

# An Experimental and Theoretical FPT/INDO Study on ${}^nJ(\text{OH},\text{C})$ , ${}^nJ(\text{OH},\text{H})$ , ${}^nJ(\text{CH})$ and ${}^nJ(\text{HH})$ NMR Couplings of Methanol, Ethanol, 2-Propanol, *tert*-Butyl Alcohol and Acetylacetone \*

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The coupling behaviour of the hydroxyl proton is studied by using model compounds representing the aliphatic, phenolic and enolic hydroxyls. The conformational and substitutional effects in ethanol and 2-propanol are estimated using the temperature dependencies of the  ${}^3J(\text{OH},\text{H})$  couplings and semiempirical MO calculations. FPT/INDO and SOS/INDO (Sum-Over-States) calculation methods are applied and compared in the interpretation of the conformational and substitutional effects: In all cases the FPT method is found to predict the general trends at least qualitatively.

${}^nJ(\text{CH})$ -couplings can yield useful conformational information if the sensitivity of instrumentation allows the measurements of the coupled  ${}^{13}\text{C}$  spectra. In this work, we have measured the couplings of typical hydroxyl protons and in the case of the phenolic hydroxyl we have used some previous data.<sup>1</sup> The substitutional and conformational behaviour of the couplings is studied also by the semiempirical MO calculations,<sup>2,3</sup> which are known to interpret the general trends quite well.<sup>4,5</sup>

The FPT<sup>2</sup> and SOS<sup>3</sup> methods are briefly compared. We are interested in the matter because the FPT method is much more expensive. Furthermore,

the SOS method is attractive because the couplings can be simultaneously computed for all the nuclei whenever a molecular orbital calculation is carried out, and with little extra effort.

In the SOS method,<sup>3</sup> the couplings are set proportional to the second-order energy due to the electron–nucleus interaction. The probability of the ground state of the molecule being mixed with an excited state is inversely proportional to the excitation energy. If the one-electron wave functions are applied, the triplet excitation energy for an electron from the  $i$ th occupied orbital to the  $j$ th unoccupied orbital is given by  ${}^3\Delta E_{i\rightarrow j} = e_j - e_i$ . If the SCF wave functions are used, the change in the coulombic interactions of the excited electron and the other electrons should be included. The simplest way to do this is to apply the first-order correction only to the excitation energies;<sup>6</sup> eqn. (1)

$${}^3\Delta E_{i\rightarrow j} = e_j - e_i - j_{ij} \quad (1)$$

where  $j_{ij}$  is the bielectronic coulombic integral.<sup>6</sup> A part of this correction can be compensated by maintaining the wave functions and thus the accurate calculations of the configuration interactions (CIs) would demand too much time to be practical. Also the inclusion of the bielectronic coulombic integrals increases the calculation time remarkably. It has been shown,<sup>7</sup> however, that many observed trends can be interpreted without including CI and, *vice versa*, that even the very complete accounting for CI does not essentially improve the results.<sup>8</sup> In this work, the coupling

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constants were calculated using the standard SOS method<sup>3</sup> and also eqn. (1). The proportionality constants used to correlate the second-order energies and the couplings were chosen to give correct values for  $^1J(\text{CH})$  and  $^3J(\text{HH})$  of benzene. This choice is quite arbitrary but it does not greatly affect the decisions made on the basis of the calculations.

In the FPT method<sup>2</sup> the second-order effects on the wave functions are calculated. The main advantage of the method is that it predicts the sign of the couplings, while the SOS method does not produce them if SCF wave functions are used. Thus the FPT method can be applied in studies on the trends in the geminal couplings.<sup>4</sup>

## EXPERIMENTAL

The samples were dissolved in acetone (30 % v/v). This solvent was chosen to prevent the association induced exchange reactions.<sup>9</sup> The acetylacetone sample was dried over Molecular Sieve 4A pellets for two days; only after that were the couplings of hydroxyl resolved. The other samples were prepared without drying, but had to be left for some hours in order to stabilize the "structures of the solutions" and to resolve the hydroxyl couplings. The spectra were run by a Jeol FX-60 PFT spectrometer, using 16K data points. A typical linewidth after 5000–10000 pulses was 0.5 Hz. The RRMS's of the spectral analysis were from 0.03 to 0.05 Hz. Temperatures were measured by the methanol method.<sup>10</sup>

