Studies of $^{13}C-^{13}C$ Coupling Constants. V. Ethyl, Isopropyl, and *tert*-Butyl Compounds[1]

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Abstract: $^{13}C-^{13}C$ coupling constants were obtained on a series of isopropyl and *tert*-butyl compounds. Spectra were obtained on natural-abundance samples using pulse-Fourier transform techniques. The results were compared with previously published data on ethyl compounds. For a given substituent, J_{CC} generally increases with increased methyl substitution. Standard arguments in terms of electronic effects seem incapable of explaining this trend. Steric factors appear to be operative.

The results of a systematic study of $^{13}C-^{13}C$ coupling constants in ethyl compounds have recently been reported.[2] That study provided basic experimental data on the effects of substituents on J_{CC} in one of the simplest hydrocarbon frameworks available. The finite perturbation–INDO method[3,4] was employed in the interpretation and led to the conclusion that the variations of $^{13}C-^{13}C$ coupling constants in the ethyl series are associated with a type of substituent characteristic that Pople and Gordon[5] refer to as "$-I^+$." The $-I^+$ label describes a substituent that withdraws electron density from the substrate carbon framework and polarizes it in the sense in which the β carbon has a higher electron density than the α carbon.

To explore the range of applicability of the trends and tentative interpretations found for the ethyl compounds, these studies were extended in the work reported here to include the effects of branching in the hydrocarbon framework. As part of a general research program on $^{13}C-^{13}C$ coupling constants, the present study was focused upon isopropyl and *tert*-butyl compounds and included an extension of the data on the ethyl system. The present work was carried out on natural-abundance samples, using the pulse-Fourier transform approach.

It is expected that with the growing use of Fourier transform techniques,[6] making it possible to obtain J_{CC} data from natural-abundance samples, the utility of and interest in that parameter will develop rapidly in the near future. Ultimately, detailed information on structural and substituent effects should be available from J_{CC} studies. Furthermore, $^{13}C-^{13}C$ coupling constants should develop as a useful aid in making ^{13}C peak assignments.[7]

Experimental Section

Materials. All materials used in this study, with the exceptions of isopropyl methyl ether and ethyl methyl ether, were obtained from standard commercial sources. Isopropyl methyl ether and ethyl methyl ether were prepared by the Williamson method.[8] Purities were checked by proton and carbon-13 nmr.

Techniques. The spectrometer employed is a Bruker Model HFX-90 which is interfaced to a Digilab FTS/NMR-3 data system and operates at 22.635 MHz for ^{13}C. The combined system was operated in the pulse-Fourier transform mode, employing the Digilab 400-2 pulse unit. Typical pulse widths were 40 μsec, and the delay time between pulses was fixed at 1.8 sec. Generally, the conditions used yielded a signal-to-noise ratio of approximately 400:1 per natural-abundance carbon, or about 5:1 for $^{13}C-^{13}C$ coupling satellites. Typically 30–120 min of data accumulation was employed. Field-frequency stabilization was maintained by locking on the ^{19}F signal from hexafluorobenzene, either dissolved (10% by vol) in the otherwise neat sample or in a 1.75-mm capillary held concentrically inside the standard 10-mm sample tube. Those samples whose spectra were obtained at other than ambient temperature (310°K) required the use of the Bruker B-ST 100/700 temperature control unit.

Results and Discussion

Figure 1 depicts a typical spectrum (the region of the CH carbon of diisopropyl ether). The truncated central peak is due to the naturally occurring molecules containing a ^{13}C isotope only at those CH positions. The satellite peaks are then due to those naturally occurring molecules with ^{13}C isotopes at the CH position and at a methyl position. The intersatellite separation measures the carbon–carbon coupling constant. Multiple determinations were made of each coupling constant to ensure reproducibility.

J_{CC} data obtained in this study, along with previously published data on J_{CC} for ethyl compounds[2] and on J_{CH} for methyl compounds,[9-13] are summarized in Table I. The $^{13}C-^{13}C$ coupling constant data in that table indicate that for each of the ethyl, isopropyl, and *tert*-butyl series a rough correlation exists between the value of the coupling constant and the "electronegativity" of the *atom* directly bonded to the hydrocarbon framework. Similar crude relationships were noted earlier for J_{CH} in substituted methanes[9] and J_{CC} in acetyl[14] and isopropenyl[15] compounds. These patterns have been taken as suggestive that similar substituent-

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[1] Supported by a grant from the Research Corporation and Biomedical Sciences Support Grant No. 5 SO5 RR07127-03 from the National Institutes of Health.

