The Structural Dependence of the Inductive Effect. Part VI.[1a] The Calculation of Vicinal Proton–Proton Spin–Spin Coupling Constants in Substituted Ethanes

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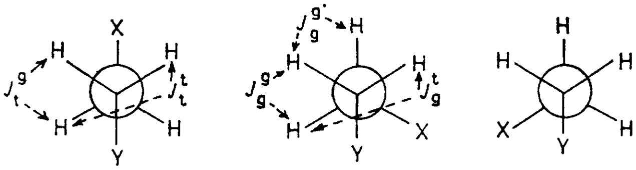
The effects of substituents upon vicinal coupling constants between protons in individual rotational isomers of some substituted ethanes are analysed by a method analogous to that developed for nuclear shielding. Equations are given which enable such coupling constants to be calculated to a satisfactorily high degree of precision (±0·18—0·27 Hz) and which explain certain trends which were not explicable by previous treatments

OUR interest in the structural dependence of the inductive effect has led us to evolve a new method of calculating chemical shifts of several different types of nuclei in a variety of molecules.[1b] A consideration of the n.m.r. parameters of the deoxyfluoro-D-glucopyranoses indicates that many of the structural parameters affecting chemical shifts also affect vicinal coupling constants,[2] and an approach similar to that used for studying chemical shifts may be fruitful.

The simplest situation in which an analysis of the inductive effects of substituents upon vicinal coupling constants may be made is that of the vicinal H–H couplings in the individual rotational isomers of substituted ethanes. A survey of the literature indicates that the only extensive and reliable data are those of Abraham and Gatti [3] on the vicinal couplings in XCH_2CH_2Y, while a theoretical consideration, using extended Hückel MO theory to calculate the effect of substituents on vicinal couplings in mono-substituted ethanes, has been made by Pachler.[4,5]

The molecule XCH_2CH_2Y has three rotational isomers and these are presented in Figure 1 using the nomenclature of Abraham; [3] superscripts denote the orientation of the coupled protons, and subscripts denote the isomer.



trans *gauche*

FIGURE 1

As in the previous work [6-10] Abraham has analysed his data by plotting the sum of the Huggins electronegativities of the substituents X and Y against the appropriate set of couplings. The results fit the equations (1)—(4).

$$J^{g}_{t} = 1{\cdot}35 + 0{\cdot}63(E_X + E_Y) \qquad (1)$$

$$J^{t}_{t} = 18{\cdot}07 - 0{\cdot}88(E_X + E_Y) \qquad (2)$$

$$J^{g}_{g} = 8{\cdot}94 - 0{\cdot}94(E_X + E_Y) \qquad (3)$$

$$J^{t}_{g} + J^{g'}_{g} = 26{\cdot}92 - 2{\cdot}03\,(E_X + E_Y) \qquad (4)$$

Using the values of $J^{g'}_{g}$ obtained from low-temperature measurements upon the spectra of cyclohexane, morpholine, and the fixed conformation of *trans*-2,3-dimethyl-1,4-dioxan the following equation was obtained:

$$J^{g'}_{g} = 10{\cdot}45 - 1{\cdot}43(E_X + E_Y) \qquad (5)$$

Subtracting (5) from (4) gives

$$J^{t}_{g} = 16{\cdot}47 - 0{\cdot}60(E_X + E_Y) \qquad (6)$$

For a monosubstituted ethane, CH_3CH_2Y, J^{g}_{t} and J^{g}_{g} are identical because of symmetry, and both equations (1) and (3) should give the same result. This is not the case as shown below.

	J^{g}_{t} calc. [eq. (1)]	J^{g}_{g} calc. [eq. (3)]
CH_3CH_3	4·12 Hz	4·80 Hz
CH_3CH_2F	5·19 Hz	3·21 Hz

The calculated values of J diverge as the electronegativity of Y increases, and equation (1) indicates that the *gauche* coupling [J^{60}_{60}, Pachler [5]] increases on changing the substituent from H to F while equation (3) predicts that it decreases in magnitude. The theoretical calculations of Pachler, however, suggest that an increase of +0·67 Hz is to be expected.

We present here an alternative analysis of the data of Abraham.

