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Perspective

Rethinking Organic Chemistry: The Dual Electronic Behavior of the Alkyl Group

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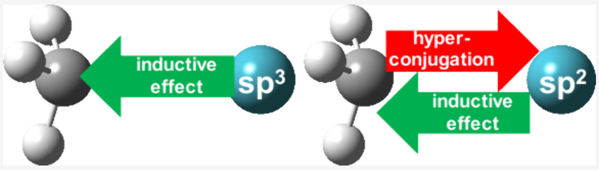

ABSTRACT: A unified framework for understanding the electronic nature of alkyl substituents is presented, resolving the contradiction between spectroscopic data and reactivity patterns typically found in organic chemistry textbooks. This framework is based on the distinct interactions of alkyl groups with σ frameworks and π systems. When attached to an sp^3-hybridized atom, as in alkanes, amines, and ethers, the alkyl group acts as an inductive electron-withdrawing substituent (relative to hydrogen). This behavior reflects the greater electronegativity of carbon than hydrogen, as evidenced by NMR chemical shifts and dipole moments. The stability trends observed for aliphatic carbanions and free radicals (ethyl < isopropyl < *tert*-butyl in both cases) are due to this electron-withdrawing character. The acidity trend of alcohols in aqueous mixtures (methanol > ethanol > 2-propanol > *tert*-butanol) correlates with the decreasing permittivities of the pure alcohols. Apparent electron-donating effects inferred from Gibbs free energy acidities of ammonium ions and substituted acetic acids arise from entropic artifacts caused by hydrophobic effects. When the alkyl group is bonded to an sp^2-hybridized atom, as in alkenes, arenes, carbonyl compounds, carboxylic acids, amides, heterocycles, and carbocations, or to an sp-hybridized atom, as in alkynes, concurrent hyperconjugative electron donation occurs, which overcomes the inductive electron-withdrawing effect in the *tert*-butyl cation. This work calls for revising textbooks to emphasize both electronic effects and to replace the misinterpreted reactivity examples with spectroscopically validated models, thereby providing a consistent framework essential for educating students and training AI systems in chemistry.

KEYWORDS: *Second-Year Undergraduate, Organic Chemistry, Misconceptions, Textbooks, Molecular Properties*

■ INTRODUCTION

A solid understanding of chemistry fundamentals requires a consistent framework of clearly defined concepts. However, current organic chemistry textbooks present an ambiguous and contradictory account of the electronic effects of alkyl substituents, with interpretations varying depending on the context. For example, alkyl groups are described as electron-withdrawing based on ^{13}C and ^{1}H NMR chemical shifts of aliphatic chains,[1−6] yet are simultaneously portrayed as electron-donating in discussions of reactivity, such as amine basicities[6−8] or radical stabilities.[5,7−11] This inconsistency persists across educational web sites and is further propagated by artificial intelligence models (ChatGPT, Copilot, DeepSeek, Gemini, Meta AI) trained on such sources, as the author has personally verified.

The electronic effects of alkyl groups have been debated for the past century. Ingold initially classified the methyl group as an inductively electron-donating substituent relative to hydrogen (+I in his notation) in 1934[12] but revised this interpretation in 1969, reclassifying it as electron-withdrawing (−I).[13] Despite this correction, current textbooks predominantly depict alkyl groups as archetypal electron-donating substituents, attributing this behavior either to pure inductive effects,[1] or to a combination of inductive and hyperconjugative contributions.[2,6,14−16] This debate has recently been reopened, as both the author's study[17] and that of Elliott's group[18] have refuted the supposed inductive electron-donating behavior of alkyl groups.

Here, the author presents a unified framework based on his previous work,[17] which reconciles reactivity patterns with spectroscopic observations. Common textbook examples of alkyl group effects on reactivity are revisited through a careful analysis of physicochemical property changes upon methylation (the formal replacement of hydrogen with a methyl group) in a way that is accessible to introductory organic chemistry students. Reactivity contributions are decomposed into enthalpic and entropic terms, with enthalpic effects further partitioned into inductive and hyperconjugative components.

Electronic substituent effects are primarily transmitted through σ bonds (inductive effects) or π bonds (resonance), though interactions through space or solvent molecules can also play a role. Inductive and resonance effects can be empirically distinguished by comparing NMR chemical shifts in systems with similar anisotropic environments. This distinction arises

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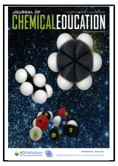


because σ bonds, which have high electron densities at atomic nuclei, strongly influence NMR chemical shifts, whereas π bonds, having nodal planes at the nuclei, contribute little to them.

■ ALKYL GROUPS BONDED TO sp^3-HYBRIDIZED ATOMS

Alkanes

Electronegativity scales indicate that carbon−hydrogen bonds are polarized as $C^{\delta-}-H^{\delta+}$, as evidenced by the electronegativity values of carbon and hydrogen based on bond energies (Pauling scale: 2.55 vs 2.20),[19] electrostatic forces (Allred−Rochow scale: 2.50 vs 2.20),[20] electron density equalization (Sanderson scale: 2.75 vs 2.59),[21] and valence electron energies (Allen scale: 2.54 vs 2.30).[22] Calculated atomic charges for methane provide further insight into the C−H bond polarization, with some methods predicting a $C^{\delta+}-H^{\delta-}$ pattern (QTAIM,[23] Wiberg),[24] but most of them supporting the $C^{\delta-}-H^{\delta+}$ arrangement (CHELPG,[25] CM4M,[26] GAPT,[27] Hirshfeld,[28] Löwdin,[26] Mulliken,[27] NBO,[29] NPA).[26] Since hydrogen is the reference substituent in Ingold's classification, the polarization of methane as $Me^{\delta-}-H^{\delta+}$ implies that the methyl group is an electron-withdrawing substituent.

