Acid-induced ^{13}C N.m.r. Chemical-shift Changes of Alcohol Carbon Atoms

By **Mikael Begtrup**, Department of Organic Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark

^{13}C N.m.r. shifts of alcohols dissolved in tetrachloromethane are displaced on addition of trifluoroacetic acid. The structure-dependent and stereoselective shift changes are useful for signal assignments, structure determination, conformational analysis, assessment of distribution of rapidly interconverting conformers, and estimation of the relative basicity of alcohols.

THE change in ^{13}C n.m.r. chemical shifts upon protonation of amines [1,2] and other organic nitrogen bases [3,4] follows certain structure-dependent trends and is useful for making ^{13}C resonance assignments. Protonation shifts up to 10 p.p.m. have been reported, with their pH dependence following classic titration curves.[4,5] Therefore, titration of nitrogen bases with acids can be monitored by ^{13}C n.m.r. spectroscopy. Carbon-13 n.m.r. protonation shift studies of other strong bases, *e.g.* phenolates [6] and carboxylates,[7] have been published, whereas reports on protonation shifts of weak bases are few and determination of their basicity using ^{13}C n.m.r. spectroscopy has been reported only for ketones.[8] The ^{13}C n.m.r. protonation shift of methanol in the extremely strong acid FSO_3H-SbF_5, diluted with SO_2, is -14.6 p.p.m.[9] (shift change $\equiv$ shift in neutral solution $-$ shift in acidic solution). Attempted basicity measurements of alcohols in aqueous acid using ^1H n.m.r. spectroscopy were hampered by association phenomena.[1c,11] In tetrachloromethane, trifluoroacetic acid (TFA) does not protonate alcohols, but rather causes proton shift changes deriving from hydrogen bonding.[12] Proton shift changes as such were not used to estimate basicity, but the proclivity to form hydrogen bonds may run parallel to the basicity as demonstrated for certain types of bases.[13-16] On this background, estimates of the relative basicity of alcohols should be obtainable from trifluoroacetic acid-induced carbon shift changes in tetrachloromethane, which does not form hydrogen bonds or associate significantly with alcohols.

RESULTS AND DISCUSSION

The ^{13}C shift changes of a 1M solution of butan-1-ol in tetrachloromethane containing trifluoroacetic acid, as a function of the alcohol : acid ratio, is shown in Figure 1.

All carbons except C-1 are shifted to higher field. At a 1 : 1 alcohol : acid ratio the shifts of C-1 and C-2 >1 p.p.m., while C-4 and C-3 are displaced by 0.5 and 0.4 p.p.m., respectively. Due to the opposite sign of the two largest shifts the most acid-sensitive parameter is δ(C-1) $-$ δ(C-2). The shift changes induced by trifluoroacetic acid in tetrachloromethane are substantially larger than those observed in aqueous trifluoroacetic acid or sulphuric acid of similar concentration (Table 1) in which neither protonation nor formation of alcohol–acid hydrogen bonds seem to be significant.

At low acid : alcohol ratios the shift displacements in tetrachloromethane solution are linearly dependent on the acid : alcohol ratio. At higher ratios the line deflects progressively with increasing ratio and the shift displacements, most strikingly that of C-1 (Table 1), seem to converge towards limiting values. This is expected when a weak base is progressively protonated by a strong acid. However, the maximum shift changes in trifluoroacetic acid–tetrachloromethane are considerably smaller than expected from extensive protonation [9] such as is observed in strong aqueous sulphuric acid (Table 1) where protonation is known to occur.[10,11] The ^{13}C n.m.r. data thus confirm that hydrogen bonding between alcohol and trifluoroacetic acid is the process of major importance in tetrachloromethane.