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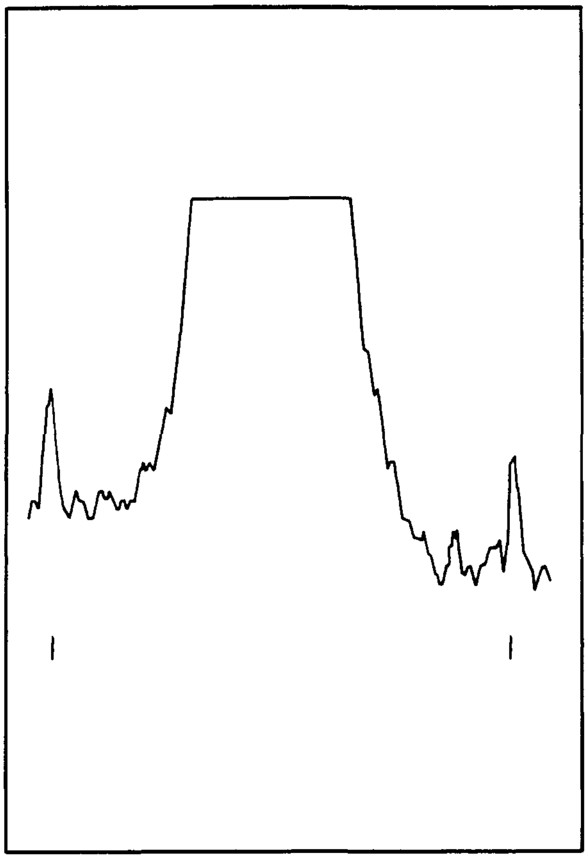

Figure 1. Spectral region of the CH carbon of diisopropyl ether.

Table I. Effects of Substituents and Branching on Directly Bonded Coupling Constants

X	J_{CC} in RX[a] Et[c]	*i*-Pr[d]	*t*-Bu[d]	J_{CH} in CH_3X	Ref[b]
CN	33.0 ± 0.5[e]		33.6[e]	136	9
CH_3	33 ± 2		33.7[f]	124.9	10
C_6H_5	34.2[d]	34.8	35.7	126	9
H	34.6	33 ± 2[c]		125	11
CO_2H	34.8	34.4	35.3[g]	130	9
$COCH_3$	35.5[d]	34.7	34.9	126	9
NO_2	35.7	36.3	37.6	146.7	12
NH_2	35.8	37.3[h]	37.6[h]	133	9
I	35.8	36.7	36.6 ± 0.5[i]	151	9
Br	36.0	37.1	37.8	152	9
Cl	36.1	37.3[j]	38.0	150	9
OH	37.7[e]	38.6	39.6[k]	141	9
OR[l]	38.9	39.9			
OCH_3	39.0[d,h]	39.9[m]	40.3	140	13

[a] Accuracy is ±0.15 Hz unless otherwise noted. [b] Reference is to source of J_{CH} data. [c] Values obtained from ref 2 unless otherwise noted. [d] Values determined in this work. [e] Values obtained from ref 14b. [f] Sample temperature, 265°K. [g] Sample temperature, 320°K. [h] Sample temperature, 296°K. [i] Determined from the separation of the central peaks in the second-order (AB) spectrum and the known value of the chemical shift, 1.4 ppm (P. C. Lauterbur, *Ann. N. Y. Acad. Sci.*, **70**, 841 (1958)). [j] Sample temperature, 290°K. [k] Sample temperature, 315°K. [l] Symmetric ether compound. [m] Sample temperature, 280°K.

effect mechanisms are operative in these various coupled systems.