Experimental IR intensities of methane also support a $C^{\delta-}-H^{\delta+}$ polarization.[30] Hydrogen effective charges derived from IR intensities are positive: +0.09 e for methane and +0.10 e for ethane.[31] The significant C−H bond polarization accounts for the intense infrared absorption band at ~2900 cm^{-1} in aliphatic compounds, which originates from changes in the molecular dipole moment during stretching vibrations.

The electron-withdrawing nature of alkyl groups in alkanes is consistent with experimental data showing that the 1s orbital of the central carbon atom in propane is lower in energy (−290.47 eV) than those of the terminal carbon atoms (−290.35 eV), owing to stabilization by the two electron-withdrawing methyl substituents.[32]

Molecular dipole moments can be decomposed into vectorial contributions from individual bonds. Although methane (**1**) and ethane (**2**) have zero total dipole moments due to their high molecular symmetry, small but measurable dipole moments are observed for propane (**3**, 0.08 D) and 2-methylpropane (**4**, 0.13 D).[33] The directions of the molecular dipole moments of these alkanes, inferred from comparison with experimental dipole moments of deuterated derivatives[35] as well as theoretical calculations,[34] reflect a slight electron-withdrawing effect of methyl groups relative to hydrogen (see Figure 1).

The inductive effect of a substituent X can be assessed by the ^{13}C and ^{1}H NMR chemical shifts of the methyl group in CH_3-X compounds.[37] For example, comparison of the ^{13}C NMR chemical shifts of methane (X = H, −2.3 ppm), ethane (X = CH_3, 7.3 ppm), and chloromethane (X = Cl, 25.6 ppm),[38] indicates that methyl group behaves as an inductive electron-withdrawing substituent, although to a lesser extent than chlorine.[39] The deshielding effect of the methyl substituent is also evident in functionalized carbon atoms ($ClCH_3$, 25.6 ppm; $ClCH_2CH_3$, 39.9 ppm).[38] Furthermore, the electron-withdrawing effect of alkyl groups is cumulative, as demonstrated by the well-known trend in NMR chemical shifts: methyl < methylene < methine < quaternary carbon (the latter only in ^{13}C NMR).[38]

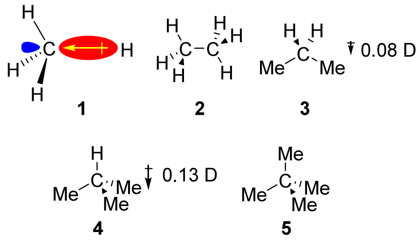


Figure 1. Structures (including dipole moments)[36] of methane (**1**, showing a polarized C−H bond), ethane (**2**), propane (**3**), 2-methylpropane (**4**), and 2,2-dimethylpropane (**5**).

Carbanions

The deprotonation of an alkane yields an aliphatic carbanion. The high negative charge concentration on the sp^3-hybridized carbanionic center can be alleviated through electron withdrawal by methyl substituents. Interestingly, basicities measured in the gas phase[40] and estimated in DMF[41] follow the irregular order methyl (**6**) < ethyl (**7**) > isopropyl (**8**) > *tert*-butyl (**9**, see Figure 2).

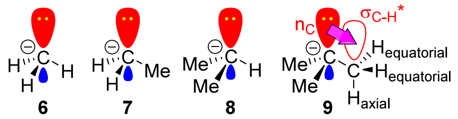


Figure 2. Structures of methyl (**6**), ethyl (**7**), isopropyl (**8**), and *tert*-butyl (**9**, showing an $n_C \rightarrow \sigma_{C-H}^*$ hyperconjugative interaction) carbanions.

Thermodynamic calculations of methylene insertion enthalpies into either methane or the methyl anion (methylation enthalpies, see Figure 3) help to rationalize this irregular trend.

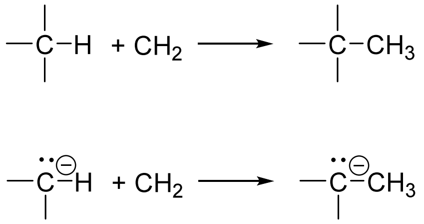


Figure 3. Methylene insertion (methylation) reactions at the central carbon of an alkane (top) and a carbanion (bottom).

Methylation of methane leads to the formation of the carbon−carbon bond of ethane (methylation enthalpy: −399.8 kJ mol^{-1}). In contrast, methylation of the methyl anion gives weaker stabilization (methylation enthalpy: −385.2 kJ mol^{-1}) because of electronic repulsion between the new C−C bond and the carbanionic lone pair.[42] As a consequence of its thermodynamic instability, the ethyl anion is more basic than the methyl anion.

Successive methylation of ethane leads to slightly higher stabilization energies (methylation enthalpies: ethane, −410.2 kJ mol^{-1}; propane, −420.8 kJ mol^{-1}). In contrast, successive methylation of the methyl anion produces larger stabilization increases (methylation enthalpies: ethyl anion, −413.1 kJ mol^{-1}; isopropyl anion, −447.2 kJ mol^{-1}) due to the combined effects of negative charge delocalization into the additional methyl substituent and the reduced electronic repulsion as the excess charge at the carbanionic center decreases. Consequently, the basicity of carbanions follows the order ethyl > isopropyl > *tert*-

butyl, which is the reverse of the trend assumed in many textbooks.[2,5,9,10]

