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Charge Distributions and Chemical Effects. 13. Ab Initio Study of the Charge Density-¹³C Nuclear Magnetic Resonance Shift Correlation for Ethylenic Carbon Atoms

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Abstract: Ab initio charge distributions in ethylene and methyl derivatives thereof are examined (1) by means of Mulliken's scheme and (2) in terms of an approximation which does not involve halving of the overlap population terms among dissimilar overlap partners. The ¹³C NMR shifts of the vinylic C atoms are linearly related to the net atomic charges obtained from the latter approximation, whereby any increase in local electron density results in an upfield shift.

Numerous and often frustrating attempts at correlating ¹³C NMR shifts, δ_c , with carbon atomic charges were presented on the premises that one of the major factors governing the shielding of a specific nucleus is its local electron density.¹ The most accurate relationship, that found for alkanes,² indicates that δ_c increases (downfield shift) with decreasing positive character of the carbon atoms of this class of compounds. This result, which is at variance with common views, best illustrates the pitfalls in the growing praxis of indiscriminately interpreting ¹³C shifts in all systems as being strictly linearly related to electron density.

Recent theoretical progress³ in the calculation of ¹³C shifts gives some insight into the various contributions that can be related to detailed features of electronic structure. While these more rigorous approaches will hopefully result in some understanding of charge density-NMR shift correlations and their limitations, it is also felt that some detailed knowledge about the trends in series of closely related compounds is desirable, despite the fact that the significance or generality of any such empirical correlation is not known.

Here we present a relationship between ¹³C NMR shifts and net charges of sp² carbon atoms in alkyl-substituted ethylenes. At this point, we wish to emphasize that the fact that this re-

lationship turns out to be simple should not be used to lend unintended support for the still unwarranted view that chemical shifts are necessarily always linearly related to atomic charges. Indeed, chemical shift is a property of the interaction of the charge density with an external magnetic field and depends, therefore, not only on the value of the integrated charge density in the neighborhood of a nucleus but also on the magnetic susceptibility of that charge density. Finally, this study illustrates the care which is required in the calculation of atomic charges if one wishes to use them in the evaluation of property-charge relationships.

Calculation of Charges

Population analyses were obtained from ab initio (STO-3G) calculations involving optimization of all (geometry and scale factor) variational parameters, along the lines described earlier;⁴ they were calculated following Mulliken's scheme,⁵ implying the half-and-half partitioning of all overlap population terms (eq 1, in standard notation),

$$N(k) = 2 \sum_i \sum_r \left(c_{ir}^2 + \sum_{l \neq k} c_{ir} c_{il} S_{rkl} \right) \quad (1)$$

thus providing sets of net charges, $\{q^0\}$, in a well-defined frame

Table I. Molecular ζ Exponents

| Atom | $\zeta(K)$ | $\zeta(L)$ |
|--|------------|------------|
| C sp ² -(H, H) | 5.67 | 1.70 |
| C sp ² -(H, CH ₃) | 5.67 | 1.71 |
| C sp ³ -(Csp ²) | 5.67 | 1.78 |
| H-(Csp ²) | 1.22 | |
| H-(Csp ³) | 1.17 | |

of reference. Then, departures from this scheme were evaluated to give charges, $\{q\}$, which do not imply the halving of all overlap population terms. For alkane carbon atoms it was shown⁶⁻⁹ that an appropriate definition of charges, leaving the mode of partitioning overlap populations to be calibrated by experiment, is essential in any comparison of properties with carbon net charges. Indeed, the use of any set of C charges other than the proper one is bound to fail in verifying any anticipated property-charge relationship.⁶ The same general approach is, therefore, followed in the present study of ethylenic carbon charges.

Standard STO-3G calculations were carried out along the

lines described by Hehre and Pople,¹⁰ using valence-shell ζ exponents for propene and the carbon inner shell exponent which is the free atom value of Clementi and Raimondi¹¹ (Table I). These exponents were held fixed in the calculations of molecular geometries (Table II).