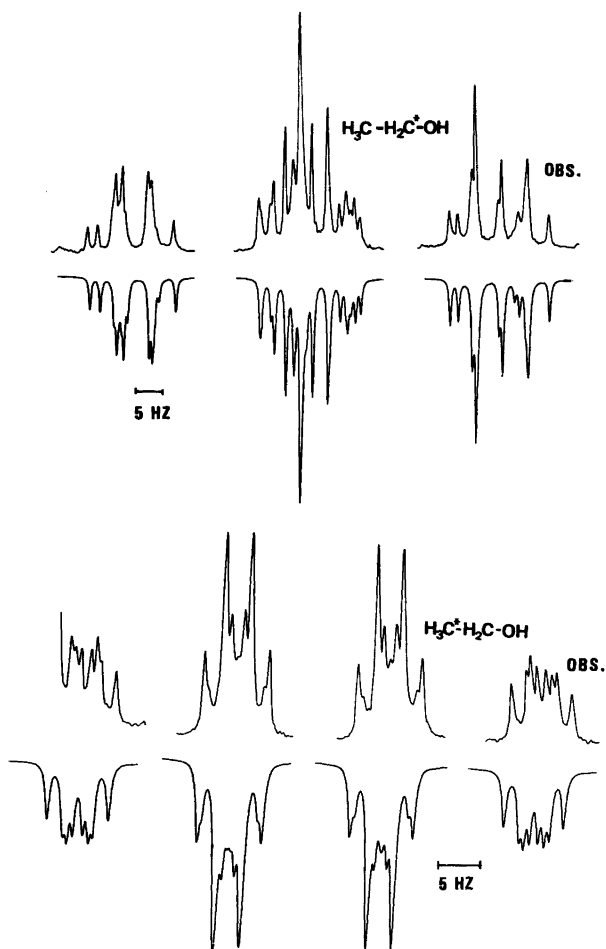


Fig. 1. The observed and simulated (with resolution 0.5 Hz)  $^{13}\text{C}$ NMR spectra of ethanol.

## Spectral analysis

The spectra of methanol and ethanol were analyzed with the program MAOCON-SC,<sup>11</sup> which is an automatically assigning version of MAOCON.<sup>12</sup> The automatic assignment-reassignment procedure worked well also in this case. Fig. 1 presents the spectra and the results from the analysis of the CH<sub>2</sub> and CH<sub>3</sub> signals of ethanol. The spectra of 2-propanol and *tert*-butyl alcohol are also slightly of second-order: the A<sub>6</sub>BCX, A<sub>3</sub>A<sub>3</sub>'BCX and A<sub>9</sub>BX spectra were analyzed with the NMR-LAOCN-4A algorithm<sup>13</sup> after it was modified to handle these large spin systems. The spectra of acetylacetone were sufficiently close to first-order to be analyzed without computer refinements.

## Molecular orbital calculations

The INDO calculations were carried out by using the CNINDO algorithm.<sup>14</sup> The standard geometries<sup>15</sup> were applied in most cases; the geometry of methanol<sup>16</sup> was applied for aliphatic hydroxyls. The geometry of the aldehyde group in salicylaldehyde was approximated with that of acetaldehyde.<sup>17</sup> The Allinger force field trial values<sup>18</sup> were

tested for the aliphatic systems, but the calculated energies were clearly greater than those given by the standard geometries.

## RESULTS AND DISCUSSION

## The conformational and substituent dependence of the couplings: Conformations of the alcohols

Table 1 contains the observed results and some selected calculations on the most important conformations. The reported INDO energies are considered to be only qualitatively correct.

*Methanol.* The three conformers are equally populated and, when the simple Karplus relationship<sup>19,20</sup>  $J = J^a \cos^2 \phi$  is applied, one obtains  $J^a(\text{OH}, \text{H}) = 10.25$  and  $J^b(\text{OH}, \text{H}) = 2.56$  Hz.  $J^a$  is the coupling of OH to the *anti*-proton in the low energy conformer,  $J^b$  the *gauche* coupling and  $\phi$  the dihedral angle HOCH. The applied Karplus relationship agrees very well with the data of Rader<sup>20</sup> for secondary alcohols and, thus, more sophisticated models are not needed in the present study.

