (+10 nm in α position, +12 nm in β position), conjugated polyenes (+5 nm) or benzene derivatives (+3.0 nm) are qualitatively consistent with effects of typical π -donor groups (e.g., chlorine).

Gas phase acid–base reactivity

Relative basicities of aliphatic amines in aqueous solution have been attributed to the assumed +I effect of alkyl group (Sorrell, 2006). Interestingly, the irregular basicity order of amines in water ($\text{Me}_2\text{NH} > \text{MeNH}_2 > \text{Me}_3\text{N} > \text{NH}_3$, as shown by the $\text{p}K_{\text{a}}$ values for the corresponding conjugated acids: $10.77 > 10.62 > 9.80 > 9.246$) (Dean, 1999) is contaminated by solvent effects as illustrated by the systematic basicity order of amines in gas phase ($\text{Me}_3\text{N} > \text{Me}_2\text{NH} > \text{MeNH}_2 > \text{NH}_3$) (Brauman, Riveros, & Blair, 1971). Although the gas phase basicity order can be attributed to the usually assumed +I alkyl effect (Carter, 2007), a decrease of the nitrogen

electron density through methyl substitution has been indeed observed by means of Molecular Electrostatic Potential calculations (Baeten, De Proft, & Geerlings, 1995), thus indicating a -I behavior for the methyl group. Actually, the gas phase basicity order of aliphatic amines should be attributed to the increasing stabilization of substituted ammonium ions due to the alkyl group polarizability (Aue, Webb, & Bowers, 1976).

Relative acidities of alcohols in aqueous solution ($\text{H}_2\text{O} > \text{MeOH} > \text{EtOH} > \text{PrOH} > \text{tBuOH}$) have also been attributed in some textbooks to the assumed alkyl +I effect (Johnson, 1999; Solomons, Fryhle, & Snyder, 2016). Since the reverse acidity order is found in gas phase, relative acidities of alcohols in water should be attributed to the lower magnitudes of solvation enthalpies for larger alkoxide anions (Brauman & Blair, 1969).

The discussion on alkyl group electronic properties can also be applied to carbanions. Thus, the 'textbook' stability order for simple carbanions (methyl > ethyl > isopropyl > *tert*-butyl) has been attributed to the assumed +I inductive effect of alkyl groups (Burrows et al., 2013; Chaloner, 2015; Roos & Roos, 2014; Smith, 2013). However, an irregular order is found for gas phase carbanion stabilities ($^t\text{Bu} > \text{Me} > \text{Pr} > \text{Et}$), in agreement with the concurrence of two opposed alkyl effects (DePuy et al., 1989): a stabilizing mechanism through alkyl polarizability (that is, $n \rightarrow \sigma^*$ hyperconjugation) and a destabilizing trend (consistently with a +R role, by assuming a *p*-like behavior for the carbon lone pair).

The stability of other reaction intermediates can also be assessed on the basis of alkyl group effects. Thus, the well-known stability order for carbocations (tertiary > secondary > primary > methyl) has been sometimes attributed to a positive inductive effect (Chaloner, 2015; Roos & Roos, 2014). Interestingly, hyperconjugation is presented in many textbooks as an alternative explanation for the stability order of carbocations (Brown, Iverson, Ansllyn, & Foote, 2013; Burrows et al., 2013) though the usual ambiguous writing prevents ascertaining whether both explanations correspond to either two different descriptions of the same phenomenon or two concurrent mechanisms playing in the same direction. Anyway, the stability order for carbocations should be attributed to hyperconjugation (hence, a +R behavior on a vacant *p* orbital, the simplest π system), though other interactions (such as alkyl polarizability) are also involved (Aue, 2011).

Free radicals show the same stability order as carbocations, thus indicating stabilization through alkyl substitution. Although such a stability order may be justified on the basis of an assumed +I behavior, the +R effect can be alternatively regarded, analogously to the stabilization of free radicals by lone pair-bearing atoms (Zipse, 2006).

Reactivity in solution

Relative acidities of simple carboxylic acids in aqueous solution (acetic acid > propionic acid > butyric acid) have been used in some textbooks to illustrate the assumed +I effect of the alkyl group (Sorrell, 2006). Interestingly, the reverse order is found when enthalpies are instead regarded

(Christensen, Izatt, & Hansen, 1967), thus indicating that the acidity order in aqueous solution should be attributed to hydration entropies. Thus, the significant lattice order of liquid water (vaporization entropy equaling $118.89 \text{ J mol}^{-1} \text{ K}^{-1}$, in contrast with typical values of *ca.* $88 \text{ J mol}^{-1} \text{ K}^{-1}$ for most liquids, Dean, 1999) can introduce sizeable changes on the reaction energetics. In particular, hydration of apolar molecules (or moieties) leads to a further solvent lattice ordering (Blokzijl & Engberts, 1993). As a consequence, alkyl group inductive effects from experimental data in aqueous solution are often masked by hydration entropies (Calder & Barton, 1971). Relative acidities of simple carboxylic acids in gas phase (Yamdagni & Kebarle, 1973) and acetonitrile (Eckert et al., 2009) are consistent with the major role played by hydration entropies.

The lower acidity of pivalic acid in comparison with acetic acid, usually attributed to the assumed +I effect of the alkyl group (Smith, 2008), is reversed when reaction enthalpies are considered (Eckert et al., 2009).

The assumed +I alkyl group effect on the acidity of simple carboxylic acids in aqueous solution can thus be attributed to an artifact derived from solvent effects. Whereas a volume increase of neutral solutes leads to a hydration entropy raise, the reverse relationship is found for ionic species (Graziano, 2009). As a consequence, alkyl substitution (through an increase of the molecular volume) leads to the stabilization (in Gibbs free energy terms) of non-ionized acid in water as well as the destabilization of the corresponding carboxylate anion, thus resulting an acidity decrease.

The larger acidity of formic acid in comparison with acetic acid in aqueous solution ($\text{p}K_{\text{a}}$ values: 3.751 and 4.756, respectively, Dean, 1999) has also been discussed in many textbooks as an example of the application of inductive effects (Hart, Hadad, Craine, & Hart, 2012; Hornback, 2006; Okuyama & Maskill, 2014; Roos & Roos, 2014). Since very similar reaction enthalpies are involved in the dissociation reactions of formic and acetic acids (Christensen et al., 1967), the larger acidity of formic acid must be indeed attributed to hydration entropy differences.

Conclusions

A clear comprehension of inductive and resonance effects is a major key for a sound learning of Organic Chemistry (Mullins, 2008). Surprisingly, the almost ubiquitous alkyl group has been incorrectly presented in many textbooks as a σ -donor (+I) group. However, a dual behavior is shown by alkyl substituents depending on the hybridization of the neighbor atom. Thus, alkyl groups bound to aliphatic chains behave as σ -acceptors (-I, consistently with the larger electronegativity of carbon relative to hydrogen), whereas those attached to π -systems act as π -donors (+R, due to hyperconjugative interactions). A number of experimental and theoretical data (dipole moments, NMR, IR, and UV spectra, reactivity) agree with such a dual behavior.

The whole analysis of all data considered here allows inferring a small -I effect as well as a significant +R behavior for the alkyl group as a feature valid in all discussions on spectroscopic and reactivity properties of organic compounds.

Conflict of interests

The author declares no conflict of interest.

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