The electron-withdrawing behavior of methyl groups in carbanions is partly due to hyperconjugation from the lone pair orbital of the anionic carbon into vacant antibonding carbon−hydrogen orbitals ($n_C \rightarrow \sigma_{C-H}^*$ interactions). Theoretical results on the *tert*-butyl anion reveal stronger interactions for axial hydrogens than for equatorial ones, as indicated by longer C−H bond lengths ($C-H_{axial}$: 1.132 Å; $C-H_{equatorial}$: 1.098 Å) and lower vibrational frequencies ($C-H_{axial}$: 2589−2656 cm^{-1}; $C-H_{equatorial}$: 2971−3016 cm^{-1}).[43]

Although the chemistry of carbanions in the gas phase is well established,[44] studies on highly basic carbanions in solution must be interpreted with caution, as counterions and other entities strongly influence their behavior. In particular, the properties of carbanions should not be directly extrapolated from those of alkyllithium compounds, whose stabilization in hydrocarbon solution arises from oligomerization.[45] Most alkyllithium compounds (including *n*-butyllithium) form hexameric aggregates, whereas *tert*-butyllithium forms tetramers because of the lower steric hindrance of the latter.[46] The higher reactivity of *tert*-butyllithium therefore results from reduced aggregation stabilization[47] rather than from any intrinsic instability of the *tert*-butyl carbanion.[48]

The Hofmann rule, which predicts preferential formation of the least substituted alkenes in elimination reactions of tetraalkylammonium cations and related substrates, is often attributed in textbooks to a presumed destabilization of a carbanion-like transition state by alkyl groups.[1,4,5,9,10,15,49] However, since alkyl substitution actually stabilizes such structures, the Hofmann rule should instead be attributed to conformational preferences of the substrate[50] and steric repulsions with the base.[51,52]

Amines

The slight electron-withdrawing character of methyl groups observed in alkanes is reinforced when bonded to heteroatoms. The experimental dipole moments of ammonia (**10**, 1.47 D) and trimethylamine (**13**, 0.61 D), combined with bond lengths and bond angles,[33] allow calculation by vector algebra of a much larger positive effective charge on hydrogen (+0.17 e in ammonia) compared with the methyl group (+0.05 e in trimethylamine). This indicates that methyl groups are less prone than hydrogen atoms to acquire a positive charge (see Figure 4).

The enhanced electron-withdrawing character of methyl groups in amines is partly due to $n_N \rightarrow \sigma_{C-H}^*$ hyperconjugation,[53] as evidenced by the lone pair *trans* effect on C−H stretching frequencies in infrared spectra.[54] Although this interaction is analogous to $n_C \rightarrow \sigma_{C-H}^*$ hyperconjugation in carbanions (which are isoelectronic), a much smaller stabilization is found for amines, as indicated by the smaller differences between calculated C−H bond lengths for axial and equatorial hydrogens (*tert*-butyl carbanion, 0.034 Å;[43] trimethylamine, 0.014 Å).[55] Clearly, hyperconjugation in amines is not driven by delocalization of a negative charge, as is the case for carbanions.

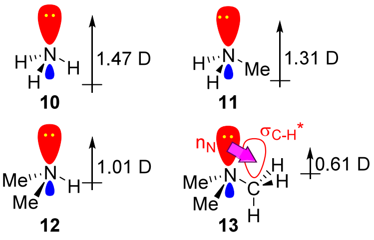


Figure 4. Structures and dipole moments (including calculated directions)[36] of ammonia (**10**), methylamine (**11**), dimethylamine (**12**), and trimethylamine (**13**, showing an $n_N \rightarrow \sigma_{C-H}^*$ hyperconjugative interaction).

Gas-phase basicities of amines are sometimes cited as evidence for the electron-donating behavior of alkyl substituents.[7,10] However, experimental and theoretical[56] gas-phase data show that methylation of amines facilitates not only protonation,[57] but also deprotonation,[58] reflecting the dominant role of polarizability (distortion of electron density under the influence of a charged atom) in gas-phase chemistry.[59] Because electrostatic interactions are especially strong in the gas phase, extrapolations to solution reactivity should be made with caution.

Since substituent effects are fundamentally enthalpic phenomena, reaction energetics should primarily be discussed in terms of enthalpy. In aqueous solution, the enthalpic basicities of amines follow the order methylamine (**11**) > dimethylamine (**12**) > trimethylamine (**13**),[60] consistent with the electron-withdrawing nature of methyl groups. An anomalous behavior is, however, observed for ammonia (**10**), which exhibits a basicity intermediate between methylamine and dimethylamine.

Whereas hyperconjugation involving the nitrogen lone pair leads to progressive stabilization of amines upon methylation, this interaction is not possible for ammonium ions. Moreover, the polarizability of cations, which plays a major role in the gas phase, is far less significant in aqueous solution.[61] These considerations justify the general rule that methylation decreases the enthalpic basicity in aqueous solution.

When considering Gibbs free energy, entropy becomes important. Upon methylation, amines show a progressive decrease in hydration entropy,[62] paralleling the trend observed for alkanes upon homologation,[63] which is attributed to hydrophobic effects.[64] Consequently, methylation of amines decreases basicity from an enthalpic standpoint but increases it from an entropic one. As a result, Gibbs free energy basicities display an irregular trend ($Me_2NH > MeNH_2 > Me_3N > NH_3$), which is misinterpreted in textbooks as evidence for the electron-donating nature of methyl groups, with trimethylamine regarded as an anomaly.[6−8,15]

Ethers

The greater electron-withdrawing ability of the methyl substituent relative to hydrogen accounts for the stronger polarization of the H−O bond compared to the C−O bond, as evidenced by the larger dipole moment of water (**14**, 1.85 D) relative to dimethyl ether (**15**, 1.30 D)[33] (see Figure 5). Based on experimental dipole moments and geometrical data,[33] the effective positive charge is calculated to be larger for the hydrogen atom in water (+0.33 e) than for the methyl group in dimethyl ether (+0.16 e), indicating that methyl groups are less prone than hydrogen atoms to acquire a positive charge.