Next, the exponents were varied in turn, using the above geometries, until the total energy was minimized. Of course, each different atom was optimized individually, both for valence-shell and carbon K-shell exponents, until stable charge distributions were obtained. Such an approach implies a large number of calculations for each molecule of interest; moreover, because of the relatively large number of variational parameters in alkyl-substituted ethylenes and lack of symmetry in most cases, stabilization of charge results is more difficult to attain than for alkanes. Indeed, for properties, such as charges, which are highly sensitive to ζ optimization, energy minimizations must be carried further: when the final L exponents are too different from their starting counterparts, an additional cycle of optimization over the set of exponents becomes necessary in order to ensure convergence of charges. The estimated uncertainty in the final carbon charges is of the order of 3 millielectron (me) units, which is much larger than for al-

Table II. Equilibrium Geometries^a

| Molecule | Symmetry constraint | Coordinate | STO-3G | Exptl | Molecule | Symmetry constraint | Coordinate | STO-3G | Exptl | | | |
|--------------------|---------------------|----------------------|-------------|---------------|-----------------------|---------------------|----------------------|---------------|---------------|----------------------|-------|--------------|
| Ethylene | D_{2h} | $r(CC)$ | 1.318 | 1.330 ± 0.005 | | | $r(C_1H_a)$ | 1.095 | 1.11 ± 0.04 | | | |
| | | $r(CH)$ | 1.080 | 1.076 ± 0.005 | | | $r(C_2H)$ | 1.092 | | | | |
| | | $\angle HCH$ | 116.6 | 116.6 ± 0.8 | | | $\angle C_1C_2C_3$ | 128.2 | | | | |
| Propene | C_s | $r(C_1C_2)$ | 1.319 | 1.336 ± 0.004 | | | $\angle C_2C_1H_s$ | 111.3 | 110.6 ± 3.6 | | | |
| | | $r(C_2C_3)$ | 1.514 | 1.501 ± 0.004 | | | $\angle C_2C_1H_a$ | 110.5 | | | | |
| | | $r(C_1H_c)$ | 1.089 | 1.091 ± 0.003 | | | $\angle H_aC_1H_a$ | 108.4 | | | | |
| | | $r(C_1H_i)$ | 1.089 | 1.081 ± 0.003 | | | $\angle C_2C_3H$ | 117.4 | | | | |
| | | $r(C_2H)$ | 1.090 | 1.090 ± 0.003 | | | 2-Methyl-2-butene | C_s | | $r(C_2C_3)$ | 1.320 | 114.5 ± 18.6 |
| | | $r(C_3H_a)$ | 1.090 | 1.085 ± 0.004 | | | | | | $r(C_3C_4)$ | 1.507 | |
| | | $r(C_3H_a)$ | 1.095 | 1.098 ± 0.014 | | | | | | $r(C_2C_1)$ | 1.514 | |
| | | $\angle H_cC_1C_2$ | 122.0 | 120.5 ± 0.3 | | | | | | $r(C_2C_5)$ | 1.516 | |
