$$d[A]/dt = k_2[\mathbf{8}] - k_1k_2[\mathbf{6}]/(k_{-1} + k_2 + k_3) \quad (31)$$

If $k_3 = 0$

$$d[A]/dt = k_1k_2[\mathbf{6}]/(k_{-1} + k_2) \quad (32)$$

Dividing eq 31 by $k_{-1} + k_2$ and setting $k_3 = k_3'[\text{LiOAc}]$, we have

$$\frac{d[A]}{dt} = \frac{\dfrac{k_1k_2}{k_{-1} + k_2}[\mathbf{6}]}{\left(1 + \dfrac{k'_3[\text{LiOAc}]}{k_{-1} + k_2}\right)} = k_{obsd}[\mathbf{6}] \quad (33)$$

which is of the same form as eq 6.

Labeling Experiments. ^{18}O-Labeled crotonaldehyde was prepared by equilibration. Freshly distilled crotonaldehyde (5 ml) was stirred for 3 days with 1.15 ml of H_2O containing 9% ^{18}O and a trace of *p*-toluenesulfonic acid. The mixture was diluted with ether and the water removed by magnesium sulfate. The crotonaldehyde was isolated by distillation and analyzed for ^{18}O content by mass spectral analysis. The ^{18}O content was 2.93%. The crotonaldehyde was reduced to the alcohol by $NaBH_4$ in aqueous NaOH. The alcohol was esterified with propionic anhydride and the ester isolated and analyzed by mass spectral analysis. The most accurate analysis of ^{18}O content of the crotyl propionate was the carbonyl oxygen using the CH_3CHCO^+ fragment (*m/e* 57).[24] The analysis of the ^{18}O content of the ester oxygen is somewhat less accurate. The carbonyl oxygen of the crotyl propionate contained 0.65% ^{18}O and the ester oxygen 2.1 ± 0.2%. Thus, some scrambling occurred on esterification.

The isomerization run was carried out on a 5-ml scale. It was started by adding 0.2 ml of the labeled crotyl propionate. At various times samples (2 ml for first sample, 1 ml for remaining samples) were withdrawn; 0.01 ml was analyzed by vpc and the remainder diluted with methylene chloride and the acetic acid, and inorganic salts were removed by washing with water. The organic phase was concentrated and the entire sample injected on vpc. The crotyl propionate and 3-buten-2-ol propionate were collected from the vpc eluent in capillary tubes which were analyzed by mass spectral analysis. For the 3-buten-2-ol propionate the most accurate analysis was also the carbonyl oxygen so this is the analysis given in Table IV.

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(24) There is little doubt that *m/e* 57 represents this fragment. No other simple fragmentation pattern will give this peak and the corresponding fragment is found in the spectra of all esters. See, for instance, R. M. Silverstein and G. C. Bossler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1963, p 14.

Positional Dependence of Substituent Effects on Long-Range Couplings in Propane Derivatives[1]

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Abstract: The effect of substituents on $^4J_{HH}$ in propane and neopentane derivatives depends on the point of attachment of the substituent to the atom chain linking the coupled nuclei, suggesting that orbitals of different symmetry types are being perturbed. The results are discussed in light of recent theoretical treatments, and it is suggested that long-range coupling constants are sensitive probes into interaction between substituents and electronic systems.

Recent studies[2-4] of substituent effects on $^4J_{Me,Me}$ in molecules of the types **1a** and **2a** indicated that

1a, R = CH_3 **2a**, R = CH_3
b, R = H **b**, R = H

the behavior of $^4J_{Me,Me}$ parallels that of $^2J_{HH}$ in the series **1b** and **2b** and that the observed trends can be rationalized in terms of a simple, qualitative molecular orbital model proposed independently by us[3] and Barfield and Chakrabarti.[5] According to this model, removal of electrons *via* a σ acceptor or back-donation of electrons by a suitably oriented π type orbital will cause an algebraic increase in $^4J_{HH}$, whereas electron withdrawal *via* a π orbital will cause $^4J_{HH}$ to decrease. Substituent effects on coupling constants therefore appear to be sensitive probes into electronic effects of substituents.