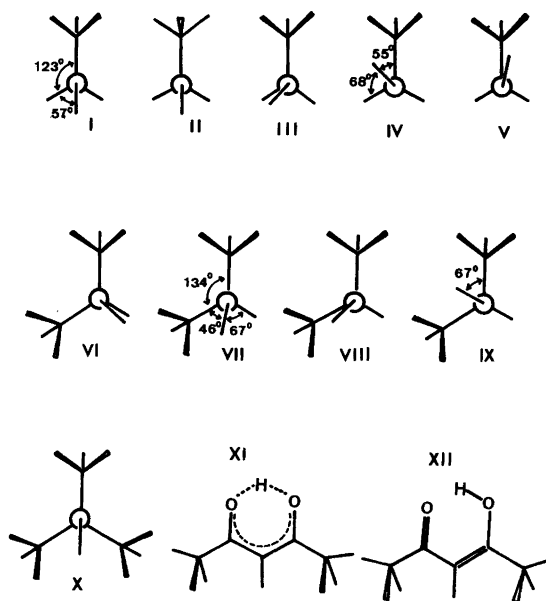


Fig. 2. The conformations of ethanol (I–V), 2-propanol (VI–IX), *tert*-butyl alcohol (X) and acetylacetone (XI–XII) discussed in the text. In the MO calculations (*cf.* Table 1) the standard dihedral angles were used: the dihedral angles given in this figure for I and IV are suggested by the molecular mechanics (Ref. 22) and in the case of VII and IX, on the basis of the considerations presented in the text.

Table 1.  ${}^nJ(\text{HH})$  and  ${}^nJ(\text{CH})$  couplings (Hz) of methanol, ethanol, 2-propanol, *tert*-butyl alcohol, acetylacetone and salicylaldehyde.<sup>a</sup> Observed and calculated values (INDO approximation).

| Structure <sup>b</sup>       |           | INDO <sup>c</sup><br>Energy<br>kJ/mol | ${}^2J(\text{OH},\text{C})$                                  | ${}^3J(\text{OH},\text{C})$ | ${}^3J(\text{OH},\text{CH})$ | ${}^2J(\text{CH}_3,\text{CH})$ | ${}^2J(\text{CH},\text{CH}_3)$ | ${}^3J(\text{CH},\text{CH}_3)$ |      |      |
|------------------------------|-----------|---------------------------------------|--|-----------------------------|------------------------------|--------------------------------|--------------------------------|--------------------------------|------|------|
| Methanol                     | staggered | —                                     | -7.41 <sup>d</sup><br>0.52 <sup>e</sup><br>1.82 <sup>f</sup> | —                           | 6.15<br>6.65<br>8.91         | —                              | —                              | —                              |      |      |
|                              | observed  | —                                     | -3.00  | —                           | 5.12                         | —                              | —                              | —                              |      |      |
| Ethanol                      | I         | 0.00                                  | -6.30 <sup>d</sup>   | 7.27                        | 0.90                         | -5.27                          | -7.39                          | 7.75                           |      |      |
|                              |           |                                       | 0.20 <sup>e</sup>  | 5.31                        | 1.46                         | 1.43                           | 0.89                           | 6.22                           |      |      |
|                              |           |                                       | -0.25 <sup>f</sup>   | 10.19                       | 0.93                         | 2.07                           | 4.33                           | 9.25                           |      |      |
|                              | II        | 7.70                                  | -6.25  | 7.75                        | 0.69                         | -5.31                          | -7.44                          | 7.74                           |      |      |
|                              |           |                                       | 0.19   | 5.75                        | 1.39                         | 1.46                           | 0.89                           | 6.11                           |      |      |
|                              | III       | 8.08                                  | -0.08  | 10.77                       | 1.10                         | 1.16                           | 4.62                           | 9.21                           |      |      |
|                              |           |                                       | -6.89  | 2.44                        | 6.44                         | -4.40                          | -7.42                          | 7.74                           |      |      |
|                              | IV        | 10.00                                 | 0.32   | 1.60                        | 5.31                         | 1.64                           | 0.87                           | 6.18                           |      |      |
|                              |           |                                       | 0.23   | 3.60                        | 8.51                         | 1.79                           | 6.48                           | 10.29                          |      |      |
|                              | V         | 12.64                                 | -7.37  | 0.63                        | 9.12                         | -4.96                          | -7.41                          | 7.52                           |      |      |
| 0.91                         |           |                                       | 2.63   | 4.05                        | 1.39                         | 0.78                           | 5.95                           |                                |      |      |
| VI                           | —         | 2.58                                  | 2.57   | 7.58                        | 1.03                         | 3.83                           | 8.80                           |                                |      |      |