| | | $\angle H_iC_1C_2$ | 122.0 | 121.5 ± 0.3 | | | | | | $r(C_4H_s)$ | 1.090 | |
| | | $\angle C_1C_2C_3$ | 125.0 | 124.3 ± 0.3 | | | | | | $r(C_4H_a)$ | 1.095 | |
| | | $\angle HC_2C_1$ | 119.7 | 119.0 ± 0.3 | | | | | | $r(C_1H_s)$ | 1.090 | |
| | | $\angle C_2C_3H_s$ | 111.3 | 111.2 ± 0.3 | | | | | | $r(C_1H_a)$ | 1.095 | |
| $\angle H_aC_3H_a$ | 108.3 | 109.0 ± 1.3 | $r(C_5H_s)$ | 1.092 | | | | | | | | |
| $\angle H_aCH_a$ | 107.2 | 106.2 ± 1.8 | $r(C_5H_a)$ | 1.095 | | | | | | | | |
| Isobutene | C_{2v} | $r(C_1C_2)$ | 1.321 | 1.330 ± 0.004 | $r(C_3H)$ | 1.091 | | | | | | |
| | | $r(C_2C_3)$ | 1.517 | 1.507 ± 0.003 | $\angle C_2C_3C_4$ | 129.0 | | | | | | |
| | | $r(C_3H_s)$ | 1.090 | 1.072 ± 0.01 | $\angle C_3C_2C_1$ | 125.4 | | | | | | |
| | | $r(C_3H_a)$ | 1.095 | 1.095 ± 0.003 | $\angle C_1C_2C_5$ | 114.3 | | | | | | |
| | | $r(C_1H)$ | 1.088 | 1.088 ± 0.002 | $\angle C_3C_4H_s$ | 112.7 | | | | | | |
| | | $\angle C_1C_2C_3$ | 122.3 | 122.3 ± 0.2 | $\angle C_3C_4H_a$ | 110.5 | | | | | | |
| | | $\angle C_2C_3H_s$ | 111.4 | 112.9 ± 1.3 | $\angle H_aC_3H_a$ | 108.4 | | | | | | |
| | | $\angle C_2C_3H_a$ | 110.9 | 110.7 ± 0.9 | $\angle C_2C_1H_s$ | 112.5 | | | | | | |
| | | $\angle H_aC_3H_a$ | 108.0 | | $\angle C_2C_1H_a$ | 110.6 | | | | | | |
| | | $\angle HC_1H$ | 116.0 | 118.5 ± 0.2 | $\angle H_aC_1H_a$ | 108.3 | | | | | | |
| | | <i>trans</i> -Butene | C_{2h} | $r(C_2C_3)$ | 1.319 | 1.347 ± 0.003 | $\angle C_2C_5H_s$ | 111.5 | | | | |
| | | | | $r(C_1C_2)$ | 1.515 | 1.508 ± 0.002 | $\angle C_2C_5H_a$ | 110.9 | | | | |
| $r(C_1H_s)$ | 1.091 | | | 1.10 ± 0.04 | $\angle H_aC_5H_a$ | 108.0 | | | | | | |
| $r(C_1H_a)$ | 1.095 | | | | $\angle C_3C_1H$ | 114.2 | | | | | | |
| $r(C_2H)$ | 1.089 | | | 1.15 ± 0.14 | 2,3-Dimethyl-2-butene | D_{2h} | $r(C_2C_3)$ | 1.328 | 1.336 ± 0.004 | | | |
| $\angle C_1C_2C_3$ | 124.8 | | | 123.8 ± 0.4 | | | $r(C_1C_2)$ | 1.525 | | | | |
| $\angle C_2C_1H_s$ | 111.3 | | | 109.0 ± 5.0 | | | $r(C_1H_s)$ | 1.086 | | | | |
| $\angle C_2C_1H_a$ | 110.9 | | | | | | $r(C_1H_a)$ | 1.094 | | | | |
| $\angle H_aC_1H_a$ | 108.0 | | | | | | $\angle (C_1C_2C_3)$ | 124.9 | | | | |
| $\angle C_3C_2H$ | 119.7 | | | 121.5 ± 4.0 | | | $\angle (C_2C_1H_s)$ | 113.0 | | | | |
| <i>cis</i> -Butene | C_{2v} | | | $r(C_2C_3)$ | | | 1.317 | 1.346 ± 0.003 | | $\angle (C_2C_1H_a)$ | 110.9 | |
| | | | | $r(C_1C_2)$ | | | 1.510 | 1.506 ± 0.002 | | $\angle (H_aC_1H_a)$ | 108.0 | |
| | | $r(C_1H_s)$ | 1.091 | | | | | | | | | |
| | | | | | | | | | | | | |