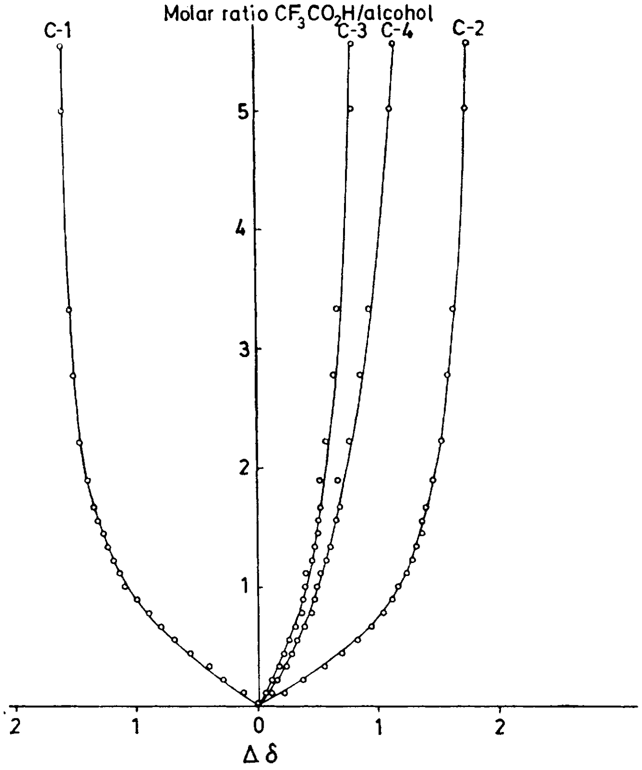

FIGURE 1 ^{13}C N.m.r. shift changes of a 1M solution of butan-1-ol in CCl_4 containing trifluoroacetic acid, as a function of the molar ratio acid/alcohol

The acid is entirely bound to the substrate in the linear region. The slopes of the lines (for C-1 −1.40 ± 0.03 and for C-2 1.78 ± 0.03 *), correspond to the theoretical shift changes for a 1 : 1 adduct. They are exceeded by the estimated limit values, due to general solvent shifts resulting from the changing medium, to incipient protonation, and/or to formation of *n* : 1 acid–alcohol adduct(s), but in any case so slightly that the shift changes of Figure 1 to a good approximation reflect the progressive bonding of one molecule of acid to one molecule of alcohol. When alcohol and acid are present in equimolar amounts the equilibrium constant *K* characterizing the extent of hydrogen bonding is given by equation (2),

$$\mathrm{ROH} + \mathrm{HA} \rightleftharpoons \underset{\mathrm{H}}{\mathrm{RO}} \cdots \mathrm{HA} \tag{1}$$

$$K = \frac{\left[\underset{\mathrm{H}}{\mathrm{RO}} \cdots \mathrm{HA}\right]}{[\mathrm{ROH}]^2} \tag{2}$$

in which $[\mathrm{ROH}]_{\mathrm{free}} = 1 - [\mathrm{ROH}]_{\mathrm{bound}}$, in its turn given by the ratio between the actual shift change and that calculated for a 1 : 1 adduct.

TABLE 1

^{13}C N.m.r. chemical shift changes (in p.p.m.) observed on addition of *n* mol of acid to a 1M solution of butan-1-ol

Solvent	Acid	*n*	Carbon atom 1	2	3	4
CCl_4	CF_3CO_2H	1	−1.11	1.16	0.39	0.49
		5	−1.60	1.73	0.79	1.11
		10	−1.62	1.89	1.00	1.49
H_2O	CF_3CO_2H	1	−0.03	0.07	0.08	0.09
		5 *	−0.42	0.07	0.08	0.33
H_2O	H_2SO_4	0.5	−0.06	0.00	−0.03	−0.04
		2.5 *	−0.59	0.17	−0.02	−0.10
92% H_2SO_4			−9.93	3.50	0.73	0.45

* The solution is inhomogeneous.