This paper presents data which indicate the effect of a substituent to depend, not only on whether it releases or withdraws electrons, but also on its point of attachment to the atom chain linking the coupled protons. The trends exhibited by our data agree with the predictions of the crude, qualitative model[3,5] and, with one exception, with the results of recent INDO calculations.[6] Support for our interpretation also stems from an empirical parallelism between two-bond and four-bond couplings which we have observed.[2-4]

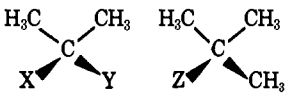
Results

Our attention was first attracted by the observation that the methyl–methylene couplings in neopentyl

(1) Presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972.
(2) D. J. Sardella, *Chem. Commun.*, 1613 (1968).
(3) D. J. Sardella, *J. Mol. Spectrosc.*, 31, 70 (1969).
(4) E. R. Curry and D. J. Sardella, *Proc. Int. Congr. Pure Appl. Chem.*, 23, 342 (1971).
(5) M. Barfield and B. Chakrabarti, *Chem. Rev.*, 69, 757 (1969).
(6) M. Barfield, *J. Amer. Chem. Soc.*, 93, 1066 (1971).

alcohol (0.05 ± 0.02 Hz[7]) and neopentyl chloride (0.15 ± 0.02 Hz[7]) are smaller than in neopentane (+0.35 Hz[8]), whereas in the series neopentane, *tert*-butyl alcohol (0.37 ± 0.03 Hz[3]), *tert*-butyl chloride (0.39 ± 0.03 Hz[3]) the reverse is true.

The same pattern of behavior is exhibited even more strikingly by the parallel series of chlorinated propane and neopentane derivatives **3** and **4**. The data, sum-



3 **4**

marized in Table I, indicate unambiguously that in-

Table I. Substituent Effects on $^4J_{HH}$ in Parallel Propane and Neopentane Series

X, Y	Z	$^4J_{Me,Me}$ in Me_2CXY	$^4J_{Me,H}$ in Me_3CZ
CH_3H	CH_3	+0.27[a]	+0.35[b]
CH_3Cl	CH_2Cl	±0.39[c]	±0.11[d]
Cl, Cl	$CHCl_2$	±0.50[c]	±0.02[d]

[a] Estimated from Figure 1 of ref 3. [b] Reference 8. [c] Reference 3. [d] This work; determined by a double resonance method to be described in detail elsewhere.

creasing electron demand produces different responses in $^4J_{HH}$, depending on the point from which electron withdrawal occurs.

Discussion

Within the framework of the LCAO-MO approximation, the coupling constant between two nuclei H and H′ can be written as[9]

$$J_{HH'} = -h^{-1}(16\pi\beta\hbar/3)^2\gamma^2\sum_i^{occ}\sum_j^{unocc}({}^3\Delta E_{i\to j})^{-1} \times \sum_{\lambda\mu\nu\sigma} c_{i\lambda}c_{j\mu}c_{j\nu}c_{i\sigma}\langle\phi_\lambda|\delta(\mathbf{r}_H)|\phi_\mu\rangle\langle\phi_\nu|\mathbf{r}_{H'}|\phi_\sigma\rangle \quad (1)$$

where β is the Bohr magneton, γ is the proton magnetogyric ratio, ${}^3\Delta E_{i\to j}$ are singlet–triplet excitation energies, and the c's are coefficients of atomic orbitals λ, μ, ν, and σ in the ith and jth molecular orbitals. The double sum extends over occupied (i) and unoccupied (j) molecular orbitals.

