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EXTENDED HÜCKEL THEORY MO CALCULATIONS OF PROTON–PROTON COUPLING CONSTANTS—II

THE EFFECT OF SUBSTITUENTS ON VICINAL COUPLINGS IN MONOSUBSTITUTED ETHANES*

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Abstract—Vicinal proton–proton couplings in a series of monosubstituted ethanes have been calculated with the Pople–Santry MO theory of coupling constants. An equation has been derived which describes the dependence of the coupling constants on the dihedral angle between coupling protons and the electronegativity of the substituent. The parameters of this equation as well as the various coupling constants in staggered and eclipsed conformations vary linearly with the electronegativity of the substituents. The theoretical results agree qualitatively with most experimentally observed trends of vicinal proton–proton coupling constants. Simple rules have been formulated, which relate the magnitude of the substituent effect to particular conformations.

INTRODUCTION

VICINAL proton–proton coupling constants in saturated organic compounds depend on a variety of molecular parameters[1,2] such as the dihedral angle between coupling protons, bond lengths and bond angles within a particular CH—CH fragment, other properties like molecular vibrations and electronic excitation energies, and furthermore on the nature and relative position of substituents attached to the CH—CH grouping. Valence bond calculations by Karplus[3] on a CH—CH fragment showed the vicinal couplings to be strongly dependent on the dihedral angle and led to the well known $\cos^2\Phi$-relationship. Changes with bond length and bond angle appear to be minor,[2] particularly in unstrained molecules like substituted ethanes for which these parameters are reasonably constant. The effect of molecular vibrations has also been found to be negligible.[4]

There is, however, ample experimental proof that the influence of substituents attached to a CH—CH fragment is the second important factor, next to the dihedral angle dependence, in determining the magnitude of vicinal coupling constants. Very few attempts have so far been made to assess this effect theoretically. Some early calculations by Hiroike[5] and Ranft[6] showed that a direct inductive effect of an electronegative substituent, which alters the C—H bond polarity, decreases vicinal proton–proton couplings by relatively small amounts. Electronegative substituents will, however, also change the hybridisation of the carbon atom to which they are attached, and this in turn should influence the coupling constants. Karplus[2] has estimated this effect for *cis*- and *trans*-couplings in an ethylene fragment and for the average vicinal coupling constants of ethyl derivatives. A decrease of the couplings with increasing electronegativity of the substituent was predicted which agreed

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* Reference 32 is considered as Part I.

qualitatively with experimental results. Further theoretical assessments of the electronegativity effect on vicinal couplings have only been reported for substituted ethylenes[7, 8] and cyclopropyl[8] derivatives.

This paper presents the results of MO calculations of vicinal coupling constants in a series of monosubstituted ethanes, elucidating the substituent effect in relation to the dihedral angle between the coupling protons and the relative position of the substituent.

METHOD OF CALCULATION

The LCAO-MO theory of coupling constants, originally developed by McConnel,[9] has recently been reformulated by Pople and Santry,[10] avoiding the mean-excitation-energy approximation. According to this theory the Fermi contact term, which is adequate to describe couplings involving protons, can be written as follows*:

$$J_{AB} = C_H \sum_{i}^{occ} \sum_{j}^{unocc} (\varepsilon_i - \varepsilon_j)^{-1} \sum_{\lambda\mu\nu\sigma} c_{i\lambda} c_{j\mu} c_{i\nu} c_{j\sigma} \, (\Phi_\lambda|\delta(r_A)|\Phi_\mu)(\Phi_\nu|\delta(r_B)|\Phi_\sigma) \tag{1}$$

with $C_H = -(8\beta\gamma_H/3)^2 h$.

Equation (1) may be simplified by retaining only one-centre integrals involving valence shell s-orbitals on nuclei A and B:

$$J_{AB} = C_H (s_A|\delta(r_A)|s_A)(s_B|\delta(r_B)|s_B) \sum_{i}^{occ} \sum_{j}^{unocc} (\varepsilon_i - \varepsilon_j)^{-1} c_{is_A} c_{js_A} c_{is_B} c_{js_B} \tag{2}$$

The successful calculation of coupling constants with these equations apparently depends on the choice of the MO method used to obtain the MO coefficients c and the orbital energies ε. Calculations with a MO theory neglecting overlap developed by Pople and Santry[11, 12] using Eq (2) failed to reproduce the negative sign of geminal H—H couplings,[13] as did the original McConnel theory. Similar calculations by Fahey, Graham and Piccioni[14] with an extended Hückel theory (EHT) gave, however, the correct signs and relative magnitudes of coupling constants in hydrocarbons. These authors could reproduce most experimentally observed trends in C—H and H—H couplings by use of the EHT method of Hoffmann[15] and Eq (1), retaining some of the more important two-centre integrals. Mainster and Memory[16] were equally successful in their efforts to calculate coupling constants in conjugated polycyclic hydrocarbons employing the method of Fahey *et al.* and estimating the π-electron contribution semi-empirically.