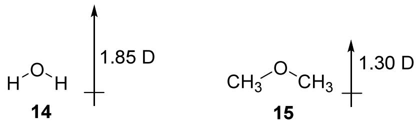


Figure 5. Structures and dipole moments[33] of water (**14**) and dimethyl ether (**15**).

Alcohols

In the gas phase, the acid−base reactivity of alcohols is primarily governed by polarizability. Thus, replacing water with methanol results in more favorable enthalpies for both deprotonation[65] and protonation.[66] Indeed, the gas-phase acidities and proton affinities of alcohols can be accurately predicted using models based solely on polarizability interactions.[67]

In solution, successive methylation at the carbon of methanol (**16**) to yield ethanol (**17**), 2-propanol (**18**), and *tert*-butanol (**19**) produces a progressive increase in the ^{13}C NMR chemical shift at the α-carbon, due to the electron-withdrawing effect of the methyl groups (see Figure 6).[68] This methylation increases the $O^{\delta-}$—$H^{\delta+}$ bond polarization in the gas phase, yielding the order MeOH < EtOH < ^{i}PrOH < ^{t}BuOH, as shown by increasing ^{1}H NMR chemical shifts of the hydroxylic proton (0.020 ppm < 0.440 ppm < 0.580 ppm < 0.584 ppm)[69] and decreasing O−H IR stretching frequencies (3681 cm^{-1} > 3665 cm^{-1} > 3655 cm^{-1} > 3644 cm^{-1}).[70] The same polarization trend is observed in CCl_4 solution (3644 cm^{-1} > 3634 cm^{-1} > 3620 cm^{-1} > 3614 cm^{-1}).[71]

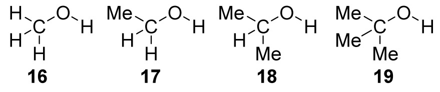


Figure 6. Structures of methanol (**16**), ethanol (**17**), 2-propanol (**18**), and *tert*-butanol (**19**).

However, O−H bond polarization in solution strongly depends on the medium permittivity.[72] Accordingly, the acidity trend in aqueous mixtures (MeOH > EtOH > ^{i}PrOH > ^{t}BuOH)[73] reflects the relative permittivities of the pure alcohols.[33] Some textbooks attribute this trend to the reduced solvation of increasingly hindered alkoxide ions,[2,7,15,74,75] although this hypothesis has been refuted in the case of carboxylic acids.[76]

Substituted Acetic Acids

Simple methylation at the α-carbon of acetic acid (**20**) to yield propanoic acid (**21**) increases the ^{13}C NMR chemical shifts: +6.8 ppm at the α-carbon and +3.4 ppm at the carboxylic carbon (see Figure 7).[38] This electron-withdrawing effect of the methyl group results in a slight decrease in the acid dissociation enthalpy (−0.51 kJ mol^{-1}), but a small increase in the Gibbs free energy change (+0.68 kJ mol^{-1}).[77] This apparent contradiction arises from a decrease in hydration entropy due to the increased molecular volume of the carboxylic acid, and more significantly, of its conjugate base.[76]

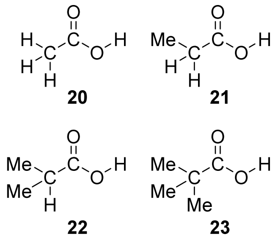


Figure 7. Structures of acetic (**20**), propanoic (**21**), 2-methylpropanoic (**22**), and 2,2-dimethylpropanoic (**23**) acids.

Charton's inductive parameter (σ_I), derived from the acidities of substituted acetic acids in Gibbs free energy terms, gives a slightly negative value for the methyl group (−0.05).[78] However, this result, which seems to support the electron-donating character of alkyl groups, is actually the consequence of an entropic artifact rather than a genuine electronic effect.

Triple methylation of acetic acid (yielding 2,2-dimethylpropanoic acid, **23**) causes larger increases in the ^{13}C NMR chemical shifts (+17.9 ppm at the α-carbon and +7.8 ppm at the carboxylic carbon). Consequently, acidity is favored enthalpically (−2.81 kJ mol^{-1}), but disfavored in terms of Gibbs free energy +1.56 kJ mol^{-1}).[77] The resulting 0.274-unit increase in pK_a should not be attributed to an enthalpic electron-donating effect of methyl groups (as is assumed in some textbooks),[8] but rather to hydration entropy effects giving the appearance of electron donation.

Free Radicals

Although a trigonal geometry is predicted for the methyl radical (**24**),[79] pyramidal geometries are calculated for the ethyl (**25**), isopropyl (**26**), and *tert*-butyl (**27**) radicals (see Figure 8).[80]

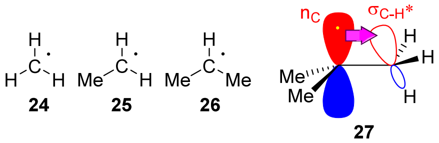


Figure 8. Structures of methyl (**24**), ethyl (**25**), isopropyl (**26**), and *tert*-butyl (**27**, showing an $n_C \rightarrow \sigma_{C-H}$* hyperconjugative interaction) radicals.

Despite these structural differences, aliphatic free radicals are discussed here as alkyl groups bonded to sp^3-hybridized atoms, because the radical center lacks low-lying vacant orbitals and therefore involves reduced hyperconjugative donation from alkyl substituents.