If only one-center integrals are retained and one-electron wave functions are used, eq 1 becomes

$$J_{HH'} = -h^{-1}(16\pi\beta\hbar/3)^2\gamma^2\langle S_H|\mathbf{r}_H|S_H\rangle\langle S_{H'}|\mathbf{r}_{H'}|S_{H'}\rangle \times \sum_i^{occ}\sum_j^{unocc}(\epsilon_j - \epsilon_i)^{-1}c_{iH}c_{iH'}c_{jH}c_{jH'} \quad (2)$$

where S_H and $S_{H'}$ are 1s orbitals centered on H and H′, respectively, and ϵ_i and ϵ_j are the energies of the molecular orbitals i and j, respectively. This equation forms the basis for the qualitative model of substituent effects on long-range HH coupling constants proposed independently by us[3] and Barfield and Chakrabarti.[5] According to the model, the overall coupling constant consists of a number of contributions which may be positive or negative, depending on the sign of the product $c_{iH}c_{iH'}c_{jH}c_{jH'}$. If the molecular orbitals are classified as symmetric or antisymmetric with respect to reflection in a plane passing through the midpoint of the coupling chain (*i.e.*, C_2 in HC_1C_2-C_3H), then terms involving orbitals of like symmetry contribute negatively to J_{HH}, while terms involving orbitals of unlike symmetry contribute positively. Despite the drastic simplifications involved in the derivation of eq 2, this model has been applied successfully to the qualitative discussion of substituent effects on long-range proton couplings in acetone and related compounds,[2] propane and isobutane derivatives,[3,6] β,β-dimethylstyrenes,[4] propenes,[5] and cyclopentenes, 2,5-dihydropyrroles, and 2,5-dihydrofurans.[10] It also formed the basis for the qualitative discussion of substituent effects on geminal HH coupling constants.[11]

Removal of electrons by a σ orbital attached to C_2 affects eight transitions, the three most heavily weighted of which contribute positively to J_{HH}. Diminution of the atomic orbital coefficients causes a positive shift in the coupling constant. Back-donation of electrons, by π-type orbitals on a substituent, into antisymmetric antibonding orbitals produces the same effect.[3,5] The data cited above support the predictions for σ withdrawal. Although fewer data are available for π back-donation, attachment of a phenyl group to C_2 causes an increase in $^4J_{Me,Me}$ to 0.38 Hz (ΔJ = +0.11 Hz)[3], whereas $^4J_{Me,CH_2}$ in neopentylbenzene appears to be well below 0.2 Hz (> −0.8 Hz), again in agreement with expectation.

In view of the uncertainties involved in deducing this behavior from the qualitative molecular orbital model,[3,5] we sought an additional line of reasoning with which to reinforce Barfield's original predictions[5] and found it in a consideration of geminal ^{13}CH coupling constants. It has been our experience that $^2J_{HH}$ parallels the behavior of $^4J_{HH}$ in symmetry-equivalent bonding situations, and we therefore felt that responses elicited by substituents in series **3** and **4** should be paralleled by those of appropriate two-bond couplings. If one considers two-bond ^{13}CH coupling constants, then in the fragment, ^{13}C–^{12}C–H, electron-withdrawal from ^{12}C should produce an *increase* in $^2J_{CH}$, while electron withdrawal from ^{13}C should produce an algebraic *decrease*. Data drawn from the literature[12] and summarized in Table II support our expectation.

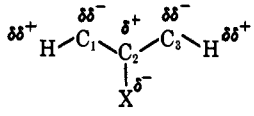
Table II

X	Y	Z	$^2J_{CH}$
		$^{13}CXYZ$-CH_3	
H	H	H	−4.5
H	Cl	Cl	(−)5.1
Cl	Cl	Cl	(−)5.9
		$Cl_2{}^{13}CH$-CHXY	
H	H		(−)5.1
Cl	H		(−)2.5
Cl	Cl		+1.2

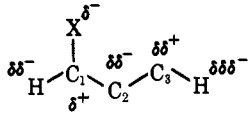
(7) Estimated by superposition on experimental line shapes of multiplets constructed from experimental singlet line shapes.
(8) H. Dreeskamp, *Z. Phys. Chem. (Frankfurt am Main)*, **59**, 321 (1968).
(9) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).
(10) M. Barfield, R. J. Spear, and S. Sternhell, *J. Amer. Chem. Soc.*, **93**, 5322 (1971).
(11) J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).
(12) C. J. Jameson and M. C. Damasco, *Mol. Phys.*, **18**, 491 (1970).