^a Distances in Å, angles in decimal degrees. Experimental geometries extracted from: (C₂H₄) K. Kuchitsu, *J. Chem. Phys.*, **44**, 906 (1966); (C₃H₆) D. R. Lide and D. Christensen, *ibid.*, **35**, 1374 (1961); (isobutene) L. H. Scharpen and V. W. Laurie, *ibid.*, **39**, 1732 (1963); (*trans*- and *cis*-butene) A. Al Menningen, I. M. Anfinson, and A. Haaland, *Acta Chem. Scand.*, **24**, 43 (1970); (2,3-dimethyl-2-butene) S. W. Eisma, C. Altona, H. J. Geise, F. C. Mijlhoff, and G. H. Renes, *J. Mol. Struct.*, **20**, 251 (1974).

Table III. Optimum Exponents and Net Charges (me)

| Molecule | Atom | $\zeta(K)$ | $\zeta(L)$ | q_{tot}^0 | q_{σ}^0 | q_{π}^0 | |
|-----------------------------------|-----------------------------------|----------------|------------|-------------|----------------|-------------|-------|
| Ethylene | C | 5.703 | 1.7105 | -128.4 | -128.4 | 0.0 | |
| | H | 1.2193 | | 64.2 | | | |
| Propene | C ₁ | 5.703 | 1.7040 | -154.6 | -120.4 | -34.2 | |
| | C ₂ | 5.703 | 1.7132 | -58.3 | -83.5 | 25.2 | |
| | C ₃ | 5.706 | 1.7731 | 29.5 | | | |
| | H _{C-} (C ₁) | 1.2122 | | 59.3 | | | |
| | H _{I-} (C ₁) | 1.2141 | | 62.7 | | | |
| | H ₋ (C ₂) | 1.2078 | | 49.3 | | | |
| | H _{a-} (C ₃) | 1.1714 | | 4.1 | | | |
| | H _{S-} (C ₃) | 1.1723 | | 3.9 | | | |
| Isobutene | C ₁ | 5.703 | 1.7004 | -173.9 | -112.2 | -61.7 | |
| | C ₂ | 5.703 | 1.7143 | -7.6 | -55.2 | 47.6 | |
| | C ₃ | 5.706 | 1.7717 | 21.9 | | | |
| | H ₋ (C ₁) | 1.2097 | | 58.5 | | | |
| | H _{S-} (C ₃) | 1.1720 | | 5.2 | | | |
| | H _{a-} (C ₃) | 1.1697 | | 2.6 | | | |
| | C ₁ | 5.706 | 1.7734 | 34.3 | | | |
| | C ₂ | 5.703 | 1.7088 | -86.3 | -78.6 | -7.7 | |
| <i>trans</i> -Butene | H ₋ (C ₂) | 1.2056 | | 46.7 | | | |
| | H _{S-} (C ₁) | 1.1706 | | 1.1 | | | |
| | H _{a-} (C ₁) | 1.1705 | | 2.1 | | | |
| | C ₁ | 5.706 | 1.7732 | 29.9 | | | |
| <i>cis</i> -Butene | C ₂ | 5.703 | 1.7090 | -86.4 | -77.6 | -8.8 | |
| | H ₋ (C ₂) | 1.2039 | | 46.4 | | | |
| | H _{S-} (C ₁) | 1.1733 | | 3.7 | | | |
| | H _{a-} (C ₁) | 1.1707 | | 3.2 | | | |
| | C ₁ | 5.706 | 1.7723 | 23.3 | | | |
| | 2-Methyl-2-butene | C ₂ | 5.703 | 1.7097 | -37.5 | -49.8 | 12.3 |
| | | C ₃ | 5.703 | 1.7053 | -106.4 | -73.8 | -32.6 |
| | | C ₄ | 5.706 | 1.7743 | 35.6 | | |
| C ₅ | | 5.706 | 1.7729 | 31.3 | | | |
| H ₋ (C ₃) | | 1.2016 | | 43.5 | | | |
| H _{S-} (C ₄) | | 1.1734 | | 2.4 | | | |
| H _{a-} (C ₄) | | 1.1700 | | 1.3 | | | |
| H _{S-} (C ₁) | | 1.1741 | | 5.9 | | | |
| H _{a-} (C ₁) | | 1.1686 | | 1.0 | | | |
| H _{S-} (C ₅) | | 1.1692 | | 0.4 | | | |
| 2,3-Dimethyl-2-butene | H _{a-} (C ₅) | 1.1678 | | -1.6 | | | |
| | C ₁ | 5.706 | 1.7713 | 23.4 | | | |
| | C ₂ | 5.703 | 1.7023 | -61.2 | -50.2 | -11.0 | |
| | H _S | 1.1768 | | 7.2 | | | |
| H _a | 1.1683 | | 0.0 | | | | |

kanes.⁴ Fortunately, in the present case such a precision turns out to be sufficient for sp² carbon atoms. The optimum exponents and atomic charges, $\{q^0\}$, obtained from the Mulliken population analysis are indicated in Table III.

These optimized charges represent now a suitable basis for the study of NMR shifts. It should be noted that this would not be the case if all ζ exponents, accounting for the changes in the atomic orbitals due to molecular environment, had not been optimized carefully. Their optimization can be kept within reasonable limits of feasibility only with the use of the minimal STO-3G basis set, which has been selected for that reason;⁴ moreover, this method has already proven adequate for calculating sufficiently accurate charges in saturated hydrocarbons.

The q^0 net charges need now to be corrected in order to satisfy a more appropriate definition^{2,7} which considers (1) that eq 1 represents a satisfactory approximation for partitioning overlap terms between partners of equal nature but (2) that such a distribution among atoms of dissimilar nature is less

valid. Appropriate corrections are made along the lines described earlier for alkanes.^{2,7} For the latter, modification of the population analysis results in the following simple approximations,

$$q_H = q_H^0 - p \quad (2)$$

$$q_C = q_C^0 + Np \quad (3)$$

where N = number of H atoms bonded to C, and p (= 30.12 me) is the departure from the usual halving of the C-H overlap population, for one carbon-hydrogen bond. These approximations have proven satisfactory for sp³ C atoms, as the charges derived in this manner enable an accurate calculation (± 0.3 ppm) of ¹³C NMR shifts in a range of over 40 ppm, from methane to adamantane.^{2,7,9}