RESULTS AND DISCUSSION

By analogy with the method previously described for chemical shifts [1b] we consider the effect upon the coupling constant of varying one substituent while the other is kept constant. This is shown graphically in Figure 2 for J^{g}_{g}, where Y is varied for particular X substituents. Here it is shown that J^{g}_{g} may increase *or* decrease with increasing electronegativity of Y, depending upon the substituent X. The slope of these lines depends linearly upon the Huggins electronegativity of X, as shown in Figure 3. Using the slopes and intercepts of these figures, J^{g}_{g} may be expressed as in equation (7). This

$$J^{g}_{g} = 3{\cdot}40 + (E_Y - 1{\cdot}93)(2{\cdot}950 - 1{\cdot}003E_X) \qquad (7)$$

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[1] (*a*) Part V, L. Phillips and V. Wray, *J.C.S. Perkin II*, 1972, **223**; (*b*) *ibid.*, p. 214.

[2] L. Phillips and V. Wray, *J. Chem. Soc.* (*B*), 1971, 1618.

[3] R. J. Abraham and G. Gatti, *J. Chem. Soc.* (*B*), 1969, 961.

[4] K. G. Pachler, *Tetrahedron Letters*, 1970, 1955.

[5] K. G. Pachler, *Tetrahedron*, 1971, **27**, 187.

[6] R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, 1963, **7**, 165.

[7] R. E. Glick and A. A. Bothner-By, *J. Chem. Phys.*, 1956, **25**, 362.

[8] C. N. Banwell and N. Sheppard, *Discuss. Faraday Soc.* 1962, **34**, 115.

[9] R. J. Abraham and L. Cavalli, *Mol. Phys.*, 1965, **9**, 67.

[10] L. D. Hall and J. F. Manville, *Chem. Comm.*, 1968, 37.

Comparison of ${}^3J_{HH}$(obs) for XCH_2CH_2Y with the calculated values from previous work [eqns. (1) and (3)] and the present work [eqns. (7) and (9)]

X	Y	J_t^g (obs)	J_t^g [eq. (1)]	J_t^g [eq. (9)]	J_g^g (obs)	J_g^g [eq. (3)]	J_g^g [eq. (7)]	J_t^t	J_g^t
C	Li	3·5	3·59	3·53				15·5	
C	Mg	4·2	3·81	3·72				14·2	
C	Al	3·9	4·00	3·91				14·2	
C	Si	4·0	4·19	4·05				13·9	
C	C	4·3	4·63	4·44	3·59	4·05	3·63	12·94	13·31
I	I	5·0	4·69	4·50	4·0	3·96	3·61	14·0	11·93
C	N	4·62	4·91	4·14	3·77	3·63	3·78	12·75	13·43
Br	Br	5·2	5·07	4·90	3·6	3·39	3·39	13·4	12·39
Cl	Br	5·1	5·19	5·06	3·3	3·21	3·19	13·0	12·77
C	O				3·87	3·21	3·94		13·07
N	N				2·98	3·21	3·28		11·57
Cl	Cl	5·4	5·32	5·20	2·9	3·02	3·15	12·5	12·86
O	N				2·84	2·78	2·77		12·12
F	Br	5·5	5·67	5·61	2·4	2·50	2·42	12·1	12·45
O	O				2·66	2·36	2·52		11·69
F	Cl	5·9	5·79	5·82	2·1	2·31	2·23	11·5	12·33
F	F	6·3	6·26	6·59	1·43	1·61	1·51		12·00
R.M.S. ±			0·21	0·27		0·28	0·18		

equation may now be tested by calculation of J_g^g in all the situations presented in the Table where the observed and calculated values are compared. The root mean deviation from the experimental values, 0·18 Hz, is better than that obtained by Abraham; of greater importance however is the fact that this equation shows that for monosubstituted ethanes (Y = substituent, X = H) J_g^g will *increase* with *increased* electronegativity of Y in agreement with the theoretical treatment of Pachler (change in J_g^g for CH_3CH_3 to CH_3CH_2F $+1{\cdot}2$ Hz) and at variance with equation (3) of Abraham. It may be noted that when X has an electronegativity of 2·99 Huggins units (~Br, 2·95) a change in the electronegativity of Y will apparently have *no* effect upon J_g^g which will stay constant at 3·40 Hz.