The Fahey-method appears to be most promising and has therefore been used in the present study. The approach is as follows: the LCAO-MO calculations are performed with the EHT method of Hoffmann, which includes all valence shell electrons and uses Slater atomic orbitals. The negative values of the valence-state ionisation potentials[17] are taken as Coulomb integrals. The off-diagonal matrix elements are calculated by the so-called Wolfsberg-Helmholtz approximation[18]

$$H_{ij} = \tfrac{1}{2}K(H_{ii} + H_{jj})S_{ij} \tag{3}$$

with $K = 1{\cdot}75$. All overlaps are included, in contrast to the method of Pople and

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* The various terms in equations (1) and (2) are defined as in reference 10.

Santry. Fahey *et al.* considered all one-centre integrals of orbitals within a certain distance of any one of the two coupling nuclei and included the significant two-centre integrals. In order to obtain a value of the carbon-2s one-centre integral consistent with SCF calculations, they chose an effective nuclear charge of 4·11 for carbon for the calculation of coupling constants.

Some preliminary calculations have been performed to assess (i) the influence of orbitals on atoms not directly bound to one of the coupling atoms and (ii) the effect of changing the effective nuclear charges as done by Fahey *et al.* Table 1 shows the results for ethane in the staggered and eclipsed conformations with effective nuclear charges on the carbon atom of 3·25 (Slater rules) and 4·11 (Fahey *et al.*), and taking into account atomic orbitals on atoms which are (a) directly bound to one of the coupling atoms, (b) less than 2 Å away, and (c) including all valence shell orbitals within the molecule under consideration.

It is seen from these results that inclusion of all two-centre integrals alters the proton-proton coupling constants by amounts up to 20%. As the effects of substituents are expected to be of the same order of magnitude, it was decided to include all one- and two-centre contact integrals of the valence shell atomic orbitals in the calculations, though this increased the computing time considerably.

TABLE 1. CALCULATED COUPLING CONSTANTS FOR STAGGERED AND ECLIPSED ETHANE WITH DIFFERENT EFFECTIVE NUCLEAR CHARGES AT THE CARBON ATOMS AND TAKING INTO ACCOUNT ORBITALS AT VARYING DISTANCES FROM THE COUPLING NUCLEI

Distance [Å]		Z_{eff}	${}^1J_{CH}$	${}^2J_{CH}$	${}^2J_{HH}$	${}^3J^{0}_{HH}$	${}^3J^{60}_{HH}$	${}^3J^{120}_{HH}$	${}^3J^{180}_{HH}$	${}^3J^{av}_{HH}$
a	1·6	3·25	34·88	−1·74	−20·52	8·35	2·04	3·33	11·97	5·35
b	2·0		37·55	−1·86	−15·37	7·59	1·83	3·21	11·34	5·00
c	∞		38·70	−1·55	−16·37	6·89	1·65	2·70	9·63	4·37
a	1·6	4·11	71·01	−3·63	−21·09	7·95	1·88	3·30	11·69	5·15
b	2·0		76·26	−3·89	−15·85	7·21	1·86	3·18	10·08	4·93
c	∞		76·86	−3·95	−16·21	7·49	1·81	3·00	10·50	4·71

Table 1 shows furthermore that a larger effective nuclear charge on the carbon atom increases the C^{13}—H couplings significantly, but has a relatively small effect on the H—H couplings. The H—H couplings are, however, strongly affected by altering the effective nuclear charge on the protons. The correct average coupling constant in ethane (8·0 Hz)[19,20] has been obtained in further test calculations with effective nuclear charges of 4·11 and 1·31 for carbon and hydrogen, respectively. The *trans/gauche* ratio (${}^3J^{180}_{HH}/{}^3J^{60}_{HH}$) of the vicinal couplings does not, however, agree with the experimental value (~ 3),[21,22] and the absolute values of the geminal couplings, which in these calculations are already appreciably larger than experimentally observed values, increase even further. The effective nuclear charges for all atoms required in this study were therefore calculated with the Slater rules in order to have a common basis for a comparison of the results.

The following molecules have been investigated: ethane, propane, ethylamine, ethanol, and fluoroethane. The parameters for the EHT MO calculations (Slater exponents and Coulomb integrals) are summarised in Table 2. Standard bond

TABLE 2. SLATER EXPONENTS AND IONISATION POTENTIALS USED IN THE MO CALCULATIONS

Atom	Slater exponent	Ionisation potential (eV) 1s	 2s	 2p
H	1·20	13·6	—	—
C	1·625	—	21·4	11·4
N	1·95	—	26·0	13·4
O	2·275	—	35·0	17·5
F	2·60	—	44·5	21·0

lengths[*] and tetrahedral bond angles have been used throughout this study, though certain angles, particularly those involving heteroatoms, are known to deviate from the ideal geometry. The substituents $—CH_3$, $—NH_2$ and $—OH$ have been taken in staggered conformations with the free electron pair of the amino group and the O—H bond *trans* to the central C—C bond in order to achieve highest possible symmetry. The vicinal proton-proton coupling constants of the ethyl fragment have been calculated as a function of the dihedral angle, which has been varied in steps of 20° over the minimum range necessary to cover a complete revolution, allowing for symmetry where appropriate.