The analogous transformation for H atoms bonded to ethylenic C atoms takes the form

$$q_H = q_H^0 - p_{CH} \quad (4)$$

where p_{CH} represents the overlap term correction for one H atom bonded to an sp² carbon. Consequently, defining now p_{CC} = correction appropriate for an sp² C atom bonded to an sp³ carbon, the modified sp² carbon net charges become

$$q_C = q_C^0 + N\Delta p + 2p_{CC} \quad (5)$$

with $\Delta p = p_{CH} - p_{CC}$. This, of course, represents the simplest possible approximation within the scheme that was found to be appropriate for alkane carbon atoms.

Comparison with ¹³C NMR Shifts

We proceed now with the comparison between atomic charges and NMR shifts, using the experimental δ_C values of Jones and Grant (Table IV).

Postulating a relationship of the form

$$\delta_C = aq_C + \delta^0 \quad (6)$$

one obtains, from eq 5, $\delta_C = 0.301 (\pm 0.016) q_C + 9.6 (\pm 1.0) \cdot N + 142.1$ ppm from Me₄Si. This result, when compared with eq 5 and 6, also indicates that $9.6 (\pm 1.0) = a\Delta p$, hence, that $\Delta p = 31.8 (\pm 4)$ me. The δ_C (1) values calculated from this correlation are in satisfactory agreement with their experimental counterparts (Table IV).

The Δp value calculated above is virtually equal to that determined earlier^{2,7} for the saturated hydrocarbons, i.e., 30.12 me with $p_{CC} = 0$. Indeed, using now $\Delta p = 30.12$ me, it follows that $\delta_C = 0.291 (\pm 0.011) q_C + 142.0$ ppm from Me₄Si, where the $2p_{CC}$ term is incorporated in the constant. The δ_C (2) values calculated from this approximation are particularly satisfactory (Table IV), as they do not involve the use of any new parameter, typical for ethylenic carbon atoms, for the recalculation of charges. This correlation is presented in Figure 1.

While it is presently difficult to assess on theoretical grounds whether the Δp correction applying to ethylenic C atoms should be identical with the correction appropriate for saturated hydrocarbons and, within the precision of the present type of analysis, no definite conclusion can be drawn in that matter, it remains that a correction of ethylenic C charges along the lines employed for alkanes yields charges which are well correlated with ¹³C NMR shifts, quite unlike their original uncorrected counterparts.

Discussion

This $\delta_C - q_C$ correlation indicates that any increase in negative charge on carbon is accompanied by an upfield shift. This trend is thus opposite to what has been observed for the positive C atoms of saturated hydrocarbons, for which any decrease in positive charge is reflected in a downfield shift. It should be noted that, for both ethylenic and sp³ C atoms, charge analyses

Table IV. Experimental and Calculated NMR Shifts

| Molecule | Atom ^e | δ_C , ppm from Me ₄ Si | | δ_C , calcd | |
|-----------------------|---------------------|--|----------------------------|--------------------|-------|
| | | Ref a-c | Ref d | (1) | (2) |
| Ethylene | C (4) | | 122.8 | 122.5 | 122.2 |
| Propene | C ₁ (2) | 115.4 ^a | 115.0 | 114.7 | 114.5 |
| | C ₂ (9) | 135.7 ^a | 133.1 | 134.1 | 133.8 |
| Isobutene | C ₁ (1) | | 109.8 | 108.8 | 108.9 |
| | C ₂ (10) | | 141.2 | 139.8 | 139.8 |
| <i>trans</i> -Butene | C ₂ (7) | 125.4 ^b | 125.8 | 125.7 | 125.7 |
| <i>cis</i> -Butene | C ₂ (6) | 124.2 ^b | 124.3 | 125.6 | 125.6 |
| 2-Methyl-2-butene | C ₂ (8) | 130.4 ^c | 131.4 | 130.8 | 131.1 |
| | C ₃ (3) | 117.9 ^c | 118.7 | 119.6 | 119.8 |
| 2,3-Dimethyl-2-butene | C ₂ (5) | | 123.2 | 123.6 | 124.2 |
| | | | | | |
| | | | Standard deviation, ppm | 1.02 | 1.00 |
| | | | Average deviation, ppm | 0.74 | 0.79 |
| | | | Multiple correlation coeff | 0.995 | 0.995 |

^a G. B. Savitsky, P. D. Ellis, K. Namikawa, and G. E. Maciel, *J. Chem. Phys.*, **49**, 2395 (1968). ^b J. W. de Haan and L. J. M. van de Ven, *Org. Magn. Reson.*, **5**, 147 (1973). ^c R. A. Friedel and H. L. Retcofsky, *J. Am. Chem. Soc.*, **85**, 1300 (1963). ^d Values of A. J. Jones and D. M. Grant, reported as personal communication in J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972. ^e The numbers in parentheses refer to the points in Figure 1. The experimental values are extracted from ref a-d.