|                              |           | -6.25                                 | 7.75   | 0.69                        | -5.31                        | -7.44                          | 7.74                           |                                |      |      |
| VII                          | —         | 0.19                                  | 5.75   | 1.39                        | 1.46                         | 0.89                           | 6.11                           |                                |      |      |
|                              |           | 0.08                                  | 10.77  | 1.10                        | 1.16                         | 4.62                           | 9.21                           |                                |      |      |
| VIII                         | —         | -2.67                                 | 2.93   | 5.03                        | -2.25                        | -4.71                          | 7.03                           |                                |      |      |
|                              |           | -2.67                                 | 2.93   | 5.03                        | -2.25                        | -4.71                          | 7.03                           |                                |      |      |
| 2-Propanol                   | VI        | 3.01                                  | -6.60 <sup>d</sup>   | 2.18                        | 8.50                         | -5.26                          | -6.65                          | 7.92                           |      |      |
|                              | VII       | 0.00                                  | -6.32  | 4.16                        | 0.93                         | -4.68                          | -6.63                          | 7.80                           |      |      |
|                              | VIII      | 7.78                                  | -6.50  | 3.29                        | 5.19                         | -4.29                          | -6.69                          | 7.58                           |      |      |
|                              | IX        | 10.13                                 | -7.00  | 0.55                        | 18.43                        | -4.57                          | -6.69                          | 7.32                           |      |      |
|                              | observed  | —                                     | -2.44  | 3.13                        | 4.27                         | -0.70                          | -4.46                          | 6.10                           |      |      |
| <i>tert</i> -Butyl alcohol   | X         | 0.00                                  | -6.08 <sup>d</sup>   | 3.13                        | —                            | —                              | -5.96                          | —                              |      |      |
|                              | observed  | —                                     | -2.12  | 2.69                        | —                            | —                              | -4.20                          | —                              |      |      |
| Acetylacetone <sup>g</sup>   | XI        | 0.00                                  | -8.53 <sup>d</sup>   | cis                         | trans                        | —                              | -0.77                          | —                              |      |      |
|                              |           |                                       |  | (CH)                        | (CH <sub>3</sub> )           |                                |                                |                                |      |      |
|                              | XII       | 4.43                                  | -2.71  | 1.99                        | 3.68                         | —                              | -2.17                          | —                              | 2.23 |      |
| observed                     | —         | (-)                                   | 3.35 <sup>h</sup>  | 2.79                        | 3.01                         | —                              | (-)                            | 2.79                           | —    | 1.65 |
| Salicylaldehyde <sup>a</sup> | —         | —                                     | -5.63 <sup>d</sup>   | cis                         | trans                        | —                              | —                              | —                              |      |      |
|                              |           |                                       |  | (CH)                        | (CH <sub>3</sub> )           |                                |                                |                                |      |      |
| observed                     | —         | (-)                                   | 4.75 <sup>h</sup>  | 4.60                        | 7.37                         | —                              | —                              | —                              | —    |      |