RESULTS

All calculated coupling constants are combined in Table 3. Graphical representations of the coupling constants as a function of the dihedral angle Φ_{HH} closely resemble

TABLE 3. CALCULATED VICINAL COUPLING CONSTANTS FOR ETHYL DERIVATIVES

Φ_{HH}	θ_{XH}	Vicinal coupling constants for CH_3CH_2X [Hz] X = −H	 $-CH_3$	 $-NH_2$	 $-OH$	 $-F$
0	−120	6·89	6·45	6·29	5·91	5·75
20	−100	6·03	5·78	5·84	5·76	5·72
40	−80	3·94	3·92	4·10	4·28	4·36
60	−60	1·65	1·77	1·97	2·21	2·32
80	−40	0·25	0·33	0·37	0·46	0·58
100	−20	0·54	0·45	0·27	0·09	0·06
120	0	2·70	2·45	2·06	1·53	1·34
140	20	5·88	5·57	5·01	4·29	3·96
160	40	8·60	8·24	7·71	7·04	6·67
180	60	9·66	9·23	8·79	8·58	8·34
200	80	8·60	8·21	7·94	8·28	8·20
220	100	5·88	5·62	5·58	6·27	6·36
240	120	2·70	2·62	2·78	3·45	3·62
260	140	0·54	0·57	0·71	1·11	1·25
280	160	0·25	0·24	0·21	0·19	0·23
300	180	1·65	1·46	1·26	0·83	0·73
320	200	3·94	3·55	3·23	2·59	2·38
340	220	6·03	5·52	5·20	4·61	4·39

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[*] Bond lengths in Å-units: C—H = 1·09, O—H = 1·00, N—H = 1·01, C—C = 1·54, C—N = 1·47, C—O = 1·43, C—F = 1·36.

the original Karplus-curve for ethane. Figure 1, showing the J/Φ relationship for ethane and fluoroethane, demonstrates various general features of interest: The curves for the ethyl derivatives are phase-shifted relative to ethane. As expected,

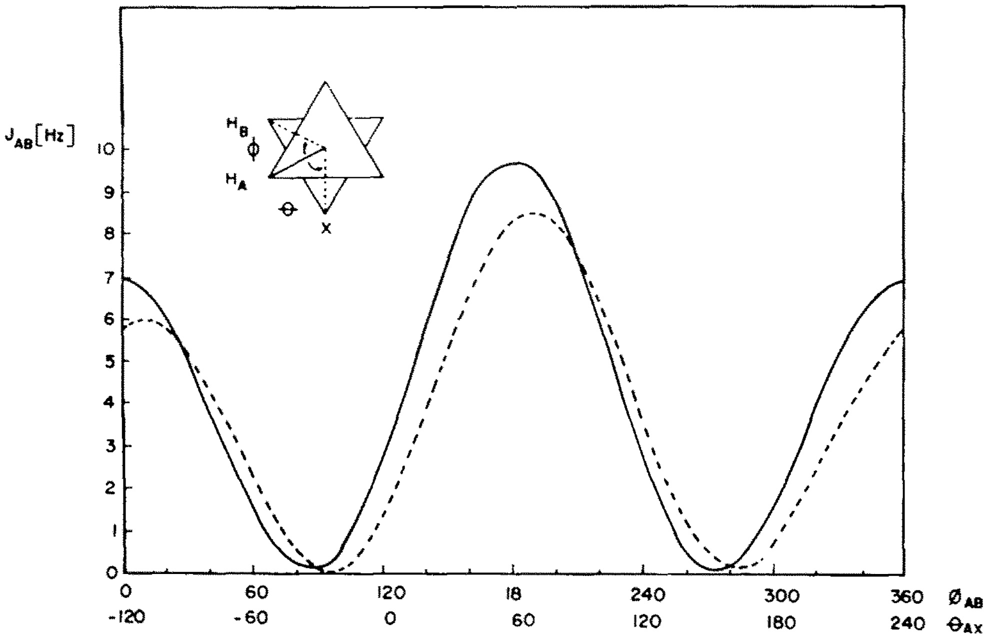

FIG 1. The calculated coupling constants for ethane and fluoroethane as a function of the dihedral angle Φ.