An increasing delocalization of the unpaired electron onto the hydrogen atoms of methyl substituents upon successive methylation is observed by electronic paramagnetic resonance (EPR) spectroscopy.[81,82] This delocalization occurs via hyperconjugative $n_C \rightarrow \sigma_{C-H}$* interactions, as supported by theoretical calculations on the *tert*-butyl radical, including natural bond orbital (NBO) analysis and C−H stretching frequencies.[43] The difference in C−H bond lengths between axial and equatorial hydrogens (C−H$_{axial}$: 1.101 Å; C−H$_{equatorial}$: 1.092 Å) in the *tert*-butyl radical (0.009 Å) is much smaller than that in the corresponding carbanion (0.034 Å), indicating weaker hyperconjugative stabilization in the free radical.

Radical stability, as inferred from C−H bond dissociation energies in alkanes, follows the order methyl < ethyl < isopropyl < *tert*-butyl.[33] This trend arises from stabilization of the aliphatic radicals through the same interaction ($n_C \rightarrow \sigma_{C-H}$*) that stabilizes carbanions. Ironically, this stability order originates from the electron-withdrawing nature of alkyl groups, not from the traditionally assumed electron-donating character frequently cited in textbooks.[5,7−11]

■ ALKYL GROUPS BONDED TO sp^2-HYBRIDIZED ATOMS

Carbocations

Methylation of the isopropyl carbocation (**28**) to yield the *tert*-butyl cation (**29**) increases the ^{13}C NMR chemical shift of the positively charged carbon (isopropyl: 320.6 ppm; *tert*-butyl: 335.2 ppm).[83] This increase arises from the inductive electron-withdrawing effect of the methyl group relative to hydrogen (see

Figure 9),[84] while hyperconjugative donation has negligible influence on the chemical shift because the nodal plane of the vacant p orbital passes through the carbon nucleus.

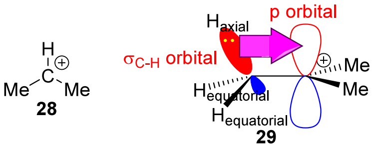


Figure 9. Isopropyl carbocation (**28**) and *tert*-butyl cation (**29**, showing a $\sigma_{C-H} \rightarrow$ p hyperconjugative interaction).

The inductive electron-withdrawal contradicts the textbook assumption of electron-donating behavior of the methyl substituent, whether through inductive effects alone[1−3,85] or in combination with hyperconjugation.[6,8,11,14,49]

Interestingly, the presence of a vacant p orbital at the carbocationic center of *tert*-butyl cation allows for hyperconjugative donation from C−H bonds ($\sigma_{C-H} \rightarrow$ p interaction),[86] as supported by its IR spectrum. This shows a typical band at 2947 cm^{-1} involving C−$H_{equatorial}$ bonds, as well as a characteristic band at 2850 cm^{-1},[87] indicating weakened C−H_{axial} bonds via hyperconjugation.[88] The methyl group in the *tert*-butyl cation thus acts as a −I +R substituent, considering hyperconjugation as a resonance-type effect.[17]

The relative stabilities of aliphatic carbocations (methyl < ethyl < isopropyl < *tert*-butyl), as inferred from gas-phase hydride ion affinities,[89] must therefore be attributed to the overall electron-donating nature of methyl groups. The *tert*-butyl cation provides a clear example in which the inductive withdrawal is outweighed by hyperconjugative electron donation.

Alkenes

Inductive effects in vinyl derivatives $CH_2{=}CH{-}X$ can be assessed through the ^{13}C NMR chemical shifts of the X-bound carbons, assuming similar anisotropic effects.[90] Accordingly, the increase in chemical shift observed upon methylation of ethylene (**30**, see Figure 10) to yield propene (**31**, ^{13}C: +12.9 ppm; ^{1}H: +0.45 ppm) indicates an inductive electron-withdrawing effect of the methyl group very similar to that found for methane methylation (^{13}C: +12.6 ppm; ^{1}H: +0.47 ppm).[37] This inductive electron-withdrawing effect of the methyl group explains the lower energy of the 1s orbital of the substituted sp^2-hybridized carbon in propene (−290.61 eV) relative to the average value for propane (−290.40 eV).[91]

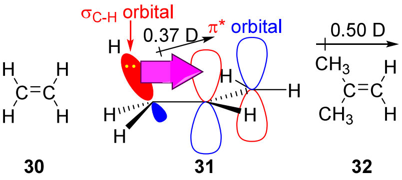


Figure 10. Structures and dipole moments of ethylene (**30**) and propene (**31**, showing $\sigma_{C-H} \rightarrow \pi^*$ hyperconjugative interaction), and 2-methylpropene (**32**), with calculated dipole moment directions.[36]

An inductive electron-donating behavior of alkyl groups in alkenes is sometimes assumed based on the lower electronegativity of sp^3-hybridized carbon relative to sp^2 carbon.[6,8] However, a direct comparison between the alkyl substituent and the vinylic moiety can be misleading. In Ingold convention, the reference is not a hypothetical substituent with negligible electron density transfer, but rather hydrogen. Accordingly, alkyl substituents should be regarded as inductive electron-withdrawing groups (relative to hydrogen) rather than inductive electron donors in an absolute sense.

Hydrogenation enthalpies of alkenes can be regarded as a measure of their thermodynamic stability relative to the corresponding alkanes, assuming similar branching and steric effects. The hydrogenation enthalpies of alkenes (ethylene, −136.4 kJ mol^{-1}; propene, −123.8 kJ mol^{-1}; (*E*)-but-2-ene, −114.3 kJ mol^{-1}; 2-methylbut-2-ene, −111.9 kJ mol^{-1}; 2,3-dimethylbut-2-ene, −110.0 kJ mol^{-1})[33] reflect progressive stabilization of olefins upon methylation.