<sup>a</sup> Ref. 1. <sup>b</sup> See Fig. 2. <sup>c</sup> Without any optimization of geometry. <sup>d</sup> FPT method. <sup>e</sup> SOS method. <sup>f</sup> SOS with the first-order CIs to excitation energies. <sup>g</sup>  ${}^4J(\text{OH},\text{CH}) = (\pm)2.79$ ; (FPT: XI; -1.81 and XII: -1.49). <sup>h</sup> Suggested signs.

*tert-Butyl alcohol.* Analogous with methanol:  $J^a(\text{OH},\text{C})=5.38$  and  $J^s(\text{OH},\text{C})=1.34$  Hz. A comparison with the values for methanol gives  $J(\text{OH},\text{C})=0.52 J(\text{OH},\text{H})$ . This simple relation is in accordance with many previous data.<sup>21</sup> However, both  $J^3(\text{OH},\text{H})$  and  $^3J(\text{OH},\text{C})$  can be used in the conformational analysis of the other alcohols only after considering the substituent effects (*cf.* below).

*Ethanol.* The molecular mechanics calculation<sup>22</sup> of the energy difference between the staggered forms I and IV (Fig. 2) gives 0.54 kJ, corresponding to 38 % of I. An approximate application of the Karplus relationship results in 36 % of I and  $\Delta E=0.29$  kJ.<sup>20</sup> If dihedral angles  $60^\circ$  and  $180^\circ$  are accepted, the calculated averaged vicinal coupling constants  $J(\text{I})$  and  $J(\text{IV})$  are 2.56 and 6.41 Hz. When dihedral angles  $\phi(\text{CCOH})=55^\circ$ ,  $\phi(\text{HCOH})=68^\circ$ , for IV, and  $\phi(\text{HCOH})=57^\circ (=180^\circ - 55^\circ - 68^\circ)$  for I<sup>22,23</sup> are applied,  $J(\text{I})=3.04$  and  $J(\text{IV})=5.84$  Hz. The dihedral angles are defined also in Fig. 2. This means that now IV would be 0.50 kJ more stable than I. A study of the model compounds of Rader<sup>21</sup> suggests that the substitution at HCOH with one aliphatic substituent increases  $J^a(\text{OH},\text{H})$  with 0.80 Hz and  $J^s(\text{OH},\text{H})$  with 0.20 Hz. Table 3 shows that also FPT calculations predict the same absolute effect on  $J^a$  (0.84 Hz), while the SOS value (0.30 Hz) is clearly smaller. The application of the observed effects results in  $J^a(\text{OH},\text{H})=(10.25+0.80)=11.05$  Hz and  $J^s(\text{OH},\text{H})=2.76$  Hz for primary alcohols, and for dihedral angles  $60^\circ$  and  $180^\circ$   $J(\text{I})=2.76$  and  $J(\text{IV})=6.90$  Hz. This corresponds to 45 % of I and 1.22 kJ for the energy difference between I and IV. The slight adjustment of the

dihedral angles as above (see Fig. 2) yields  $J(\text{I})=3.28$  Hz,  $J(\text{IV})=6.30$  Hz, 42 % of I and  $\Delta E=0.92$  kJ.

In order to get a more accurate picture of the angular and substitutional effects, the temperature dependence of the couplings was applied; eqn. (2).

$$^3J(\text{OH},\text{H}) = [J(\text{I}) \exp(\Delta E/RT) + 2J(\text{IV})]/(2 + \exp(\Delta E/RT)) \quad (2)$$

The measurement of the couplings at temperatures 196, 229, 251, 273, 293 and 316 K gave the values 4.86, 4.95, 4.99, 5.01, 5.05 and 5.07 Hz within about  $\pm 0.03$  Hz. Unfortunately, only two of the unknown parameters  $J(\text{I})$ ,  $J(\text{IV})$  and  $\Delta E$  can be determined simultaneously because of the internal correlations between them. The plotting of  $^3J(\text{OH},\text{H})$  vs.  $1/T$  gives the straight line in Fig. 3, and the extrapolation of the line to  $1/T=0$  gives  $(J(\text{I})+J(\text{IV}))/3=5.40 \pm 0.05$  Hz. The error limits are at 90 % confidence level, represented by the hyperbola in Fig. 3. The simple assumption, as above for methanol, gives now  $J^a(\text{OH},\text{H})=10.80 \pm 0.10$  Hz,  $J^s(\text{OH},\text{H})=2.70 \pm 0.03$  Hz ( $=J(\text{I})$ ),  $J(\text{IV})=6.75 \pm 0.10$  Hz, 43  $\pm 1.5$  % of I and  $\Delta E=1.02 \pm 0.17$  kJ. In these calculations possible deviations from the ideal dihedral angles are not included as they are opposite to each other and to a great extent compensate each other.

If no substitutional effects on  $^3J(\text{OH},\text{C})$  are supposed and the percentage of I is supposed to be 43 %, the use of the values of *tert*-butyl alcohol gives  $3.07 \pm 0.06$  Hz (observed 2.93 Hz). The substituent effects on  $^3J(\text{OH},\text{C})$  can be approximately estimated from the simple relation<sup>21</sup>  $J(\text{CH})=0.5 J(\text{HH})$ . By using values 0.30 (that is about  $(10.80 - 10.25)/2$ ) and 0.07 Hz for the effects on  $J^a$  and  $J^s$ , one obtains, after the effects are applied twice on the values of *tert*-butyl alcohol,  $J^a(\text{OH},\text{C})=4.78$  and  $J^s(\text{OH},\text{C})=1.27$  Hz. The effects are in accordance with the FPT values 0.5 and 0.1 Hz (*cf.* Table 2).  $^3J(\text{OH},\text{C})$  for ethanol now becomes  $2.78 \pm 0.08$  Hz. This value is, however, very sensitive to changes of the dihedral angle  $\phi(\text{HOCC})$ , and the observed value 2.93 Hz is obtained with the angle  $55 \pm 2^\circ$ . This value is in good agreement with previously suggested values<sup>22,23</sup> (see Fig. 2).

The FPT calculations show, furthermore, that the rotation of the  $\text{CH}_3$  group has an effect on the vicinal coupling (see Table 1 and Fig. 2, structure II). Because of the low rotational barrier, as derived on the basis of the MO calculations comparable with that of methanol,<sup>16</sup> some effects are expected to be due to the tilting of  $\text{CH}_3$ .