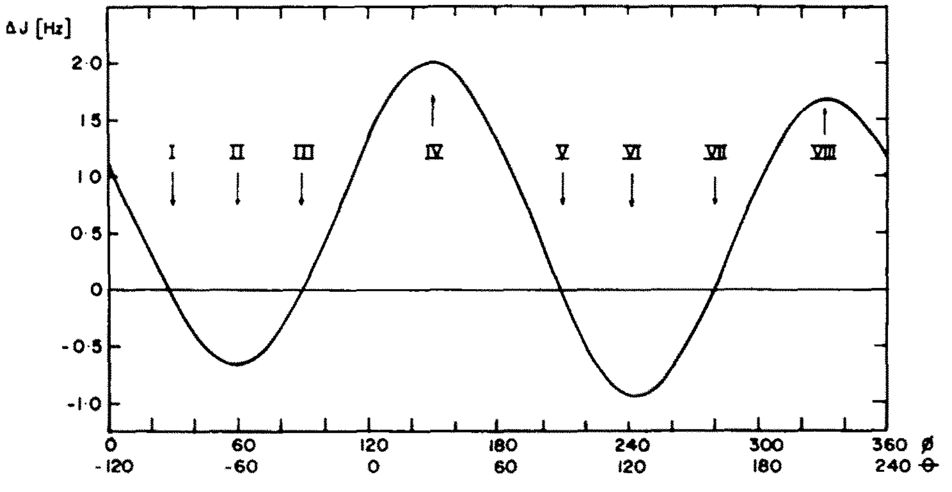

FIG 2. The difference $\Delta J = J_{\text{ethane}} - J_{\text{fluoroethane}}$ as a function of the dihedral angle Φ.

these deviations increase gradually with increasing electronegativity of the substituent. The asymmetry of the curves for monosubstituted ethanes results in two different coupling constants for equivalent H—H angles depending on the corresponding angle θ_{XH} between the β-proton under consideration and the substituent X. This demands an unambiguous defination of these two angles, which are measured here relative to the proton H_A such that $\theta_{AX} = \Phi_{AB} - 120°$ (*cf* Fig 1). Two further points of important emerge which are better illustrated by the difference between the ethane and the fluoroethane values ($\Delta J = J_{\text{ethane}} - J_{\text{fluoroethane}}$) shown as a function of the dihedral angle in Fig 2, which is representative for all difference curves of monosubstituted ethanes. Although an electronegative substituent decreases the average vicinal coupling constant, it is seen that the substituent effect is, firstly, strongly angle-dependent and, secondly, of opposite sign for certain ranges of the H—H angle, leading to an increase of the coupling with increasing electronegativity of the substituent.

DISCUSSION

It is experimentally well established that average vicinal proton-proton coupling constants decrease linearly with increasing electronegativity of substituents attached directly to a particular CH—CH fragment.[23, 24] The electronegativity effect, however, also depends on the relative configuration of the substituent and the coupling protons, and is thought to be largest in a *trans*-coplanar arrangement. This was first observed for staggered conformations in rigid compounds such as steroids[25] and derivatives of cyclohexane and heterocyclic six-membered rings,[26] and later in acyclic compounds during investigations of 1,2-disubstituted ethanes.[27] Extensive studies of rigid bicyclic systems with eclipsed —CH_2—CHX-groupings[28, 29] resulted in different linear relationships between the coupling constants J_0 and J_{120} with dihedral angles of 0° and 120°, respectively, and the electronegativity of the substituent X. An increase of vicinal coupling constants with increasing electronegativity of a substituent was first noted for the *gauche* coupling in 3,3-dimethylbutyl derivatives,[30] existing entirely in the *trans* conformation, and a similar observation was subsequently made for 1,2-dihaloethanes.[31] Very recently Abraham and Gatti[31] have derived equations for the electronegativity dependence of the various coupling constants in staggered arrangements and have established beyond any doubt that the *gauche* coupling in the *trans* conformer of 1,2-disubstituted ethanes increases with increasing electronegativity of the substituents.

All these experimental observations are evident in the MO calculations. Integration over the difference curves, as shown in Fig 2 for fluoroethane, adequately weighted by a potential function of three-fold symmetry, gives the expected decrease of the average vicinal coupling constants with increasing electronegativity of the substituent. Three different vicinal coupling constants are found for staggered conformations (*cf.* Fig. 1); a *trans* coupling ($\Phi = 180°$, $\theta = 60°$) with the substituent in *gauche* position, and two *gauche couplings* ($\Phi = 60°$ and 300°) with X—H angles of 60° and 180°, respectively. A decrease of the *trans* coupling and one of the *gauche* couplings ($\Phi = 300°$, $\theta = 180°$), but an increase of the other *gauche* coupling on substitution is predicted by the MO calculations (*cf* Fig 2). The study of Abraham and Gatti[31] contains experimental values for the individual conformers of 1,2-disubstituted ethanes and a number of selected six-membered ring compounds which may be assumed to be truly staggered. These values can be compared to the theoretical results if additivity of the substituent effects is assumed. Figure 3 shows the various types of couplings

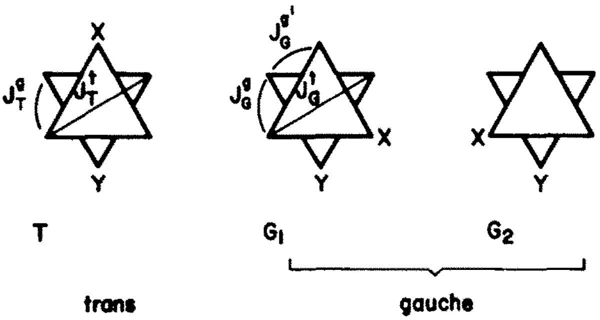

FIG 3. The staggered conformers of 1,2-disubstituted ethanes and the individual coupling constants.

found in the *trans* and *gauche* conformers of 1,2-disubstituted ethanes. The couplings in the ring compounds correspond to those in the *gauche* conformations.