Several types of hyperconjugation interactions can occur in alkyl-substituted alkenes. Theoretical calculations attribute the conformational preference of propene mainly to $\sigma_{C-H} \rightarrow \pi^*$, $\pi \rightarrow \sigma_{C-H}^*$, and $\sigma_{C-H} \rightarrow \sigma_{C-H}^*$ interactions.[92] At the same time, the increased HOMO energy upon methylation, as evidenced from the ionization energy of propene (9.73 eV) compared with ethylene (10.51 eV),[93] can be ascribed to $\sigma_{C-H} \rightarrow \pi^*$ hyperconjugative donation from the methyl substituent.[3,15,75] This increase in HOMO energy upon alkylation accounts for the enhanced reactivity of alkyl-substituted alkenes in peracid epoxidation reactions.[3,14]

The dipole moments of methylated alkenes (propene, 0.37 D; 2-methylpropene, **32**, 0.50 D)[33] suggest significant charge transfer from the methyl group to the π system. Molecular Orbital calculations indicate that the dipole moment of propene arises primarily from polarization of the π system, with only minor hyperconjugative donation from the methyl group.[93]

According to C 1s orbital photoelectron spectroscopy, the effect of adding a methyl group to 1,3-butadiene to form 1,3-pentadiene is very similar to ethylene methylation, indicating an inductive electron-withdrawing effect.[91] At the same time, hyperconjugative electron donation from methyl groups is evidenced by bathochromic shifts in the $\pi \rightarrow \pi^*$ UV spectra of alkyl-substituted polyenes (+5 nm)[38] and by the increased reactivity of methylated dienes in Diels−Alder reactions.[15]

Arenes

Inductive effects in substituted benzenes can be assessed using the ^{13}C chemical shift of the *ipso* carbon.[95] An inductive electron-withdrawing behavior for the methyl group (see Figure 11) can be inferred from the increased shift from the carbons of benzene (**33**, 128.5 ppm) to the *ipso* carbon of toluene (**34**, 137.7 ppm), which increases upon methylation at the α carbon of toluene (ethylbenzene, 140.2 ppm; isopropylbenzene, 148.7 ppm).[38] The inductive effect is strongest at the *ipso* position but attenuates rapidly along the aromatic ring, as shown by the ^{13}C NMR chemical shifts of toluene (*ipso*, 137.7 ppm; *ortho*, 129.2 ppm; *meta*, 128.4 ppm; *para*, 125.5 ppm).[2]

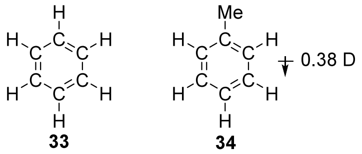


Figure 11. Structures of benzene (**33**) and toluene (**34**, showing experimental dipole moment[33] and calculated direction).[36]

The inductive electron-withdrawing effect of the methyl group is further supported by the lower energy of the 1s orbital of the *ipso* carbon of toluene (−290.30 eV) compared to the carbons of benzene (−290.24 eV).[96] However, some textbook authors have attributed to the methyl group in toluene an inductive electron-donating effect, either alone[8,15] or in combination with hyperconjugation.[7]

On the other hand, the methyl group donates electron density to the aromatic π-system through hyperconjugative $\sigma_{\mathrm{C-H}} \to \pi^*$ interactions,[97] as evidenced by changes in ionization energies (benzene: 9.24 eV; toluene: 8.83 eV)[93] and UV absorption maxima (benzene: 198 nm; toluene: 208 nm).[38] Interestingly, the slight π-electron donation of the methyl group in toluene coexists with a dominant σ-electron-withdrawing effect, such that a net electron withdrawal is predicted by theoretical calculations.[98,99]

The dipole moment of toluene (0.38 D) is consistent with small π-density transfer from the methyl group arising from hyperconjugation.[94] The direction of the toluene dipole moment results from the combination of positive charge at the *ipso* position, caused by the inductive electron withdrawal of the methyl group, and negative charge at the *para* position, generated through resonance originated from hyperconjugative donation.

The electron-withdrawing effect of the methyl group explains slight decreases in acid dissociation enthalpies for phenol upon methylation at the *meta* (−0.59 kJ mol^{-1}) and *para* (−0.67 kJ mol^{-1}) positions.[100] However, when Gibbs free energies are considered, slight increases are instead observed (*meta*: +0.46 kJ mol^{-1}; *para*: +1.46 kJ mol^{-1}). Some textbooks interpret this as evidence of a net electron-donating behavior of the methyl group,[6] although this reversal arises from entropic contributions overriding the electron-withdrawing effect.

Hammett constants for substituents are derived from acidity of benzoic acid upon substitution at the *meta* (σ_m) and *para* (σ_p) positions. The electron-withdrawing character of the methyl group leads to slightly increased ^{13}C NMR chemical shifts at the carboxylic carbons (*meta*: +0.18 ppm; *para*: +0.15 ppm, respectively)[101] and, correspondingly, decreased acid dissociation enthalpies (*meta*: −0.10 kJ mol^{-1}; *para*: −0.28 kJ mol^{-1}).[102]

However, increases are observed instead when Gibbs free energies of dissociation are considered (*meta*: +0.28 kJ mol^{-1}; *para*: +1.09 kJ mol^{-1}, respectively).[102] This behavior is reflected in negative values of the Hammett constants for the methyl group ($\sigma_m = -0.07$; $\sigma_p = -0.17$),[103] which some textbooks interpret as evidence of an electron-donating behavior effect,[3,14] when in fact they merely reflect entropic artifacts.