In the most elaborate theoretical investigation thus far, Barfield[6] performed INDO calculations on cyano- and fluoropropanes and -propenes. While the signs of the couplings are not infallibly predicted, the trends in $^4J_{HH}$ with substitution are faithfully reproduced. The only exception is that $^4J_{Me,CH_2}$ in 1-fluoropropane is predicted to be slightly more positive (−0.22 Hz) than $^4J_{Me,Me}$ in propane (−0.28 Hz).

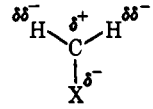
Very recently, Williamson, Mosser, and Stedman[13] have reported a similar sensitivity of $^3J_{HF}$ to the point of attachment of the substituent in mono- and difluorocyclopropanes. They ascribe this behavior to alternating substituent-induced charge densities, an effect first noted in the CNDO calculations of Pople and Gordon.[14] In terms of Williamson's explanation, electron withdrawal from the central carbon in a propanic fragment would result in the pattern of induced charges shown below.



By contrast, removal of electrons from either C_1 or C_3 would result in the following pattern.



One should therefore expect differently placed substituents to exert opposite effects on $^4J_{HH}$, as we observe. However, we feel the explanation to be inadequate to explain our data in two respects. First, accepting Williamson's assumption that greater electron density is associated with greater coupling, we anticipate increasingly electronegative substituents at C_2 should decrease $^4J_{HH}$, while electron withdrawal from C_1 or C_3 should cause an increase. The opposite is true. Second, application of the alternating charge density argument to geminal HH couplings leads to the prediction that $^2J_{HH}$ and $^4J_{CH_3,CH_3}$ should respond



differently to electron withdrawal, $^2J_{HH}$ becoming more positive while $^4J_{CH_3,CH_3}$ becomes more negative. In fact, their parallel behavior is striking.[2-4] We feel, therefore, that an explanation based solely on variations in electron density is too crude to explain the data and that we must consider the nature of electron redistribution at the orbital level.

Both experiment and calculations point up the extreme sensitivity of substituent effects on long- (and short-) range coupling constants to the position of attachment of the substituent to the atom chain through which coupling occurs. This suggests that orbitals of different symmetry types[15] are being affected, and this in turn suggests that long-range coupling constants may serve as sensitive probes into interactions between substituents and molecular electronic systems at the orbital level.

Experimental Section

Nmr spectra were recorded on a Varian Associates HA-60-IL spectrometer operating at 60 MHz in the frequency-swept mode. Magnitudes of long-range coupling constants were determined either directly (*e.g.*, in the series Me_3CX^2), or by construction of unresolved multiplets by superposition of experimental singlet line shapes, or by a double resonance method developed in our laboratory and which will be described in detail elsewhere. Precision of the measurements exceeded ±0.03 Hz in all cases. Samples were undegassed.

Acknowledgment. This work was supported in part by a Boston College Summer Faculty Fellowship, which is gratefully acknowledged.

(13) K. L. Williamson, S. Mosser, and D. E. Stedman, *J. Amer. Chem. Soc.*, 93, 7208 (1971).

(14) J. A. Pople and M. Gordon, *ibid.*, 89, 4253 (1967).

(15) The term "symmetry" in this context is meant to refer to the idealized symmetry which the group orbital in the molecular fragment HCCCH would possess if it were isolated from the asymmetric perturbation imposed by the rest of the molecule.