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IS 100% s-CHARACTER NECESSARY?

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There has been considerable interest in correlations between the %s character in a C-H or C-C bond and other chemical properties such as acidity, bond strength, and ir stretching frequency.[2] The %s character of a C-H bond has customarily been found via correlation of this value with the ^{13}C-H coupling constant. That is, $J_{CH} = a(\%s) - b$ Hz where the precise values of a and b may vary with the original reference cited.[3] (We choose the values a = 5.70 and b = 18.4 as given in reference 4.) The %s character of a C-C bond may likewise be expressed through the functional form $^1J_{CC} = c(\%s_A)(\%s_B) - d$ Hz[3,4] where c and d are likewise "variable". (We choose the values c = 0.0621 and d = 10.2 as given in reference 4.) Let us concentrate on C-C bonds, and although quantum chemical calculations on numerous hydrocarbons exist,[4] let us take a purely empirical approach.

Let us initially discuss neopentane, $C(CH_3)_4$ as it is tetrahedral and so contains one type of C-H and one type of C-C bond. From the two different reported experimental C-H coupling constants, 124.9 or 130.3 Hz,[5] we deduce the C-H bond has 25.1 or 26.1 %s character. Following the normal, if implicit, assumption of 100%s character around a given carbon, we deduce the CH_3 in the CH_3-C bond is contributing an orbital which is 24.7 or 21.7 %s. We may now connect the C-C coupling constant and the %s of the bonds from the central carbon. Using the above $^1J_{CC} = 0.0621(\%s_A)(\%s_B) - 10.2$ Hz, the experimental coupling constant (35.7 Hz)[5b] and $\%s_A$ (= 24.7 or 21.7%) from above, we deduce the %s of the bonds from the central carbon to be 29.9 or 34.1 %s. We so conclude that this central bond does not have 100%s character around it but rather 120 or 136 %s! Alternatively, we may assert that this central carbon is clearly sp^3 hybridized and so derive the %s character on the methyl carbons. This gives us a value of 29.6 %s, which given the above information about the C-H bonds in neopentane gives a total %s character for the methyl carbons to be 105 or 108%, again in disagreement with the 100% s character assumption.

Using this latter procedure, the individual errors per carbon seem to be small, and we are reminded of the scatter of points in the various references cited in footnotes 3 and 4. However, noting the small %s difference between sp^3 and sp^4

and yet the great differences between propane and cyclopropane makes us leery of this exoneration. Furthermore, implicit in fitting our equations for %s character and coupling constants is the assumption that CH_4 is sp^3 hybridized. This assumption has been recently challenged via ab-initio quantum chemical calculations: it has been argued that s-p hybridization is irrelevant for the tetrahedral geometry for this species[6] but rather nuclear repulsion between the hydrogens is the dominant effect.[7] Because of the high symmetry, both methane and neopentane might be viewed as special cases although one would have thought that the 100%s character assumption would be most valid here.

Let us now qualitatively show why this assumption should not be assumed true in general. Consider a carbon atom and four substituents bonded to it, i.e. some CTUVW molecule. In the simplest model,[8] we have four orbitals from the carbon, the 2s, $2p_x$, $2p_y$ and $2p_z$, and one orbital each from the four groups, t,u,v and w. From these eight atomic and substituent orbitals, we now construct eight molecular orbitals. Following conventional assumptions, we place two electrons in each of the new orbitals until all eight electrons have been used in this bonding. We thus have four occupied orbitals. While symmetry might imply constraints (e.g. for tetrahedral species three of these four must have p-like or T_2 symmetry), we are not forced to utilize the carbon 2s orbital the same as the $2p_x$, $2p_y$ or $2p_z$ orbitals. This utilization applies equally to each bond individually and to the molecule: equivalently, we need not average 25% s character per bond nor have 100%s character around the central carbon.

Table I presents a collection of molecules and the %s character around each carbon as deduced by varying assumptions.

It is to be seen that the %s character rarely totals to 100% and also varies with the assumptions made. Analogous results could have been presented for many additional hetero derivatives but the necessary constants for determining %s character of many types of carbon-hetero bonds are lacking. The known properties of fluorocarbons indicate that the hybridization of CF_4 does not correspond to sp^3 [5a,8,9] and thus our warnings are clearly even more important in hetro derivatives.

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Table I

Calculated Total s-Character of Selected Carbon Atoms [a]

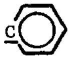
Molecule	$^1\underline{J}_{CH}$(Hz)	$^1\underline{J}_{CC}$(Hz)	Total %s-Character[a]	Comments [b,c]
$\underline{C}H_3 - CH_3$	+125.0	34.6	102.5	
$\underline{C}H_2 = CH_2$	+156.2	67.2	96.5	
$H\underline{C} \equiv CH$	+248.7	170.6	100.9	
$H\underline{C} \equiv C\ C_6H_5$	251	175.9	102.0	Assume symmetrical triple bond
H - 	159	57.0	96.9	
$CH_2 = C = \underline{C}H_2$	168	98.7	100.5	Assume central carbon is sp hybridized (Ref. 10)
$\underline{C}H_3 - C_6H_5$	136.2	44.2	107.6	Assume sp^2 hybridized aromatic carbon
$\underline{C}H_3 - C \equiv C - C_6H_5$	131.3	68.6	104.3	Assume sp hybridized acetylene carbon
$\underline{C}H_3 - C \equiv CH$	131	67.4	105.4	Use $^1J_{CH} = 247.6$ Hz for ≡ C-H and assume the same hybridization for $\equiv C\text{-}CH_3$ acetylenic carbon
$\underline{C}H_3 - C \equiv CH$			103.6	Assume $\equiv C\text{-}CH_3$ acetylenic carbon is sp hybridized
$\underline{C}H_3 - CN$	136	56.5	102.8	Assume CN is sp hybridized
$\underline{C}H_3 - C(CH_3)_2CN$	129	33.6(CH_3-C) 56.5(C-CN)	110.5	Assume CN is sp hybridized and calculate out toward methyl group (Ref. 11)
$(CH_3)_3\ \underline{C}\ CN$			116.3	Assume -CN is sp hybridized and $-CH_3$ carbon uses 1.00 s orbital
			106.1	Assume -CN is sp hybridized and $-CH_3$ is sp^3 hybridized

Table I continued

Molecule	$^{1}J_{CH}$ (Hz)	$^{1}J_{CC}$ (Hz)	Total %s-Character[a]	Comments[b,c]
CH_3- $\underline{C}H_2$- CN	135.5	33.0(CH_3-C) 55.2(C-CN)	102.9	Assume CN is sp and $-CH_3$ is sp^3 hybridized (Ref. 11)
H - 	152	53.5	91.5	Assume C_3 is sp^2 hybridized (Ref. 12)

a) The equations presented by Newton and Schulman[4] are used in conjunction with experimental nmr coupling constants to obtain s-character;

b) Data from Ref. 5 or J.W. Emsley, J. Feeney and L.H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1966, Chapter 12, unless otherwise indicated.

c) It should be pointed out that about half of the entries in the table still calculate to other than 100% s-character even when allowance is made for the standard deviations in the equations.

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