The coupling J^g_T has both substituents *gauche* to the coupling protons and the increase of the coupling with increasing electronegativity of the substituents predicted by theory is, indeed, observed. The couplings J^t_T, J^t_G, and J^g_G have all substituents in positions which should lead to a decrease of the coupling with increasing substituent electronegativity and this is also found experimentally. A discrepancy exists only for the remaining coupling J^g_G. In the conformer $G1$ of Fig 3 the substituent X would

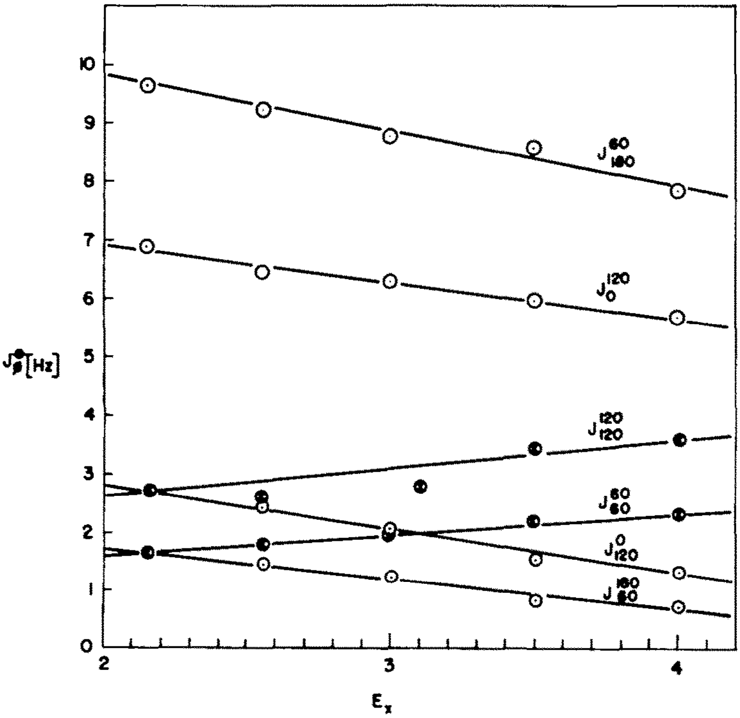

FIG 4. The coupling constants in staggered and eclipsed conformations as a function of the electronegativity E_X of the substituent.

cause a decrease and Y an increase of the coupling constant J^g_G. A small change with electronegativity would therefore be expected in contrast to the experimentally observed strong decrease.

Two of the couplings in eclipsed systems [J_0 ($\Phi = 0°$, $\theta = -120°$) and J_{120} ($\Phi = 120°$, $\theta = 0°$) in Fig 2] are predicted to decrease with increasing electronegativity of the substituents, and this is well supported by experimental evidence, in particular the investigations by Williamson[28] on hexachlorobicyclo[2.2.1]heptenes and by Laszlo and Von Ragué Schleyer[29] on 5-endo derivatives of bicyclo[2.2.1]heptene. If both the H—H and X—H angles are 120° ($\Phi = 240°$, $\theta = 120°$ in Fig 2) MO theory predicts an increase of the coupling constants on electronegative substitution. Though there is some experimental support for this effect, couplings in the corresponding model compounds are usually subject to other disturbing influences such as conformational changes and the contributions by lone-pair electrons, as pointed out in a preliminary account of this study.[32]

Figure 4 shows the various calculated coupling constants in CH_3CH_2X compounds corresponding to those discussed above as a function of the electronegativity of the substituent X. The relationships are linear and can be expressed as

$$J(E_X) = J - aE_X \tag{4}$$

The constants J and a for different types of couplings are compared to the corresponding experimental values in Table 4. Empirical relationships are converted to conform with equation (4), assuming additivity of the substituent effects. The ratios of the constants J and a, given in Table 4, are consistently smaller than one, the only exception being one of the ratios for the values of the *trans* coupling J^{60}_{180}. This figure is, however, based on a set of experimental data which includes couplings in compounds assumed to be entirely in the *trans* conformation, though even small percentages of the *gauche* conformer would affect that J^{60}_{180} coupling appreciably. Using