TABLE 2

^{13}C N.m.r. chemical shift changes (in p.p.m.) observed on addition of 1 molar equivalent of CF_3CO_2H to a 1M solution of an unbranched alcohol in CCl_4

Alcohol	Carbon atom [a] 1	2	3	4	5	6	7	8	9	10	11	12
Methanol	0.23											
Ethanol	−1.42	1.30										
Propan-1-ol	−1.03	1.05	0.65									
Butan-1-ol	−1.15	1.21	0.40	0.49								
Pentan-1-ol	−1.11	1.17	0.52	0.36	0.43							
Hexan-1-ol	−1.09	1.17	0.47	0.38	0.30	0.36						
Heptan-1-ol	−1.12	1.16	0.46	0.46	0.30	0.19	0.27					
Octan-1-ol	−1.12	1.15	0.46	0.58	0.26	0.22	0.17	0.24				
Nonan-1-ol	−1.15	1.20	0.49	0.51	0.17		0.16	0.14	0.22			
Decan-1-ol	−1.13	1.17	0.47					0.14	0.11	0.19		
Undecan-1-ol	−1.11	1.16	0.46						0.11	0.11	0.16	
Dodecan-1-ol	−1.12	1.15	0.46							0.07	0.07	0.16
Mean value [b]	−1.12	1.17	0.47									

[a] Assignments according to J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Amer. Chem. Soc.*, 1970, **92**, 1338.
[b] Calculated using shift displacements of alcohols with more than three carbon atoms.

The effect of structural and stereochemical factors on the magnitude of the trifluoroacetic acid-induced carbon shift changes and the hydrogen-bonding constants is apparent from the results of Tables 2—5. In unbranched alcohols the shift displacements of C-1, C-2, C-3, and C-4, respectively, are almost constant (Table 2). Only ethanol shows slightly larger shift changes. The magnitude of the shift displacement of C-1 (negative) and C-2 (positive) are similar, while C-3 and C-4 (both positive) are displaced roughly half as much. From C-4 the shift displacements seem to decrease steadily towards the terminal carbon atom, which exhibits a slightly larger displacement, observable even when 11 carbon atoms separate it from the hydroxy-group.

Branched alcohols also exhibit consistent acid-induced carbon shift displacements (Table 3). The shift displacement of the hydroxy-carbon atom increases almost equidistantly in the series methanol, primary, secondary, and tertiary alcohols. It is virtually constant in secondary and tertiary alcohols, while in primary alcohols it depends on the branching of the alkyl group. A methyl group at the α, β, or γ position causes a *ca.* 35% decrease, a *ca.* 10% increase, or a slight decrease, respectively, of the hydroxy-carbon shift displacement (Table 4). The effect of more branchings is approximately additive, unless a quaternary α-carbon atom results. This may be due to the steric compression so frequently encountered in ^{13}C n.m.r.

The methyl-substituted α, β, or γ carbon atoms themselves are decreasingly influenced by the branching, α-carbon atoms independent of the type of alcohol, and β-carbon atoms invariably in primary and secondary alchols. Adjacent carbon atoms are less sensitive to methyl groups, except β-carbon atoms of secondary alcohols which, like hydroxy-carbon atoms of primary alcohols, are significantly influenced by α-branching.

Prediction of the acid-induced shift displacements of the individual carbon atoms of any, not excessively sterically crowded, acyclic alcohol is now possible. After characterization of the alcohol the hydroxy-carbon shift displacement is assessed using the incre-