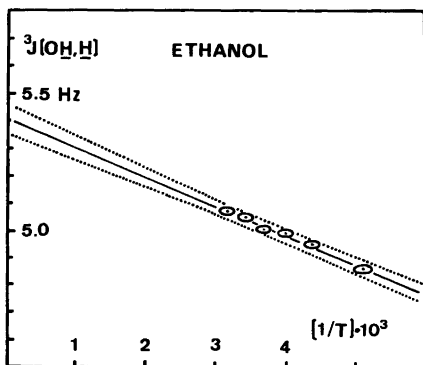


Fig. 3. The temperature dependence of  $^3J(\text{OH},\text{H})$  of ethanol. The dotted lines represent the 90 % confidence hyperbola.

Table 2. The calculated  $J^a(\text{OH},\text{H})$ ,  $J^b(\text{OH},\text{H})$ ,  $J^a(\text{OH},\text{C})$  and  $J^b(\text{OH},\text{C})$ 's of various conformations of aliphatic alcohols.

| Structure <sup>a</sup> |          | $J^a(\text{OH},\text{H})$ | $J^b(\text{OH},\text{H})$ | $J^a(\text{OH},\text{C})$ | $J^b(\text{OH},\text{C})$ |
|------------------------|----------|---------------------------|---------------------------|---------------------------|---------------------------|
| MeOH                   | eclipsed | 16.60 <sup>b</sup>        | 0.92                      | —                         | —                         |
|                        |          | 12.38 <sup>c</sup>        | 1.39                      | —                         | —                         |
| EtOH                   | I        | —                         | 0.90                      | 7.27                      | —                         |
|                        |          | —                         | 1.46                      | 5.31                      | —                         |
|                        | IV       | 17.44                     | 0.81                      | —                         | 0.68                      |
|                        |          | 12.68                     | 1.28                      | —                         | 0.48                      |
| 2-PrOH                 | VII      | —                         | 0.93                      | 7.77                      | 0.55                      |
|                        |          | —                         | 1.41                      | 5.56                      | 0.56                      |
|                        | IX       | 18.44                     | —                         | —                         | 0.55                      |
|                        |          | 13.03                     | —                         | —                         | 0.41                      |
| <i>t</i> -BuOH         | X        | —                         | —                         | 8.30                      | 0.54                      |
|                        |          | —                         | —                         | 5.82                      | 0.51                      |

<sup>a</sup> See Fig. 2. <sup>b</sup> FPT method. <sup>c</sup> SOS method, without CI.

The observed substituent effects due to the CH<sub>3</sub> group are, in this case, opposite to those observed in HCCH fragments.<sup>24</sup> In order to check the validity of the FPT calculations, we calculated also the couplings in ethane and its methyl-substituted derivatives. The calculated effects were  $-0.2$  and  $-0.3$  Hz for propane *vs.* ethane and butane *vs.* propane, respectively. This is in qualitative agreement with the observed value of  $-0.65$  Hz.<sup>24</sup>

*2-Propanol.* The considerations of Rader<sup>20</sup> give for 2-propanol about 87% of VII and 13% of IX, corresponding to  $\Delta E = 3.0$  kJ. Similar considerations on the basis of  $^3J(\text{OH},\text{C})$  couplings of *tert*-butyl alcohol result in 89% of VII. The microwave measurements<sup>25,26</sup> and molecular mechanics calculations<sup>22</sup> suggest clearly smaller  $\Delta E$ , 1.4 and 1.0 kJ, respectively. However, as in the case of  $^3J(\text{OH},\text{C})$  of ethanol,  $^3J(\text{OH},\text{H})$  coupling in 2-propanol is very dependent on the dihedral angle HOCH. The measuring of the  $^3J(\text{OH},\text{H})$  at temperatures 194, 228, 250, 286 and 298 K gave the values 3.61, 3.91, 4.03, 4.15 and 4.27 Hz, which result in  $(2J(\text{VII}) + J(\text{IX}))/3 = 5.40 \pm 0.20$  Hz. The large (90%) confidence limits are due to the fact that, in this case, the widths of doublets were measured instead of triplets, as in the case of ethanol.  $J(\text{IX})$  can be supposed to be about  $11.75 \pm 0.5$  Hz on the basis of the model compounds of Rader<sup>20</sup> and the previous considerations on ethanol. This corre-

sponds to  $J(\text{VII}) = 2.22 \pm 0.40$  Hz,  $78 \pm 3\%$  of VII,  $\Delta E = 1.4 \pm 0.5$  kJ and  $\phi(\text{HOCH}) = 65 \pm 2^\circ$  in structure VII.