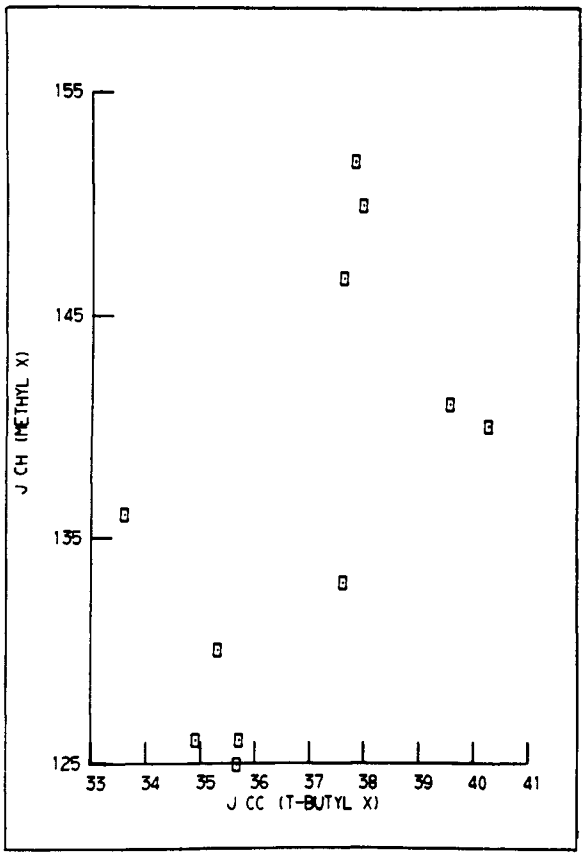

Figure 2. Relationship of J_{CH} in CH_3X to J_{CC} in $(CH_3)_3CX$ as the substituent X is varied. X values as J_{CH} increases are: CH_3, $COCH_3$, C_6H_5, CO_2H, NH_2, CN, OCH_3, OH, NO_2, Cl, Br.

The most popular prevailing view of such mechanisms is that formulated originally by Muller and Pritchard[9] for the dependence of J_{CH} in substituted methanes on the nature of the substituent. According to that view, an electron-withdrawing influence of a substituent tends to increase the 2p character of the carbon hybrid orbital involved in the σ bond to the substituent. This, in turn, tends to enrich the 2s character of the carbon hybrid orbital in the C–H bond, which, according to simple views of Fermi contact coupling, tends to increase the value of J_{CH}. This same type of argument has been applied with some qualitative success in interpreting J_{CC} data.[16] Using their limited data on ^{13}C–^{13}C couplings in the *tert*-butyl series, Grant and Litchman[17] suggested a near-linear relationship between J_{CH} in a series of substituted methanes and J_{CC} in the corresponding *tert*-butyl compounds. This was suggestive that simple views in terms of hybridization parameters might be applicable to ^{13}C–^{13}C coupling constants, at least in the system studied. A more complete and accurate set of J_{CC} data from this study, on the same system, is plotted in Figure 2; clearly, no such linear relationship exists. This lack of correlation supports previous suggestions[2,14,15] that *literal* interpretations of substituent effects based on Muller and Pritchard's simple view are not generally justified in these J_{CC} systems.

Examination of J_{CC} data in Table I shows that all substituents except those containing a carbonyl group (CO_2H, $COCH_3$) and possibly the methyl and cyano groups, obey the rule $J_{CC}^{Et} < J_{CC}^{i\text{-}Pr} < J_{CC}^{t\text{-}Bu}$. Furthermore, with one additional exception ($X = C_6H_5$), all of the other substituents have J_{CC} values for the ethyl case *higher* than that of ethane itself. On a

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general qualitative basis, this pair of patterns is at first somewhat surprising. For whatever the nature of a substituent's effect on the hydrocarbon framework, one might expect the effect to be dissipated somewhat as the number of methyl groups attached to the α carbon increases. That is, one might expect the effect of the substituent to become "diffused" over an increasing number of equivalent C–C bonds in going from ethyl to isopropyl to *tert*-butyl. This view rests on the assumption that a C–CH_3 moiety can accommodate more of a given substituent's perturbing influence than can a C–H moiety in the analogous position. For those substituents that cause an increase in J_{CC} relative to the parent hydrocarbon within a given series, this type of reasoning would lead to anticipation of the order $J_{CC}^{Et} > J_{CC}^{i\text{-}Pr} > J_{CC}^{t\text{-}Bu}$ for a given substituent. Experimentally, this is not the case. However, the ranges of J_{CC} in all three series are about the same, which would tend to imply that a given change of substituent has approximately the same effect on a C–C moiety, regardless of whether there are hydrogens or methyl groups attached to the α carbon.

The situation can be treated from a slightly different standpoint by focusing on the C–C bond in an ethyl compound and considering the effects on that bond as methyl groups are substituted for hydrogens. This treatment will, of necessity, be somewhat speculative for the specific relationship between electronic factors in a C–C moiety and the carbon–carbon coupling constant is as yet not well understood. For purposes of exploring the characteristics of the approach, the supposition here will be that electron withdrawal from the C–C moiety enhances the s character in the C–C bond and, based on the Fermi contact mechanism, increases J_{CC}.