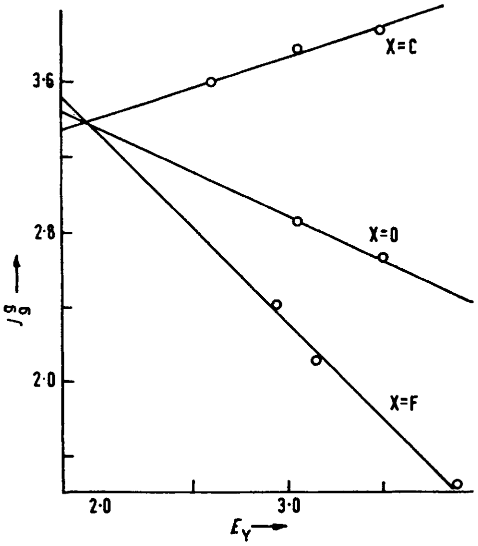

FIGURE 2 J_g^g in XCH_2CH_2Y plotted against E_Y for particular X substituents

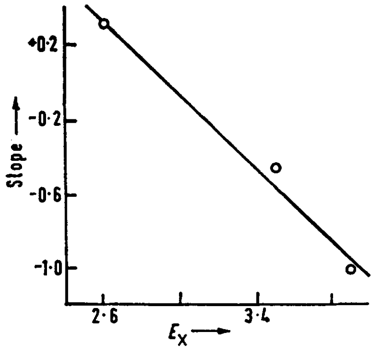

FIGURE 3 Slopes from Figure 2 plotted against E_X

The effect upon J_g^g of varying X for particular Y substituents is shown in Figure 4. Here it is clear that the value of J_g^g always decreases with increasing electronegativity of X and is almost independent of Y. Thus a straight plot of J_g^g against E_X gives a satisfactory correlation (Figure 4) with an equation of the form

$$J_g^g = 7{\cdot}47 - 1{\cdot}39\,E_X \qquad (8)\,*$$

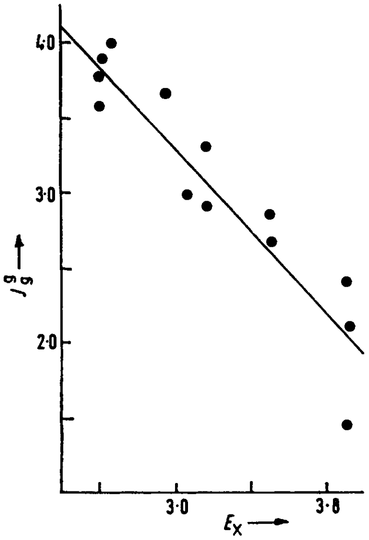

FIGURE 4 J_g^g in XCH_2CH_2Y plotted against E_X for particular Y substituents

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* This is less precise than equation (7). It is included to illustrate the sensitivity of such a coupling constant to changes in X (which is *trans* to one of the coupled species) and the relative insensitivity to Y (which bears a *gauche* relationship to a coupled nucleus).

The other gauche couplings may be analysed similarly and the results are shown graphically for J^{g}_{t} in Figures 5 and 6, while $J^{g'}_{g}$ will be given by equation (5); J^{g}_{t} will be given by an equation analogous to (7):

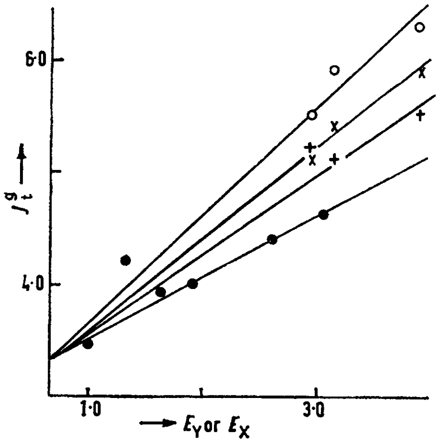

FIGURE 5 J^{g}_{t} in XCH_2CH_2Y plotted against E_Y (or E_X) for a particular X (or Y) substituent; ○ = F, × = Cl, + = Br, ● = C

$$J^{g}_{t} = 3{\cdot}51 + (E_Y - 0{\cdot}91)(0{\cdot}367E_X - 0{\cdot}402) \quad (9)$$

Using equation (9), all the values of J^{g}_{t} may be calculated and these are compared with the experimental values in the Table. The r.m.s. of 0·27 is acceptable (Abraham 0·21). It may be seen that J^{g}_{t} would be 3·51 Hz and show *no* variation with the change of one substituent if the other had an electronegativity of 1·10 and would indeed decrease if E_X was less than 1·10, a situation difficult to realise in practice. Equation (9) predicts an increase in J^{60}_{60} (ref. 5) on going from CH_3CH_3 to CH_3CH_2F with comparable values to those from equation (7) as shown below.