If the values of *tert*-butyl alcohol and the percentages obtained above are applied directly, without including angular or substituent effects,  $^3J(\text{OH},\text{C}) = 2.91 \pm 0.05$  is obtained, while the observed value is 3.13 Hz. By applying the substituent effect  $-0.3$  Hz to the value of *tert*-butyl alcohol, one obtains the still lower value of 2.78 Hz. However, if dihedral angles  $\phi(\text{HOCH}) = 67^\circ$ ,  $\phi(\text{HOCC}) = 46^\circ$  (in VII) and  $\phi(\text{HOCC}) = 65^\circ$  (in IX, see Fig. 2) are applied to the equation  $J = (5.38 - 0.30) \cos^2 \phi$ , the experimental value  $^3J(\text{OH},\text{C}) = 3.13 \pm 0.05$  Hz is obtained. Also the  $\phi(\text{HCOH})$  of VII is in agreement with the value suggested above and with molecular mechanics calculations.<sup>18,22</sup> In addition, FPT calculations (Table 2) suggest that the substituent effects do not operate on  $J^b$  as much as on  $J^a$ , which means that the simple Karplus relationship used is not satisfactory. To summarize, no very reliable evidence on the magnitude of the substituent effects is available in this case.

*Acetylacetone and salicylaldehyde.* These cases represent the enolic and phenolic protons, or more generally, the hydroxyls bonded to *sp*<sup>2</sup> carbons. The conformational behaviour of the phenolic hydroxyls has been well documented and discussed earlier.<sup>1</sup> It appears, also in this case, that the FPT

method predicts the conformational behaviour quite well (Table 1). In the case of acetylacetone, the calculations were carried out for structures XI and XII.<sup>27</sup> In XII the bond lengths for localized single and double bonds were used<sup>15</sup> and in IX the corresponding average values were applied. The results suggest that XII is the more real structure, although the low energy difference between the forms XI and XII, and also the too low calculated value of  ${}^2J$  in XII (especially when compared to the correlation in the other cases) suggest that the hydrogen-bonding has an effect on the structure of the hydroxyl group. The effect is, however, overestimated in the structure XI.

### The geminal couplings

The magnitudes of the geminal HH couplings are governed by three factors: Inductive and hyperconjugative substituent effects and conformational factors.<sup>4,28</sup> The simple correlation between HH and CH couplings<sup>21</sup> suggests that the same factors are operating in both couplings.<sup>21,29</sup> In the case of simple aliphatic systems, the trends in  ${}^2J(\text{CH})$  couplings may be interpreted on the basis of inductive effects of substituents and hybridization of the carbon.<sup>30</sup> Comparing the data reviewed by Jameson and Damasco<sup>30</sup> and our own data, one easily discovers that the  ${}^2J(\text{OH},\text{C})$ 's compare well with  ${}^2J(\text{C}_{\text{sp}^3}\text{H},\text{C})$ 's. A similar conclusion can be drawn also for the vicinal couplings, the absolute values of  ${}^3J(\text{OH},\text{C})$  couplings being systematically smaller than the corresponding  ${}^3J(\text{CH},\text{C})$  couplings.<sup>31,24</sup>

The trends observed by Jameson and Damasco can be summarized as follows: (i) The absolute value of the coupling  ${}^2J(\text{XH},\text{C})$  (X is C or O) is proportional to the *s*-nature of electron densities at H and C, and (ii) the more of *s*-character in the CX bond,

the more negative is the coupling. In other words, the value of the couplings should be dependent on the *s*-bond-orders of C-COH and CC-OH bonds, for  ${}^2J(\text{CH}_3,\text{CH})$  and  ${}^2J(\text{OH},\text{CH})$ , respectively. The *s*-CC-OH (and *s*-C-COH) bond-orders of salicylaldehyde, methanol, ethanol, 2-propanol and *tert*-butyl alcohol are 0.2175 (-), 0.1787 (-), 0.1777 (0.2580), 0.1740 (0.2539) and 0.1724 (0.2476), respectively. The conformational ratios derived above are used in these values. A comparison of these values with the observed ones shows that the rule (ii) is approximately obeyed in this case.

The electron density variations and also the coupling correlations are connected with the double-bond nature of CO bond. In salicylaldehyde the  $\pi$ -bond-order of CO is 0.312, in methanol it is 0.183 and ethanol about 0.170 (in the conformation IV, as in all conformations of 2-propanol and *tert*-butyl alcohol, the  $\pi$ -type orbitals are slightly mixed with  $\sigma$ -orbitals). Furthermore, there is a clear correlation between the couplings and the *s*-electron densities, as shown in Table 3 and Fig. 4.