TABLE 4. THE CALCULATED AND EXPERIMENTALLY OBSERVED CONSTANTS FOR EQUATION (4) IN STAGGERED AND ECLIPSED CONFORMATIONS

Coupling constant[a]	J_{calc}	a_{calc}	J_{exp}	a_{exp}	Reference[b]		J_{calc}/J_{exp}	a_{calc}/a_{exp}
J^{60}_{180}	11·80	−0·98	16·18	−0·88	(31)	(J^t_T)	0·73	1·11
			18·10	−1·30	(31)[c]		0·64	0·75
J^{180}_{60}	2·90	−0·58						
J^{60}_{60}	0·85	0·38	2·70	0·63	(31)	(J^g_T)	0·32	0·60
J^{120}_{0}	8·15	−0·63	12·6	−1·40	(28)	(J_{cis})	0·65	0·45
			11·3	−1·00	(29)	(J_{cis})	0·72	0·63
J^{0}_{120}	4·15	−0·70	8·8	−1·70	(28)	(J_{trans})	0·47	0·41
J^{120}_{120}	1·60	0·50						
$\frac{1}{2}(J^{180}_{60} + J^{60}_{60})$	1·87	−0·10	6·92	−0·94	(31)	(J^g_G)	0·27	0·11
			5·48	−0·50	(33)	(J_{cis})	0·34	0·20
$\frac{1}{2}(J^{60}_{180} + J^{180}_{60})$	7·35	−0·78	11·28	−1·02	(31)	($\frac{1}{2}(J^t_G + J^g_G)$)	0·65	0·76
			11·40	−1·05	(33)	(J_{trans})	0·64	0·74

[a] Subscripts are H—H angles, superscripts X—H angles.

[b] In brackets: the corresponding couplings in the references quoted.

[c] From 1,2-dihalo-ethanes only.

values for the properly analysed 1,2-dihaloethanes only, the ratio in question is reduced to 0·75, consistent with all the other values.

The range of J and a ratios in Table 4 is surprisingly narrow, considering the approximations inherent in the MO theory and the crude assumption of additivity made in evaluating the experimental data. The relatively low J ratio for the J_{60}^{60} coupling may be due to the small absolute value of the corresponding calculated coupling (0·85 Hz). A serious discrepancy is noted for the ratios of the couplings $\frac{1}{2}(J_{60}^{180} + J_{60}^{60})$. This may indicate a breakdown of the additivity in a situation where two opposing substituent effects are present. The good overall correspondence between the calculated values and the observed trends of coupling constants, however, encourages a more detailed discussion of the theoretical results.

The calculated coupling constants for all compounds investigated are well represented by a trigonometric function of the form:

$$J = A + B\cos\Phi + C\cos 2\Phi + D\sin\Phi + E\sin 2\Phi, \tag{5}$$

in which the sin-terms had to be added to the original Karplus-equation in order to

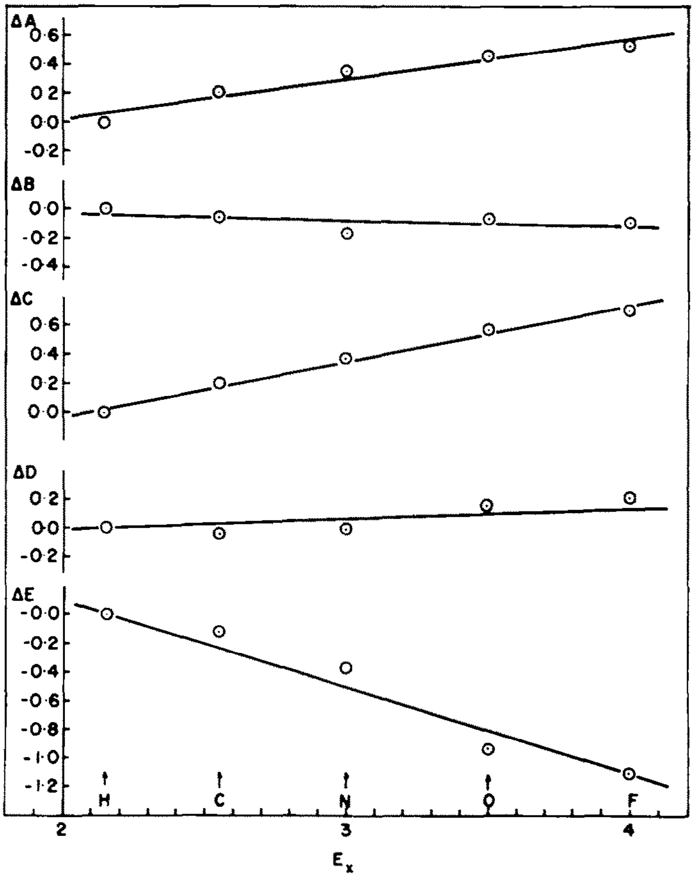

FIG 5. The various constants ΔK as a function of the electronegativity E_X of the substituent and the straight lines fitted by least-squares.

account for the asymmetry of the curves with respect to $\Phi = 0°$. Table 5 contains the parameters obtained from a least-squares fit and the corresponding RMS errors. The substituent effects relative to ethane ($\Delta J = J_{\text{ethane}} - J_{\text{ethyl X}}$) can be expressed by an analogous equation, in which all constants are replaced by the corresponding difference ($\Delta K = K_H - K_X$).