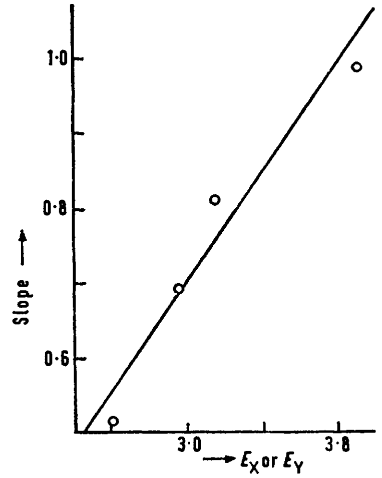

FIGURE 6 Slopes from Figure 5 plotted against E_X (or E_Y)

	C_2H_6	C_2H_5F	Difference
J^{g}_{g} (Hz)	3·60	4·86	+1·26
J^{g}_{t} (Hz)	4·03	4·72	+0·75
		4·84	

The behaviour of $J^{g'}_{g}$ and J^{g}_{g} with respect to changes in the electronegativity of X and Y is interesting. $J^{g'}_{g}$ Is a coupling between two protons, and the group X is in a *trans*-coplanar relationship to one of them and Y is in a *trans*-coplanar relationship to the other; its magnitude decreases linearly with increase of electronegativity of both X and Y. On the other hand, J^{g}_{g} is a coupling between two protons only one of which has a *trans*-substituent, X, while the other is in a *gauche* relation to Y; the magnitude of J^{g}_{g} is much more sensitive to changes in X than to changes in Y. A plot of J^{g}_{g} against E_X has a similar slope to a plot of $J^{g'}_{g}$ against $E_X + E_Y$ (−1·39 *cf.* −1·43), and the relationship clearly verifies the postulate of Booth and others [11,12] that substituents exert a maximum effect when they are in a *trans*-coplanar relationship with respect to either of the coupled nuclei. We have recently shown that vicinal substituent effects upon nuclear shielding are also at a maximum when a *trans*-coplanar arrangement exists between the substituent and the nucleus, and this has been analysed in terms of geminal and 'primary vicinal' σ electronic delocalisation interactions; [1a] the same interpretation holds for coupling constants.

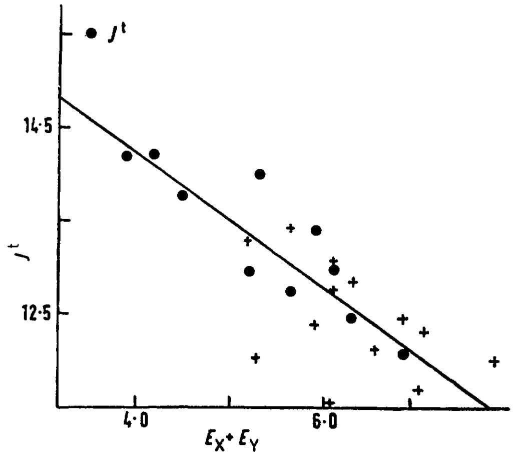

FIGURE 7 J^t in XCH_2CH_2Y plotted against $E_X + E_Y$; J^{t}_{t} = ●, J^{t}_{g} = +

Neither of the nuclei involved in the couplings designated as J^{t}_{t} and J^{t}_{g} has a *trans*-substituent; it would, therefore, be expected that they should show very similar dependence upon substituent electronegativity. Abraham has concluded, however, that the influence of substituents is much greater upon J^{t}_{t} than upon J^{t}_{g}. A plot of values of J^{t}_{t} and J^{t}_{g} against $(E_X + E_Y)$ is shown in Figure 7, [J^{t}_{g} values are calculated using equation (5) and experimental values of $J^{t}_{g} + J^{g'}_{g}$ (Table)]. It may be concluded that the plot is linear within experimental error and that both sets of coupling constants lie on the same line, which is in accord with the present picture.

Pachler [5] has discussed Abraham's results qualitatively by assuming an additivity of substituent effects. The

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[11] H. Booth, *Tetrahedron Letters*, 1965, 411.

[12] N. S. Bhacca and D. H. Williams, 'Applications of N.M.R. Spectroscopy in Organic Chemistry,' Holden-Day, San Francisco, 1964.

present work indicates that for J^{g}_{g} such an assumption is invalid, as the magnitude of the variation in coupling with substituent change depends upon the other substituents present in the molecule. This type of phenomenon would also account for the remarkable variation in $^{3}J_{\mathrm{HH}}$ couplings in the fluoroethanes recently observed by Abraham and Kemp.[13]

An extension of the above approach to $^{3}J_{\mathrm{HF}}$ is clearly necessary although a further difficulty arises in that molecules with identical groups show different values for the same coupling depending upon whether the substituent is attached to the CH end or CF end of the CH·CF fragment.[2,13] By analogy with previous studies upon nuclear shielding, this may arise from different 'secondary geminal' delocalisation interactions of the substituent with H and F.[1b] Such an approach is impending.

[1/1790 *Received, 29th September,* 1971]

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[13] R. J. Abraham and R. H. Kemp, *J. Chem. Soc.* (*B*), 1971, 1240.