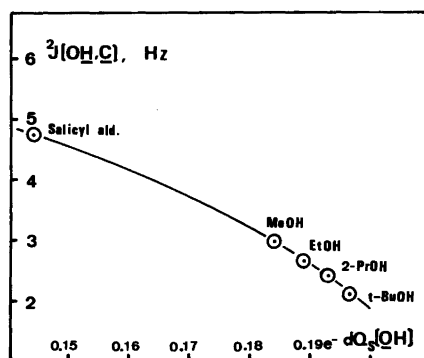


Fig. 4. The  ${}^2J(\text{OH},\text{C})$  couplings of some alcohols vs. the INDO *s*-electron excesses at OH's.

Table 3. The electron excesses ( $dQ_s$  and  $dQ_p$  in  $e^-$ , for *s*- and *p*-electrons) at OH, OH, COH and CCOH's of the aliphatic alcohols and salicylaldehyde. The values are calculated with INDO method and the conformational effects are included using the conformational ratios given in the text.

|                            | OH     |        | OH      |        | COH     |         | CCOH   |         |
|----------------------------|--------|--------|---------|--------|---------|---------|--------|---------|
|                            | $dQ_s$ | $dQ_p$ | $dQ_s$  | $dQ_p$ | $dQ_s$  | $dQ_p$  | $dQ_s$ | $dQ_p$  |
| Salicylaldehyde            | 0.1442 | 0.1768 | -0.2034 |        | 0.0157  | -0.2868 | -      | -       |
| Methanol                   | 0.1842 | 0.1170 | -0.1698 |        | 0.0500  | -0.3015 | -      | -       |
| Ethanol                    | 0.1891 | 0.1229 | -0.1645 |        | 0.0201  | -0.2703 | 0.0504 | -0.0660 |
| 2-Propanol                 | 0.1932 | 0.1275 | -0.1604 |        | -0.0029 | -0.2384 | 0.0540 | -0.0717 |
| <i>tert</i> -Butyl alcohol | 0.1965 | 0.1322 | -0.1577 |        | -0.0208 | -0.2054 | 0.0578 | -0.0776 |

The only general correlation, *i.e.* valid also for salicylaldehyde, exists between  ${}^2J(\text{OH},\text{C})$ 's and the *s*-electron densities at OH (Fig. 4) or OH.

The FPT method appears to predict the general trends very well after inclusion of the conformational effects. The calculated values of  ${}^2J(\text{OH},\text{C})$  for our material are  $-7.41$ ,  $-6.90$ ,  $-6.47$  and  $-6.08$  Hz, corresponding to the observed values  $-3.00$ ,  $-2.67$ ,  $-2.44$  and  $-2.12$  Hz. The methyl substituent effects 0.51, 0.43 and 0.39 correspond, at least qualitatively, to the observed values 0.33, 0.23 and 0.32 Hz. A similar trend is observed also in the case of  ${}^2J(\text{CH},\text{CH}_3)$ 's and approximately for the two  ${}^2J(\text{CH}_3,\text{CH})$ 's (see Table 1). In the case of  ${}^2J(\text{OH},\text{C})$  the inclusion of the conformational effects is necessary, thus indicating that the FPT method can predict also the conformational effects correctly. In the case of  ${}^2J(\text{CH}_3,\text{CH})$ , the FPT results are not very good, indicating some deformations of the bond-angles, suggested also above in the case of the vicinal couplings for 2-propanol.

## CONCLUSIONS

The comparison of the behaviour of  ${}^3J$  and  ${}^2J$  of the OH proton with that of corresponding couplings of  $\text{CH}_3$  proton, suggests that their coupling behaviour is similar although the absolute values of the couplings are clearly smaller for the OH group. For example, when ethane and methanol are compared,  ${}^3J^a(\text{HH})$ 's are about 16.0 and 10.2 Hz, and  ${}^2J(\text{CH})$ 's are  $-4.5$  and  $-3.0$  Hz, respectively.<sup>2</sup>

The FPT calculations and the consideration of the conformations suggest that both the  ${}^3J$  and  ${}^2J$ 's are substituent dependent, and that the substituent effects must be taken into account when the couplings are used in conformational analysis. Generally, the FPT calculations appear to interpret the most important trends correctly, while the SOS methods fail in the case of  ${}^2J$  couplings. The inclusion of the first-order corrections to the excitation energies (on the basis of eqn. (1)) does not improve the results at all.

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