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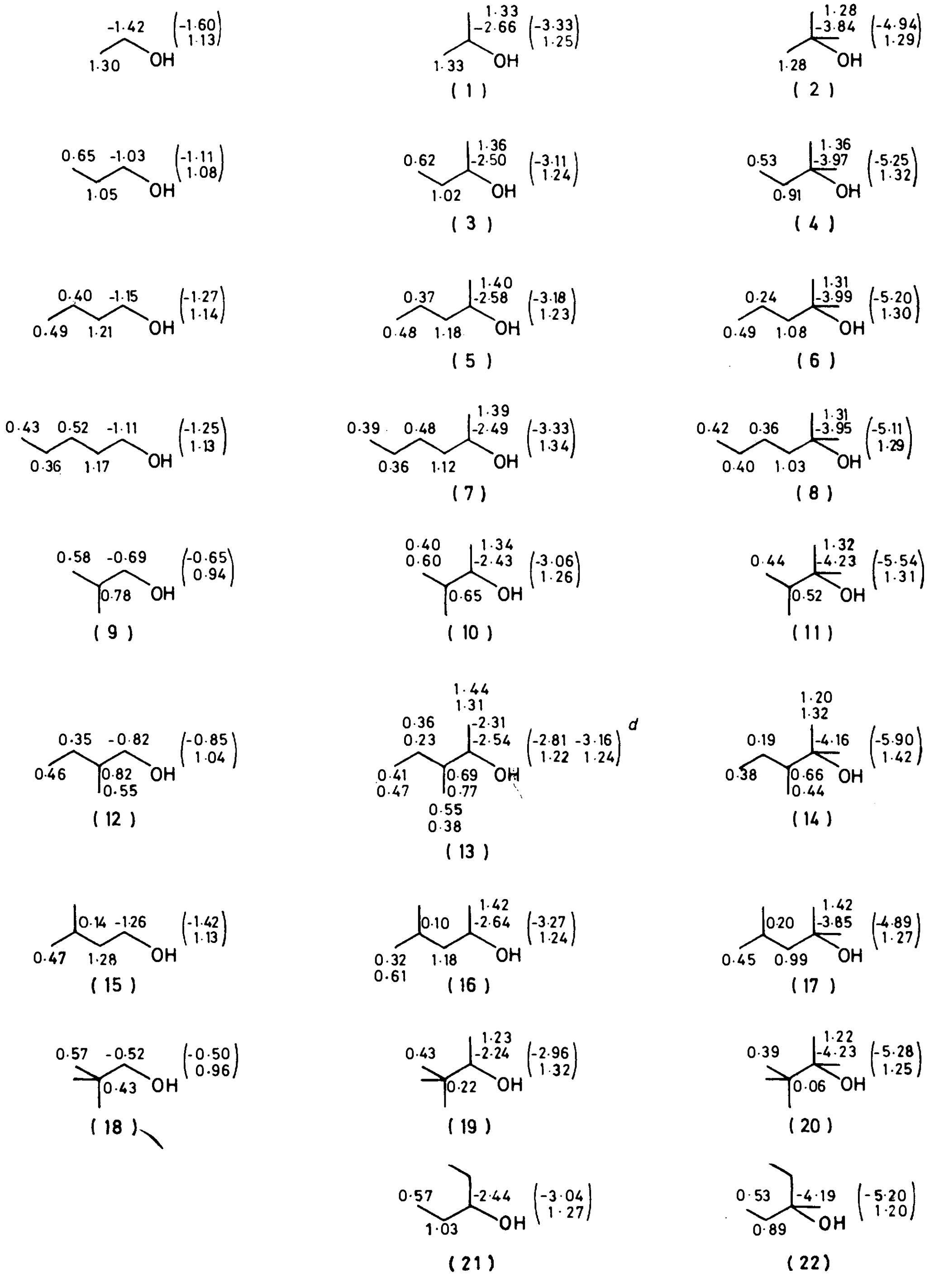
* Obtained by a least-squares calculation from shift changes observed on stepwise addition of ten 0.01 molar aliquots of trifluoroacetic acid to the butanol solution.

TABLE 3

^{13}C N.m.r. shift displacements (p.p.m.) of a 1M solution of alcohol and CF_3CO_2H in CCl_4,[a] extrapolated hydroxy-carbon shift displacements of a 1 : 1 alcohol-CF_3CO_2H adduct,[b] and K values[c] in l mol^{-1} (in parentheses above and below, respectively)



[a] The ^{13}C n.m.r. spectra were assigned following J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Amer. Chem. Soc.*, 1970, **92**, 1338, with the following exceptions: compounds (8), (14), and (17) (see Experimental section); compounds (6), (13), and (22) (K. L. Williamson, D. R. Clutter, R. Emch, M. Alexander, A. E. Burroughs, C. Chua, and M. E. Bagel, *J. Amer. Chem. Soc.*, 1974, **96**, 1471); and compound (20) (L. M. Jackmann and D. P. Kelly, *J. Chem. Soc.* (*B*), 1970, 102). [b] Obtained from a least-squares calculation using shift displacements observed on stepwise addition of 0.05 molar equivalents of CF_3CO_2H to a 1M solution of alcohol in CCl_4. Accuracy better than ±0.02. [c] Calculated as described in the text. [d] The *erythro*- (upper and left figures) and the *threo*-isomer were investigated in *ca.* 1 : 1 mixture. This may give rise to slightly erratic shift displacements.