Carbonyl Compounds

The comparison of ^{13}C NMR chemical shifts upon successive methylation of formaldehyde (formaldehyde, **35**: 197.0 ppm; acetaldehyde, **36**: 200.5 ppm; acetone, **37**: 206.7 ppm)[37] indicates an inductive electron-withdrawing character of the methyl group,[57] in contrast with the inductive electron-donating behavior assumed in some textbooks (see Figure 12).[4,85]

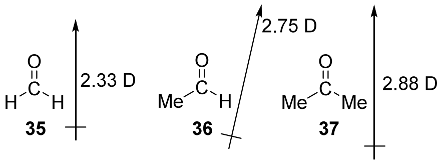


Figure 12. Structures and dipole moments (with calculated orientations)[36] of formaldehyde (**35**), acetaldehyde (**36**), and acetone (**37**).

Dipole moments of carbonyl compounds (formaldehyde: 2.33 D; acetone: 2.88 D)[33] reveal a strong molecular polarization. Nevertheless, the magnitude of the dipole moment increase by dimethylation of formaldehyde (0.55 D) is similar to that observed for 1,1-dimethylation of ethylene (0.50 D),[33] consistent with a small hyperconjugative donation from methyl groups.

The hydrogenation enthalpies of these carbonyl compounds (formaldehyde, −92.4 kJ mol^{-1}; acetaldehyde, −68.6 kJ mol^{-1}; acetone, −55.5 kJ mol^{-1})[33] reveal progressive thermodynamic stabilization upon methylation, in line with the decreasing equilibrium constants of hydration in aqueous solution (formaldehyde, 2000; acetaldehyde, 1.4; acetone, 0.002).[104]

Formic Acid vs Acetic Acid

The comparison of the ^{13}C NMR chemical shifts of the carboxylic carbon in formic acid (**38**, 165.4 ppm) and acetic acid (**20**, 176.0 ppm) indicates an inductive electron-withdrawing character of the methyl group, in contrast to some textbooks that assume an inductive electron-donating effect (see Figure 13).[4,9]

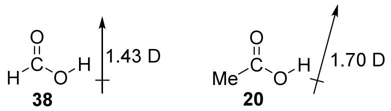


Figure 13. Structures and dipole moments (with calculated orientations)[36] of formic acid (**38**) and acetic acid (**20**).

In contrast, the increase in dipole moment upon methylation (formic acid: 1.43 D; acetic acid: 1.70 D)[36] supports an electron-donating effect of the methyl group through hyperconjugative donation. This net donation reduces the polarization of the O−H bond, as evidenced by the increase in the gas-phase IR ν_{OH} stretching frequencies (formic acid: 3567 cm^{-1}; acetic acid: 3583 cm^{-1}).[105] This electron-donating behavior is further reflected in the higher acid dissociation energy for acetic acid relative to formic acid, both in terms of enthalpy (+0.25 kJ mol^{-1}) and Gibbs free energy (+5.73 kJ mol^{-1}).[77]

N-Methylamides

The dual behavior of the alkyl group can also be illustrated by the successive N-methylation of formamide. The inductive electron-withdrawing behavior lowers the energy of σ molecular orbitals, as revealed by resonant inelastic X-ray scattering (RIXS) data.[106] In contrast, the hyperconjugative electron-donating effect raises the energy of the occupied π molecular orbitals, as evidenced by decreases in ionization energies (formamide, **39**: 10.16 eV; *N*-methylformamide, **40**: 9.83 eV; *N*,*N*-dimethylformamide, **41**: 9.12 eV, see Figure 14) and redshifts in the $\pi \to \pi^*$ UV absorption maxima (formamide: 173 nm; *N*-methylformamide: 175 nm; *N*,*N*-dimethylformamide: 199 nm).[107]

Heterocycles

Methylation at the nitrogen atom of pyrrole (yielding 1-methylpyrrole, see Figure 15) extends the study of nitrogen-bound methyl groups to heterocycles. An inductive electron-

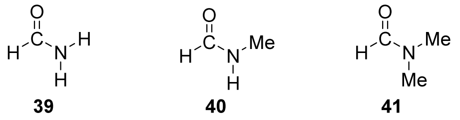
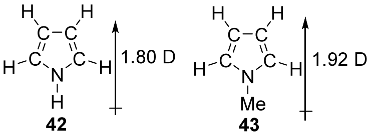


Figure 14. Structures of formamide (**39**), *N*-methylformamide (**40**), and *N*,*N*-dimethylformamide (**41**).



42 **43**

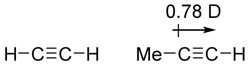
Figure 15. Structures and dipole moments (with calculated orientations)[36] of pyrrole (**42**) and 1-methylpyrrole (**43**).

withdrawing effect of the methyl group can be inferred from ^{15}N NMR chemical shifts (pyrrole, **42**: −238.8 ppm; 1-methylpyrrole, **43**: −235.2 ppm).[108] At the same time, hyperconjugative donation from the methyl group to the π system (see Figure 15) is demonstrated by ionization energies (pyrrole, **42**: 8.22 eV; 1-methylpyrrole, **43**: 7.95 eV),[109] UV absorption maxima (pyrrole: 205 nm, 1-methylpyrrole: 210 nm),[110] dipole moments (pyrrole: 1.80 D; 1-methylpyrrole, 1.92 D),[33] and theoretical calculations.[111] As discussed for toluene, no net electronic methyl effect can be deduced from the increased dipole moment upon pyrrole methylation.