It is interesting to note that the sum of the couplings of H_B (*cf* Fig 1) with all three protons in the methyl group is constant and equal to 3A in any particular conformation. This is easily derived from equation (5) since the sum of every one of the trigonometric terms for Φ, $\Phi + 120°$, and $\Phi - 120°$ vanishes. The same applies to the sum of all substituent effects on the couplings of a particular proton with all protons on a neighbouring Me group. In this case the sum is 3 ΔA.

The various ΔK values are plotted in Fig 5 as a function of the electronegativity of the substituents. The following conclusions can be drawn: (i) the electronegativity dependence is mainly reflected by changes of the constants A, C and E; (ii) the constant B varies only slightly; (iii) the value of ΔD remains very small. Assuming a linear relationship between these constants and the electronegativity of the substituents, the calculated values in Table 5 can be fitted by least-squares methods to linear equations of the type:

$$K = K_0 - kE_X \tag{6}$$

The resulting values are given in Table 6 and the straight lines in Fig 5 are obtained with these constants. The deviations are less than 0·1 Hz except for the ΔE values (*cf* Fig 5). It should therefore be possible to describe the dependence of vicinal proton-proton coupling constants on the dihedral angle between the coupling protons and on the electronegativity of a substituent by a general formula of the following type:

$$\begin{aligned} {}^3J^{HH}(\Phi, E_X) = {} & (A_O - k_A E_X) + (B_O - k_B E_X)\cos\Phi \\ & + (C_O - k_C E_X)\cos 2\Phi + (D_O - k_D E_X)\sin\Phi \\ & + (E_O - k_E E_X)\sin 2\Phi \end{aligned} \tag{7}$$

The various constants for ethane and for the ethyl derivatives calculated from Eq (6) are also given in Table 6. Comparison of the calculated coupling constants in Table 3 with those obtained from Eq (7) using the constants in Table 6 results in the RMS errors also shown in Table 6. These are only slightly larger (by an average of 0·05 Hz) than those for the individually fitted MO calculations of the ethyl derivatives (Table 5). Figure 6 depicts the curve calculated with Eq (7) and the corresponding J-values of

TABLE 5. THE CONSTANTS FOR EQUATION (5) OBTAINED FROM A LEAST-SQUARES FIT OF THE CALCULATED COUPLING CONSTANTS

X	E_X	A	B	C	D	E	RMS
H	2·15	4·21	−1·30	4·06	0·0	0·0	0·08
CH_3	2·55	4·00	−1·27	3·84	0·04	0·12	0·12
NH_2	3·0	3·85	−1·13	3·68	0·01	0·38	0·13
OH	3·5	3·75	−1·24	3·49	−0·15	0·94	0·10
F	4·0	3·68	−1·21	3·35	−0·20	1·12	0·08

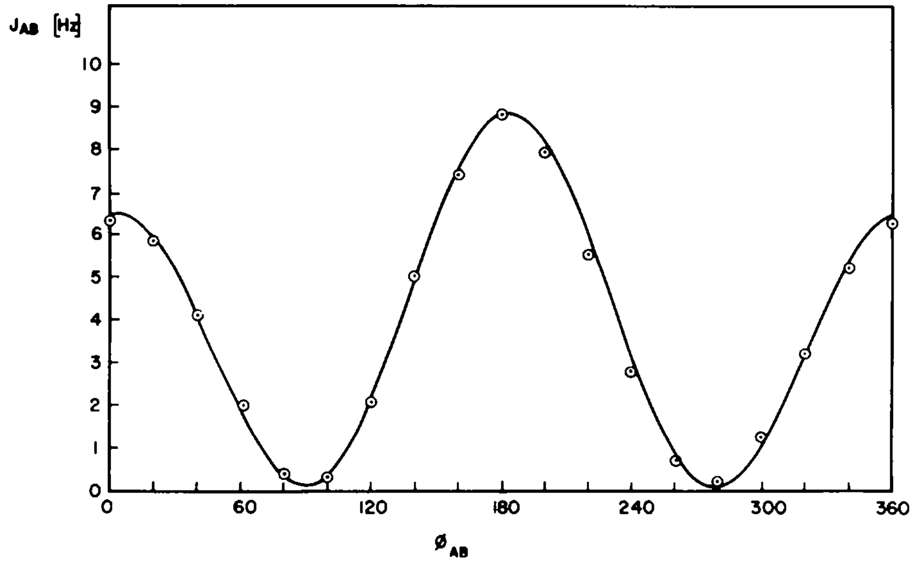

FIG 6. The coupling constant in ethylamine as a function of the dihedral angle Φ. Solid line according to Eq (7), points from the MO calculation.

the theoretical calculations from Table 3 for ethylamine, the compound with the largest discrepancies. The excellent agreement leads to the conclusion that all vicinal proton-proton coupling constants of monosubstituted ethanes computed in this study by MO methods are represented fairly accurately by Eq (7) using the corresponding constants in Table 6. It should—hopefully—be possible to describe experimentally observed coupling constants by a similar equation incorporating empirical constants.