TABLE 4

The effect of branching on CF_3CO_2H-induced alcohol carbon shift displacements. Mean values in p.p.m. extracted from Table 3. If values are scattered the interval is given. A negative sign indicates a numerical decrease of shift displacement

Alcohol	Position of branch	C-OH	Carbon atom		
			C-α	C-β	C-γ
Primary	C-OH	1.15—1.75	−0.1	−0.05	0
	C-α	−0.35	−0.3	−0.05	−0.05
	C-β	0.1	0.1	−0.25	0
	C-γ	−0.05	−0.05	0.1	−0.15
Secondary	C-OH	1.3—2.0	−0.1	−0.1	0
	C-α	−0.05 to −0.25	−0.4	−0.1	−0.05
	C-β	−0.1 to 0.1	0.1	−0.15	0
	C-γ	−0.1	−0.05	0.1	−0.1
	C-α′		0	−0.05	
Tertiary	C-α	0.2	−0.4	−0.1	−0.05
	C-β	−0.1	−0.15 to 0.15	−0.2	−0.1
	C-γ	−0.1	−0.1	0.1	−0.1
	C-α′		0.05	0	

ments of Table 4. Estimation of the individual alkyl carbon shift displacements is based on values obtaining for the longest straight chain (Table 2), corrected for branching increments (Table 4).

Two examples may serve to illustrate the procedure and its accuracy. The hydroxy-carbon shift displacement of 2,4-dimethylpentan-3-ol is estimated from the shift displacement of propan-2-ol (−2.66 p.p.m.), corrected for the influence of four α-substituents (4 × 0.15 p.p.m.) to give −2.05 p.p.m. (observed −2.41 p.p.m.). The α-carbon shift displacement is calculated from that of propan-1-ol (1.05 p.p.m.) corrected for the influence of a hydroxy-carbon, an α-, and two α′-substituents (−0.1, −0.40, and 2 × 0 p.p.m., respectively) to give 0.65 p.p.m. (observed 0.45 p.p.m.). The β-carbon shift displacement is derived from that of propan-1-ol (0.65 p.p.m.), corrected for the influence of the substituents above (−0.05, −0.05, and 2 × −0.05 p.p.m.) to give 0.40 p.p.m. (observed for the diastereotopic β-carbon atoms, 0.40 and 0.43 p.p.m.). The calculated and observed (in brackets) carbon shift displacements for 3,5-dimethylhexan-3-ol also agree reasonably well; C-1 0.55 (0.40); C-2 0.90 (1.02); C-3 −4.05 (−4.12); C-4 1.05 (1.06); C-5 0.1 (0.21); C-6 0.4 (two diastereotopic carbon atoms, 0.40 and 0.43); Me at C-3 1.2 (1.37 p.p.m.).