Two views of the electronic functionality of alkyl groups as substituents currently find acceptance. The older of these[18] is based on the inductive model, whereby the methyl group is thought to be electron releasing (compared to hydrogen). Most of the data cited in support of this view have come from relative reactivity studies in solution, and the importance of solvation effects received no explicit treatment. More recent work,[19,20] particularly gas-phase studies, indicate that the methyl group acts as a generally polarizable species, able to donate or accept electronic charge as the situation demands. Thus, for example, the order of relative acidities of alcohols observed in the gas phase, neopentyl > *tert*-butyl > isopropyl > ethyl > methyl > water[20] is *reversed* from that observed in solution. Additional methyl groups tend to stabilize the anion in the gas phase, while in solution they apparently hinder solvation, thereby reducing the stability.

Based on the supposition mentioned above, relating J_{CC} to electronic effects in the C–C fragment, applying either theory of the electronic effect of the methyl substituent (relative to hydrogen) to the carbon–carbon coupling constants in these series leads to the same qualitative result. Since the electronegative substituent X in an ethyl compound (CH_3CH_2X) produces an electron deficiency in the C–C moiety, one would expect that substitution of a methyl group for a hydrogen on the α carbon would tend to counteract the effect of the electron-withdrawing substituent X, whether this occurs for a "classical" inductive reason or due to polarizability of the methyl group. Counteracting the electron-withdrawing ability of the X substituent would reduce the s character in the C–C bond and, from simple Fermi contact views, reduce the coupling constant. Further application of this type of argument for the effect of successive substitutions of methyl groups for α hydrogens on a substituted ethane can be made, leading to the same prediction given above; namely, that the order of coupling constants for a given X substituent would be $J_{CC}^{Et} > J_{CC}^{i\text{-}Pr} > J_{CC}^{t\text{-}Bu}$. And as noted previously, the reverse of this order is generally observed.

Our initial suppositions, in conjunction with popular views of the electronic functionality of methyl substituents, seem incapable of explaining the experimental observations. One possible explanation is that the major effect of adding methyl groups at the α position is a steric one. The bulk of a methyl group relative to a hydrogen can cause a redistribution of s character in the bonds of the carbon to which it is attached. That is, the CCH angle on the α carbon of an ethyl compound is likely to be smaller than the CCC angle on the corresponding isopropyl compound, which in turn would be expected to be smaller than the CCC angle on the analogous *tert*-butyl compound. Therefore, associated with this progression from ethyl to isopropyl to *tert*-butyl would be an increase in the s character in the C–C bonds. A corresponding increase in the $^{13}C-^{13}C$ coupling constant would be expected. Support for this argument comes from theoretical calculations.

Finite perturbation–INDO calculations of J_{CC} were carried out for ethyl compounds previously.[2] In the present work we employed the finite perturbation–INDO method to compute J_{CC} values for a series of isopropyl and *tert*-butyl compounds. Similar criteria were employed in this study for choosing conformations for calculation as had been used in the ethyl case. As in the calculations on the ethyl series, geometries used in the computations were based on Pople and Gordon's "standard geometrical model."[5] According to that model, all angles about a tetravalent carbon assume the tetrahedral value. When these geometries were used, it was found that although in many cases the method predicted $J_{CC}^{i\text{-}Pr} > J_{CC}^{Et}$ for a given substituent, the value for $J_{CC}^{t\text{-}Bu}$ was almost invariably lower than the corresponding isopropyl value and, in many cases, lower than J_{CC}^{Et}. The computed results are summarized in Table II.

Data on the actual geometries of the compounds considered here are in most cases not available, precluding their use in the computations. However, a perusal of what data are available[21] for these and related compounds indicates that use of an expanded CCC angle is certainly in order, at least for *tert*-butyl compounds. Increases in the CCC angle in going from an isopropyl compound to the corresponding *tert*-butyl species are 2–6°, based on the sketchy data available. In order to explore the effect of an increase in CCC angle, calculations on *tert*-butyl compounds were

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Table II. Results of Finite Perturbation–INDO Calculations on Ethyl, Isopropyl, and *tert*-Butyl Compounds, C_B–C_A–X^a