Difference curves very similar to that one, shown in Fig 2 for fluoroethane, are obtained for the other ethyl derivatives with the amplitudes decreasing from ethanol to propane. The graphs for propane and ethylamine appear somewhat distorted, but as the substituent effects in these compounds are relatively small, this may simply be due to the limited accuracy of the calculations, or to different effects of the lone-pair electrons and the X—H bonds. These distortions are eliminated in the set of curves obtained from Eq (7).

It is quite revealing to interpret the extrema and zero points of Fig 2 in terms of the corresponding conformations I–VIII as shown in Fig 7. Two of the four zero points

TABLE 6. THE CONSTANTS FOR EQUATIONS (6) AND (7)

	K_0	k	$X = H$	C	N	O	F
A	4·75	0·28	4·15	4·03	3·91	3·77	3·63
B	−1·34	−0·04	−1·25	−1·24	−1·21	−1·20	−1·18
C	4·86	0·38	4·03	3·89	3·72	3·53	3·34
D	0·15	0·07	0·00	−0·03	−0·06	−0·10	−0·13
E	−1·27	−0·60	0·00	0·24	0·51	0·81	1·11
RMS	---	--	0·11	0·18	0·18	0·15	0·16

coincide with conformations (I and V) where the C—X bond forms a right angle with the C—H_A bond ($\Phi = 30°$ and 210°). The other zero points ($\Phi \simeq 90°$ and 280°) correspond approximately to conformations with negligibly small couplings (III and VII). The maximum decrease of the couplings is interestingly found when both the C—X and C—H_B bonds are perpendicular to the two bonds not involved in coupling with the proton H_B (conformations IV and VIII). The maximum increase is observed in the staggered conformation II and the totally eclipsed form VI. Here the C—X bond is either opposite to or eclipsed with one particular C—H bond not involved in the coupling. The effect of an electronegative substituent X on the vicinal coupling constant between two protons A and B, where B is in an α-, A in a β-position relative to X, can be summed up by the following rules: (i) the maximum decrease is observed if the dihedral angle between A and B is 30° or 150°, provided the substituent X is not perpendicular to the proton A; (ii) no effect is found at dihedral angles of 30° or 150° when X is perpendicular to A, or at an AB dihedral angle of 90°; (iii) the maximum increase of a coupling is obtained in either staggered conformations in which neither B nor X are *trans* to A, or in eclipsed conformations, in which neither B nor X are eclipsed with A.

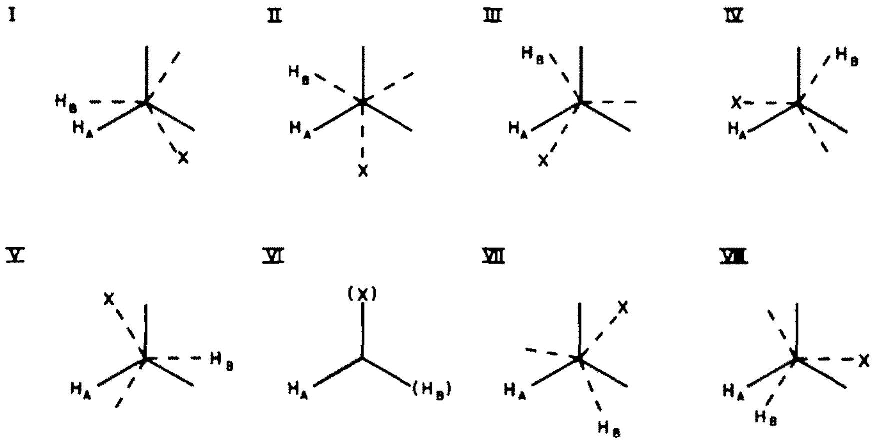

Fig 7. The various conformations corresponding to extrema and zero points of Fig 2.

A discussion of the results in terms of the electronic structure of the molecules appears to be difficult because of the delocalised nature of the molecular orbitals. Attempts to reduce the interpretation to those molecular orbitals contributing most to the couplings using one-centre integrals failed. In fact, these predicted an increase of *cis*-couplings with increasing electronegativity of the substituents in obvious contradiction to the complete results and to experimental evidence.

CONCLUSION

MO calculations of the effect of substituents on vicinal proton-proton coupling constants with the Pople-Santry theory appear to be very promising. The results obtained in this study with the extended Hückel theory of Hoffmann are in qualitative agreement with most experimentally observed trends in vicinal couplings. More sophisticated MO techniques are required if qualitative significance of the theoretical calculations is to be achieved.

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