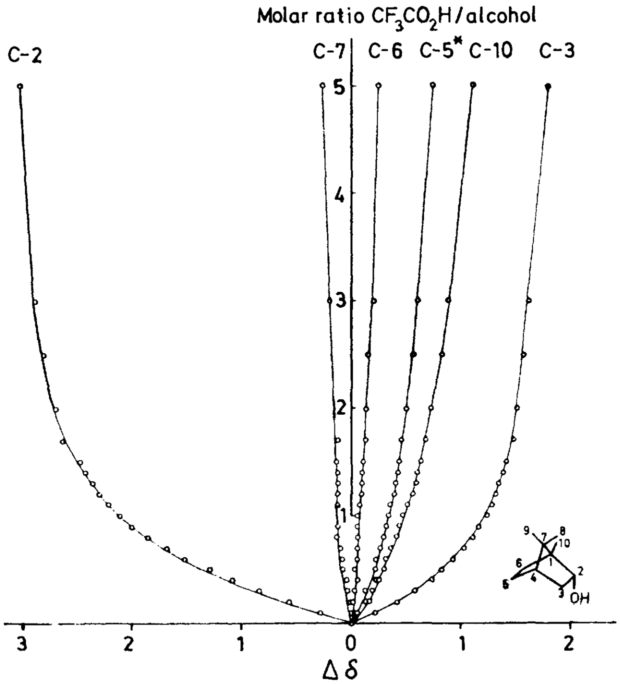


FIGURE 2 ^{13}C N.m.r. shift changes of a 1M solution of borneol in CCl_4, containing trifluoroacetic acid, as a function of the molar ratio acid/alcohol (* C-4 and C-5 display almost identical shift displacements)

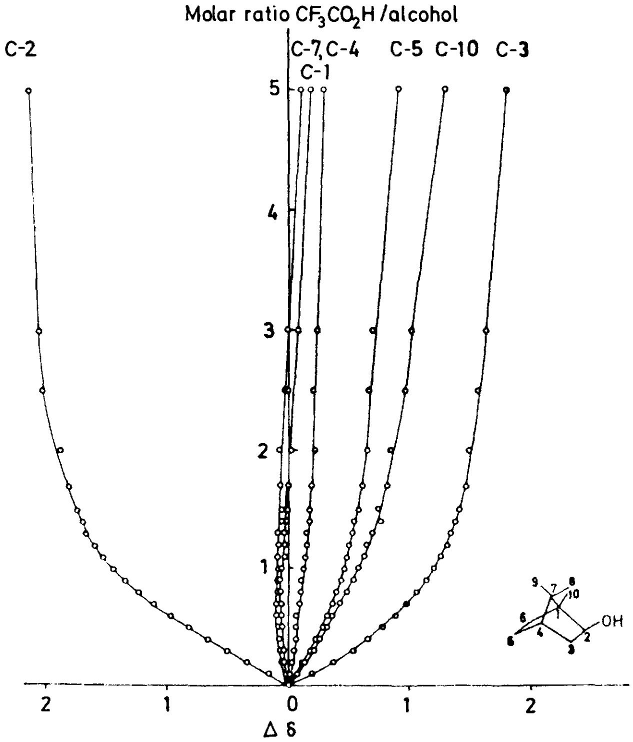


FIGURE 3 ^{13}C N.m.r. shift changes of a 1M solution of isoborneol in CCl_4, containing trifluoroacetic acid, as a function of the molar ratio acid/alcohol

In contrast to structural changes, the steric orientation of the hydroxy-group significantly influences the hydroxy-carbon shift displacement of secondary alcohols; compare borneol and isoborneol (Table 5) and the conformationally rigid *cis*- and *trans*-4-t-butylcyclohexanol. These empirical differences can be a useful aid to distinguish between *e.g. exo*- and *endo*-hydroxybornanes or between equatorial and axial orientation of hydroxy groups in cyclohexanes.

γ-Substitution of alcohols effects the hydroxy-carbon shift displacement so little that pentan-3-ol can be regarded as a conformationally mobile analogue of cyclohexanol. Accordingly, its hydroxy-carbon shift displacement equals the mean value of those of *cis*- and

TABLE 5

^{13}C N.m.r. shift displacements (p.p.m.) of a 1M solution of cyclic alcohol and CF_3CO_2H in CCl_4, extrapolated hydroxy-carbon shift displacements of a 1 : 1 alcohol-CF_3CO_2H adduct[a] (in parentheses), conformer distribution, and K values[b]