	Ethyl[b]				Isopropyl				*tert*-Butyl			
X	$J_{CC}{}^b$	$P_{s_{C_A}s_{C_B}}{}^2$	$P_A{}^c$	P_B	J_{CC}	$P_{s_{C_B}s_{C_A}}{}^2$	P_A	P_B	J_{CC}	$P_{s_{C_A}s_{C_B}}{}^2$	P_A	P_B
CO_2H	39.3	0.0596	4.0186	3.9272	40.6	0.0574	4.0181	3.9315	39.2	0.0545	4.0138	3.9294
$COCH_3$	40.0[d]	0.0593	4.0066	3.9338	39.8	0.0570	3.9935	3.9292	40.5	0.0549	3.9996	3.9308
CN	40.7	0.0588	3.9397	3.9378	40.7	0.0566	3.9336	3.9382	39.9	0.0539	3.9353	3.9374
									(41.1)[e]	(0.0548)		
H	41.5	0.0620	3.9457	3.9457	42.1	0.0602	3.9391	3.9453	42.0	0.0578	3.9398	3.9439
									(43.3)	(0.0589)		
C_6H_5	41.6	0.0599	3.9410	3.9417	44.1	0.0586	3.9422	3.9458	42.0	0.0553	3.9513	3.9404
NO_2	41.9	0.0624	3.9430	2.9488	44.1	0.0610	3.9368	3.9525	43.0	0.0582	3.9325	3.9503
CH_3	42.1	0.0602	3.9391	3.9453	42.0	0.0578	3.9398	3.9439	41.0	0.0550	3.9461	3.9418
NH_2	47.0	0.0644	3.8223	3.9682	47.2	0.0620	3.8270	3.9657	45.5	0.0586	3.8432	3.9652
OCH_3	47.6[d]	0.0660	3.7478	3.9857	50.8	0.0643	3.7657	3.9860	48.9	0.0610	3.7771	3.9809
									(50.3)	(0.0620)		
OH	49.6	0.0672	3.7495	3.9798	48.7	0.0638	3.7668	3.9858	47.6	0.0608	3.7764	3.9777
F	49.6	0.0679	3.6787	4.0000	50.1	0.0655	3.6890	3.9968	48.7	0.0622	3.7053	3.9933

[a] J_{CC} values in Hz. [b] Taken from ref 2 unless otherwise noted. [c] Valence-shell atomic electron density of carbon A, *i.e.*, $P_{2s2s} + P_{2p_x2p_x} + P_{2p_y2p_y} + P_{2p_z2p_z} = P$. [d] Determined in this study. [e] Values in parentheses correspond to calculations in which the C_B–C_A–C_B angle is 115°.

carried out for selected substituents using CCC angles larger (by 5.5°) than the tetrahedral value. The resulting shifts in J_{CC}, shown in Table II, are of the appropriate sense so as to bring the computed results into more general qualitative agreement with experiment. It was found that the majority of the increase in computed J_{CC} upon expanding the CCC angle is accounted for, as expected, by altered carbon hybridization, as manifested by changes in $P_{s_{C_A}s_{C_B}}{}^2$, the square of the bond order between the 2s orbitals of the coupled carbons.[22]

The experimental data and computed results of this study are consistent with the following view of substituent effects on ^{13}C–^{13}C coupling constants in the ethyl, isopropyl, and *tert*-butyl series. Within a given series, an electron-withdrawing substituent may be considered qualitatively to enhance the s character of the C–C bond and thus to increase the Fermi contact coupling. For a given substituent, substitution of methyl groups for hydrogens at the α carbon tends to increase the s character in the C–C bond by sterically inducing minor changes in bond angles and hence in hybridization. Thus the coupling constant goes up with the number of methyl groups attached to the α carbon. Studies of ^{13}C–^{13}C coupling constants in *n*-propyl, isobutyl, and neopentyl compounds would be useful in testing this interpretation. Experiments to this end are under way. It can be noted that preliminary data on *n*-propyl compounds support the interpretation based upon steric effects.

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Anomalous Kinetic Hydrogen Isotope Effects on the Rate of Ionization of Some Dialkyl Substituted Ketones

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Abstract: The rates of hydroxide catalyzed H^+, D^+, and T^+ transfer from 2,4-dimethyl-3-pentanone and 3,5-dimethyl-4-heptanone have been measured over a temperature range. The Arrhenius plots are linear and the deuterium isotope effects are normal. These results suggest that tunneling is not significant in these reactions. The rates of H^+ and T^+ transfers are similar and apparently there is no tritium isotope effect. The results suggest that in detritiation, T^+ transfer is not the rate determining step. A mechanism for tritium–hydrogen exchange has been proposed.

It was reported[1] that the Arrhenius plot for the bromination of 2,4-dimethyl-3-pentanone catalyzed by hydroxide ion exhibited pronounced curvature at temperatures below 20°. This deviation was ascribed to tunneling of the proton through the energy barrier.[1] The Arrhenius plot for the hydroxide ion catalyzed detritiation[2] of 2,4-dimethyl-3-pentanone showed a sharp break at approximately 40°. This was attributed to a

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