ALKYL GROUPS BONDED TO sp-HYBRIDIZED ATOMS

Alkynes

Propyne (**45**, see Figure 16) serves as a key example of a methyl group bonded to an sp-hybridized carbon. Compared to acetylene (**44**), the ^{13}C NMR chemical shift of the central carbon in propyne increases by +8.5 ppm, indicating a small inductive electron-withdrawing effect of the methyl group, similar to those observed for ethane (+9.6 ppm) and propene (+12.9 ppm).[38] This electron-withdrawing behavior is consistent with the estimated 0.32 eV stabilization of the 1s orbital of an acetylene carbon upon methyl substitution, inferred from photoelectron spectroscopy.[112]



$H{-}C{\equiv}C{-}H$ $\quad$ $Me{-}C{\equiv}C{-}H$

44 **45**

Figure 16. Structures of acetylene (**44**) and propyne (**45**, including calculated dipole moment orientation).

At the same time, hyperconjugative donation from the methyl group into the π system can be observed, as supported by the lower ionization energy of the HOMO π orbital in propyne (10.37 eV vs 11.40 eV for acetylene).[1] The dipole moment of propyne (0.78 D, directed from the methyl group toward the terminal carbon) can be attributed to significant π-system polarization[113] arising from a modest hyperconjugative donation.[114]

CONCLUSION

The prevailing framework in organic chemistry textbooks for understanding the effects of alkyl substituents is based on a contradictory view: alkyl groups are considered electron-withdrawing in spectroscopic contexts but electron-donating in reactivity-based scenarios. Textbooks have long relied on examples that appear to support this dichotomy, while counterexamples have been largely overlooked. A reevaluation of classic textbook reactivity examples, now aligned with spectroscopic data, leads to a revised framework for understanding the electronic properties of alkyl groups.

The key point of the framework presented here is that alkyl groups display a dual electronic effect. When attached to an sp^3-hybridized atom, an alkyl group acts as an inductive electron-withdrawing substituent, consistent with the higher electronegativity of carbon relative to hydrogen. This electron-withdrawing character accounts for the characteristic NMR chemical shifts observed in aliphatic compounds. The same electron-withdrawing behavior is also evident in ethers and amines, as reflected in their molecular dipole moments.

This electron-withdrawing effect contradicts some generalized textbooks examples assuming an electron-donating behavior. Thus, the enthalpic basicities of aliphatic carbanions and amines follow the trend primary > secondary > tertiary, which supports the electron-withdrawing influence of alkyl groups. The increased enthalpic acidities of methylated ammonium ions and substituted acetic acids are likewise explained by the inductive electron-withdrawing nature of alkyl groups. Meanwhile, the apparent electron-donating character suggested by Gibbs free energy acidities is indeed an artifact arising from hydration entropies. The relative stabilities of free radicals (tertiary > secondary > primary > methyl) also reflect the electron-withdrawing character of alkyl groups, which facilitates spin delocalization across the substituents.

At the same time, when an alkyl group is bonded to an sp^2-hybridized atom, electron donation through hyperconjugation from σ_{C-H} orbitals to vacant p or π^* orbitals occurs. Although little transfer is usually observed for hyperconjugative donation in neutral molecules, significant polarization of π systems can be generated, as shown by the dipole moments of methylated unsaturated compounds.

In carbocations, the hyperconjugative donation can outweigh concurrent inductive electron withdrawal. Consequently, alkyl groups concurrently stabilize carbanions and free radicals (by inductive electron withdrawal), as well as carbocations (through hyperconjugative donation).

The framework proposed here calls for a substantial revision of organic chemistry textbooks. Pedagogically, no new concepts are required to explain the dual electronic behavior of alkyl groups. Inductive effects can be introduced using NMR chemical shifts of monosubstituted alkanes,[37] whereas hyperconjugation can be illustrated through the conformational analysis of ethane. Moreover, the dual behavior of substituents is already embedded in organic chemistry teaching (for instance, chlorine substituent on benzene deactivates the ring while directing substitution to the *ortho* and *para* positions).

The introduction of alkyl group electronic effects can be effectively illustrated by comparing dipole moments (e. g., methane/propane vs formaldehyde/acetone). NMR chemical shifts of aliphatic compounds highlight the inductive electron-withdawing character of the alkyl group, whereas the stability of the *tert*-butyl carbocation provides an example of predominant hyperconjugative donation.

Traditional textbook examples that seemingly support an inductive electron-donating nature for alkyl groups should be reinterpreted or removed. The Supporting Information includes several tables of experimental and theoretical data to aid educators in developing new examples and problems based on the authentic electronic properties of alkyl groups.

Textbook authors should strive a clear and consistent explanation of the electronic effects of alkyl substituents, explicitly distinguishing between inductive and hyperconjugative contributions, much as is already done when discussing inductive versus resonance effects for other substituents.

Crucially, the dual behavior of alkyl groups should be introduced even at the introductory level.

A deeper understanding of the electronic effects of alkyl groups will enable both educators and AI models to explain their influence on chemical reactivity in a way consistent with spectroscopic properties. Updating educational resources to reflect these effects will provide a more rigorous and coherent foundation for organic chemistry, thereby improving the learning process for both students and artificial intelligence systems.

The electronic nature of the alkyl substituent is not the only misconception in organic chemistry textbooks. Other errors, such as the attribution of the *endo* rule for Diels−Alder reactions to Secondary Orbital Interactions[1−3,10,48] (rather than a combination of other effects),[115] or the depiction of the ethyl carbocation as containing one sp^3-hybridized carbon and one sp^2 carbon[4−6,14,15] (instead of two equivalent carbons),[116] should also be corrected.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.5c00936.

Physicochemical properties of the numbered entities (PDF)

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Notes

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