	Carbon atom											Percentage of conformer with axial hydroxy-group (previous determinations in parentheses)
Alcohol[c]	1	2	3	4	5	6	7	8	9	10	K/ l mol^{-1}	
1,7,7-Trimethyl-*endo*-bicyclo[2.2.1]heptan-2-ol (borneol)[d]	0.06	−2.12 (−2.81)	1.23	0.34	0.34	0.08	−0.12	0.31	0.35	0.47	1.33	
1,7,7-Trimethyl-*exo*-bicyclo[2.2.1]heptan-2-ol (isoborneol)[e]	−0.06	−1.45 (−1.66)	1.19	0.12	0.45	0.21	−0.09	0.46	0.39	0.57	1.14	
Cyclohexanol	−2.22 (−2.77)	1.16	0.33	0.62							1.25	20 (23[f])
1-Methylcyclohexanol	−4.10 (−5.19)	1.01	0.59	1.70	0.26						1.27	
cis-2-Methylcyclohexanol	−2.58	0.21										*ca.* 85[g] (78[h])
trans-2-Methylcyclohexanol	−1.99	0.76										*ca.* 0[g] (8[h])
cis-3-Methylcyclohexanol	−1.90	1.39										*ca.* 0[g] (2[i])
trans-3-Methylcyclohexanol	−2.52	1.28										*ca.* 75[g] (85[i])
cis-4-Methylcyclohexanol	−2.66	1.23										100 (80[i])
trans-4-Methylcyclohexanol	−2.04	1.15										0 (2[i])
cis-4-t-Butylcyclohexanol	−2.66 (−3.41)	1.23	0.33	0.49	0.15	0.37					1.28	100[j]
trans-4-t-Butylcyclohexanol	−2.11 (−2.57)	1.21	0.34	0.39	0.18	0.28					1.22	0[j]

[a] Calculated by the method of least squares using shift displacements observed by stepwise addition of six 0.05 molar equivalents of CF_3CO_2H to the alcohol solution. [b] Calculated using equation 2. [c] Previous assignments of signals as in Table 2 footnote *a*, unless otherwise stated. [d] J. Briggs, F. A. Hart, G. P. Moss, and E. W. Randall, *Chem. Comm.*, 1971, 364. [e] O. A. Gansow, M. R. Willcott, and R. E. Lenkinski, *J. Amer. Chem. Soc.*, 1971, **93**, 4295. [f] A. H. Lewin and S. Winstein, *J. Amer. Chem. Soc.*, 1962, **84**, 2464. [g] More accurate determination requires information about the influence of axial with respect to equatorial methyl groups on the hydroxy-carbon shift displacement. [h] J. Sicher and M. Tichy, *Coll. Czech. Chem. Comm.*, 1967, **32**, 3687. [i] See ref. 19. [j] Assumed.

trans-t-butylcyclohexanol. This suggests that a shift-displacement analysis may allow assessment of the distribution of rapidly interconverting conformers. In fact, the hydroxy-carbon shift displacement of cyclohexanol when compared with those of *cis*- and *trans*-4-t-butylcyclohexanol, representing the individual conformers of cyclohexanol, signals the presence of 80% of the *trans*-conformer (Table 5). This agrees with a reported conformational energy of 3.1 kJ mol^{-1} under similar experimental conditions.[17,18] Determination of the conformer distribution in *cis*- and *trans*-2-, 3-, and 4-methylcyclohexanol with reference to the hydroxy-carbon shift displacement of *cis*- and *trans*-4-t-butylcyclohexanol also agrees with previous results (Table 5).

Hence, hydroxy-carbon shift displacements can be valuable when assessing the distribution between rapidly interconverting conformers with differently oriented hydroxy-groups. Steric influence on shift displacements also appears from the different changes displayed by diastereotopic carbon atoms and by *erythro*- and *threo*-3-methylpentan-2-ol (Table 3).

TABLE 6

Previously unassigned ^{13}C n.m.r. spectra of alcohols studied in the present paper (1M solution in CCl_4; p.p.m. relative to external dioxan at 67.40 p.p.m.)

