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ON THE HYBRIDIZATION-DEPENDENCE OF DEUTERIUM-INDUCED ^{13}C NMR ISOTOPE SHIFTS OVER ONE BOND: DATA FOR ETHANE, ETHYLENE, AND ACETYLENE^{+}

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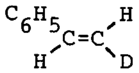
Abstract: *One-bond $^{2}H/^{1}H$ isotope effects on ^{13}C chemical shifts in ethane, ethylene, and acetylene correlate linearly with the fractional s-character of the corresponding CD bond hybrid.*

There are a number of reports in the literature on the s-character dependence of $^{2}H/^{1}H$ isotope effects on ^{13}C chemical shifts, $^{1}\Delta(^{13}C)$,[1)] and a decrease of $^{1}\Delta(^{13}C)$ with increasing s-character of the CD bond hybrid has been calculated[2)] and measured.[3)] However, conclusive experimental results from a study that includes aliphatic, olefinic as well as acetylenic CD bonds have not yet been obtained. Earlier attempts failed because of the lower experimental accuracy available at that time[4)] or the neglect of substituent effects on $^{1}\Delta(^{13}C)$ data.[5)]

We now observed an excellent linear correlation between $^{1}\Delta(^{13}C)$ and the fractional s-character, s(i), of the corresponding CD bond hybrid for the two series of compounds 1 - 3 and 4 - 6, respectively (Table 1). The mono-deuterated species were prepared by standard techniques as 3:1 mixtures with isotope-free material.[6)] NMR isotope effects were measured at 100.61 MHz under ^{1}H broad-band decoupling and ^{2}H decoupling where necessary.[7)] The fractional s-character was calculated from the observed one-bond $^{13}C,^{2}H$ coupling constants by the modified Muller-Pritchard relation[8)] $s(i) = (\gamma_H/\gamma_D) \times {}^{1}J(^{13}C,^{2}H)/500$, with $\gamma_H/\gamma_D = 6.5144$.[9)] A graphical representation of the results (Table 1) is given in Fig. 1.[10)]

Our data clearly demonstrate that a linear correlation between $^{1}\Delta(^{13}C)$ and the fractional s-character of the corresponding CD bond hybrid exists for compounds

Table 1. One-bond $^{2}H/^{1}H$ ^{13}C NMR Isotope Shifts (ppb, exp. error ± 0.5), $^{13}C,^{2}H$ Coupling Constants (Hz, exp. error ± 0.03), and Calculated Fractional s-Character of 1 - 6

	H_3C-CH_2D 1	$H_2C=CHD$ 2	$HC\equiv CD$ 3	$C_6H_5-CH_2-CH_2D$ 4	 $C_6H_5HC{=}CHD$ 5	$C_6H_5-C\equiv CD$ 6
$^{1}\Delta(^{13}C)$	284.0	273.6	226.7	296.0	283.2	252.7
$^{1}J(^{13}C,^{2}H)$	19.23	23.95	37.97	19.40	24.55	38.45
s(i)	0.250	0.312	0.495	0.253	0.320	0.501

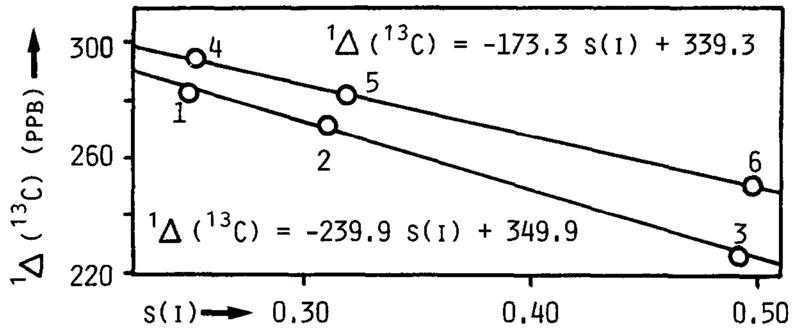


Fig. 1. Correlation between ^{13}C NMR isotope shifts over one bond, $^1\Delta(^{13}C)$ (ppb), and the fractional s-character of the corresponding CD bond hybrid in 1 - 6 (data from Table 1).

of closely related structure. The different slopes and intercepts obtained for 1 - 3 and 4 - 6, respectively, (Fig. 1) are - at least in part - a consequence of the different temperatures, solvents, and concentrations used,[11] but the effect of phenyl-substitution in 4 - 6 is certainly a major factor. The strong influence that structural variations have on $^1\Delta(^{13}C)$ is most convincingly demonstrated by the fact that methane ($^1\Delta(^{13}C)$ = 187.0 ppb[12]) does not fit into the correlation since it lacks an α-carbon substituent.[13] Empirical correlations like the above equations are thus less general than the Muller-Pritchard relation for $^1J(^{13}C,^1H)$ coupling constants.

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References and Notes:

+) *Dedicated to Professor Dr. W. Lüttke on the occasion of his 65th birthday.*

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6) *1: from ethyl magnesium bromide with H_2O/D_2O (1:3); 2: from vinyl magnesium bromide as before; 3: from CaC_2 by hydrolysis as before, resulting in a product mixture of $C_2H_2/C_2HD/C_2D_2$ (1:2:2); 4: hydrolysis of β-phenyl-methyl magnesium bromide as before; 5: J.P.Quintard and M.Pereyre, J.Label.Compounds 14, 653 (1978); 6: from phenylacetylene by reaction with n-butyllithium and subsequent hydrolysis as before.*

7) *BRUKER WH-400 FT-NMR Spectrometer with ASPECT 2000 data system.*

8) *N.Muller and D.E.Pritchard, J.Chem.Phys. 31, 768, 1471 (1959).*

9) *P.Diehl and T.Leipert, Helv.Chim.Acta 47, 545 (1964).*

10) *The use of the empirical constant 500 in the Muller-Pritchard relation neglects any primary isotope effects on $^1J(^{13}C,^2H)$. These effects are, however, small (< 1%) (cf. ref. 5 and footnote 16 in ref. 3) and therefore well within the error limits of the empirical constant.*

11) *1 and 2 were measured at 173 K in CD_2Cl_2/CS_2 (ca.20 Vol%); 3 at 213 K in acetone-d_6 (ca. 50 Vol%); 4 - 6 at 310 K in $CDCl_3$ (1 M).*

12) *M.Alei, Jr., and W.E.Wageman, J.Chem.Phys. 68, 783 (1978).*

13) *We found that $^1\Delta(^{13}C)$ in polymethyl- and polyphenyl methanes changes systematically with the number of methyl and phenyl groups, respectively (J.R.Wesener, Diploma thesis, Siegen 1982).*

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