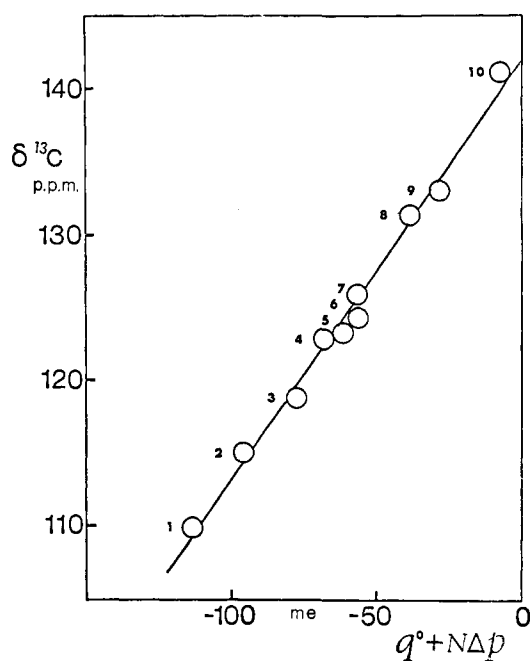


Figure 1. Comparison of ¹³C NMR shifts with corrected carbon net charges, using $\Delta p = 30.12$ me. The radius of the circles corresponds to an uncertainty of 0.7 ppm or 3.5 me.

are those derived from optimized STO-3G calculations and that in both cases the $\Delta p \sim 30$ me correction term is the only one permitting a monotonic dependence of ¹³C NMR shifts on carbon charges. This follows from the fact that the sets of corrected (q_C) and uncorrected (q_C^0) carbon charges (eq 5) are not linearly related one to another and, hence, that one has to choose only between two alternatives, i.e., (1) a virtually linear relationship with $\Delta p \sim 30$ me or (2) no relationship at all between ¹³C shifts and theoretical atomic charges of sp² carbon atoms, with any $\Delta p \neq \sim 30$ me. These conclusions are easily derived from the crudest possible approximation, i.e., that expressed in Figure 1.

The modified charges (eq 5) reveal interesting effects resulting from the substitution of methyl for hydrogen at the trigonal centers, i.e., a downfield shift at the substituted C atom and an upfield shift at the β carbon. The behavior at the substituted atom may seem surprising, at first, in the perspective of a methyl group viewed as a better electron donor than H, and considering that an increase in electron density at a center

results in an upfield shift. Now the calculated atomic charges (corrected for $N\Delta p$) indicate, indeed, a decrease in electron density at the point of substitution and an accumulation of negative charge in β position. This polarization offers an explanation for Markownikoff's rule.

The verification that methyl is, indeed, electron releasing relative to hydrogen follows from the corrected net charge of a methyl group, $q(\text{CH}_3) = q^0(\text{CH}_3) - p_{\text{CC}}$ and from eq 4: a positive difference $q(\text{CH}_3) - q_{\text{H}} = q^0(\text{CH}_3) - q_{\text{H}}^0 + \Delta p$ verifies this statement. For example, using the charges of Table III, the propene methyl group has a net charge $q^0(\text{CH}_3) = 41.5$ me and q_{H}^0 in ethylene is 64.2 me; therefrom, with $\Delta p = 30.12$ me, $q(\text{CH}_3) - q_{\text{H}} = 7.4$ me. Similarly, in tetramethylethylene, $q^0(\text{CH}_3) = 29.5$ me and q_{H}^0 in trimethylethylene is 42.9 me; hence, $q(\text{CH}_3) - q_{\text{H}} = 17.5$ me. In all cases one methyl appears to be a better electron donor than one hydrogen, under comparable conditions. It would be false, therefore, to interpret the fact that the chemical shifts of ethylene and tetramethylethylene are very similar as an indication that methyl is not a better electron donor than hydrogen, because it must always be considered that in multiple substitution of methyl for hydrogen the electron-attracting power of partially methylated vinylic groups with respect to both H and CH₃ changes as the number of substituents is varied.

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References and Notes

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