	Carbon atom						
Alcohol	1	2	3	4	5	6	Me
2-Methylhexan-2-ol (8)	30.10	70.96	44.52	27.27	24.05	14.87	
2,3-Dimethylpentan-2-ol (14)	27.09 27.99	73.57	47.01	24.90	14.68		13.76
2,4-Dimethylpentan-2-ol (17)	30.91	71.54	53.29	25.20	25.60		
2,4-Dimethylpentan-3-ol	17.81 20.72	31.31	81.98				26.63
3,5-Dimethylhexan-3-ol	9.13	36.03	73.53	50.84	25.80	24.85 25.64	27.59

The K values calculated from equation (2) using extrapolated and observed hydroxy-carbon shift displacements * of 1 : 1 alcohol–trifluoroacetic acid mixtures † display minor, but consistent variations in the primary alcohols (Table 4). α-Methyl branching leads to a *ca.* 5% reduction of the K value while β-branching causes a *ca.* 5% increase; γ-branching is without significant effect. The K values increase in the series

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* The hydroxy-carbon shift displacement was chosen since at increasing TFA concentration this most conspicuously converges against a vertical asympote; increasing, yet slight, inclinations are observed for carbon atoms progressively removed from the carbinol carbon atom (see Figures 1 and 2).

† As in butan-1-ol, discussed above, the extrapolated values are normally exceeded by the estimated limit values, but the difference decreases in the series primary, secondary, and tertiary alcohols.

primary, secondary, and tertiary alcohols, but are less sensitive to structural changes in the two latter series. The increase in the K value corresponds to the relative basicity of primary, secondary, and tertiary alcohols,[13] indicating that the K values, in addition to their ability to form hydrogen bonds, reflect the relative basicity of the individual alcohols.

In contrast to structural variations, the steric orientation of the hydroxy-group markedly influences the K value of secondary alcohols. Thus, the K values of borneol and isoborneol indicate that the *exo* is more basic than the *endo*-hydroxy-group, and the K values of *cis*- and *trans*-4-t-butylcyclohexanol reveal that the equatorial hydroxy-group is more basic than the axial (Table 5). The K values, like the shift displacements of pentan-3-ol and cyclohexanol fall between those of the rigid cyclohexanols.

Conclusions.—The magnitude of the trifluoroacetic acid-induced ^{13}C n.m.r. shift displacement of alcohol carbon atoms follows structure-dependent trends which makes it possible to distinguish between primary, secondary, and tertiary alcohols, and to obtain information about their structure using increments characteristic of the position of branching. The shift displacements are stereoselective, permitting a distinction between *endo* and *exo* or between axial and equatorial hydroxy-groups, as well as estimation of the composition of rapidly equilibrating mixtures of such conformers. Finally, the shift changes seem to provide information about the relative basicity of alcohols and its dependence on structural and steric factors.

EXPERIMENTAL

All compounds are commercially available (Fluka), except (14), (20), 2,4-dimethylpentan-3-ol, 3,5-dimethylhexan-3-ol, and 1-methylcyclohexanol, which were prepared by conventional Grignard reactions.[20,21] 2-Methyl-, 3-methyl-, and 4-t-butyl-cyclohexanols are available as *cis*-*trans* mixtures. *trans* 4-t-Butylcyclohexanol was isolated *via* its hydrogenphthalate.[22] The *cis*-isomer was obtained by chromatography on a column of acidic alumina.[22] The *cis-trans* mixtures of 2- and 3-methylcyclohexanol were not separated, but investigated in *ca.* 1 : 1 mixtures. This may give rise to slightly erratic shift displacements. All liquid alcohols were distilled from barium oxide. The accuracy in concentrations of substrates was better than 2%.

^{13}C N.m.r. spectra were recorded in the Fourier-transform mode on a Bruker WH-90 instrument at 28 °C. 25—50 Scans were accumulated with 3- or 6-s (tertiary alcohols) repetition time and a 45° tilt angle. A concentric tube contained the lock substance (deuterium oxide) and the chemical shift standard (dioxan). An accuracy to ±0.01 p.p.m. in chemical shifts was attained using a digital resolution of 2.68 points Hz^{-1} combined with signal position assessment using parabolic three-point interpolation.

^{13}C N.m.r. data of (8), (14), (17), 2,4-dimethylpentan-3-ol, and 3,5-dimethylhexan-3-ol have not been reported previously. The signals were assigned from coupled spectra through multiplicity of one-bond C–H splittings. If ambiguity then persisted the multiplicity due to two- and three-bond couplings was employed to secure the assignment.

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