Tetrahedron Vol. 34, pp. 2947–2951

0040-4020/78/1001-2947/$02.00/0

ROTATIONAL ISOMERISM—22[1]

AN NMR STUDY OF OH.. π BONDING AND THE CONFORMATIONS OF BENZYL ALCOHOL AND DERIVATIVES

R. J. Abraham
The Robert Robinson Laboratories, The University of Liverpool, Liverpool, England

and

J. M. Bakke
The Chemistry Department, The University of Trondheim, NLHT, N-7000 Trondheim, Norway

(*Received in UK* 12 *January* 1978; *accepted for publication* 14 *April* 1978)

Abstract—The conformations of benzyl alcohol, the *ortho* and *para* nitro and methoxy derivatives and benzyl methyl ether have been investigated by NMR in CCl_4 and DMSO solutions. The ^3J(CH.OH) and ^2J(H.C.H) couplings (the latter via the ^2J(H.C.D) coupling) and the OH chemical shift (in DMSO and ∞ dil^n in CCl_4) were used as conformational probes. The δ_∞ (OH) for ROH (R = Me, Et, iPr) is also given.

The results provide no support for the existence of an intramolecular H-bond in benzyl alcohol. The *endo* conformation of the OH proton (*anti* to a CH proton) is favoured by *ca.* 1 kcal mole^{-1} over the *exo* conformation (H *anti* to phenyl) and these conformers are responsible for the separate OH frequencies observed in the IR spectrum. The results do not support an extreme conformation of the phenyl ring (C.C.C.O dihedrals of 0 or 90°) but are consistent with either an ~60° conformation of the phenyl ring or a freely rotating model. In *ortho* nitrobenzyl alcohol intramolecular H-bonding is present, but in *ortho* methoxy benzyl alcohol little or no bonding to the substituent occurs.

The observation of two OH stretching bands in the IR spectrum of aryl alcohols $C_6H_5(CH_2)_nOH$ in dilute solution has been generally interpreted as evidence for intramolecular OH...π bonding.[2-5] In benzyl alcohol itself the OH frequencies (3635 and 3615 cm^{-1}) are so similar to those of ethanol (3637 and 3623 cm^{-1}) that an alternative interpretation that these are merely those characteristic of a primary alcohol has been proposed.[6]

An IR study of substituted benzyl alcohols showed that H-bonding to the *ortho* substituent was weak or non-existent, only the *ortho* nitro group giving a definite effect.[7] In contrast, in 1,2-diphenyl ethanols the more favourable substituent -OH geometry produced a strong intramolecular H-bond.

NMR investigations should complement these studies, and Schaefer *et al.* have used NMR and MO techniques, in particular the ^6J (CH_2, p-H) coupling to deduce the conformations of a number of benzyl derivatives.[8,9] In *o*-fluorobenzyl alcohol *ab-initio* (STO-3G) calculations predicted a number of populated conformations which gave calculated NMR couplings in reasonable agreement with the observed values.[10] In 3,5 dichlorobenzyl alcohol the ^6J (CH_2, p-H) coupling (−0.59 Hz) was interpreted on the basis of a preferred in plane orientation of the O atom but only by 0.3 (±0.2) kcal mole^{-1}.[11] Due to the strongly coupled ring proton spectra, this method is not applicable to the parent compound and was not applied to very dilute solutions. The result agreed with MO (STO-3G) calculations on benzyl alcohol[12] which gave a preference for the in-plane conformer of 0.2 kcal mole^{-1}. In contrast very recent ED results suggest that the favoured conformer in the gas phase has a ring-CO dihedral angle of *ca.* 60° with a significant barrier to inversion.[13]

With the advent of FT NMR spectrometers it is now possible to overcome the sensitivity problem and study by NMR H-bonded systems in as low concentrations as in the IR studies. Thus it was decided to investigate these systems by NMR using as conformational probes the OH chemical shift, CHOH coupling and the CH_2 geminal coupling. We report here our results for benzyl alcohols. As the basic data required for these dilute solutions (i.e. the OH chemical shift and coupling constant) has not been previously reported to the accuracy we required, we give also for comparison this data for the simple alcohols.

Conformer geometries of benzyl alcohol

The benzyl alcohol molecule is defined by two dihedral angles, the $C_1C_2C_3O_4$ (θ) and $C_2C_3O_4H$ (φ) (Fig. 1). We may reasonably consider only the staggered conformations of the C.O bond, i.e. φ equals ±60° and 180°, as the 3-fold barrier to rotation will be similar to that in methanol (1.07 kcal mole^{-1}).[14] However the low intrinsic barrier to rotation of the Ph–CH_2 bond (toluene, $\Delta G^{\neq}$ 0.014 kcal mole^{-1})[12] means that all values of θ must be considered. We will restrict our discussion for ease of presentation to considering the extreme cases of the planar ($\theta = 0°$) and orthogonal ($\theta = 90°$) conformations. 1A..D (Fig. 1) and the ED conformations (1E) and (1F).

MO (STO-3G) calculations on 1A..D ((1E) and (1F) were not considered) gave relative energies of 0.0 (1C), 0.06 (1B), 0.22 (1A), and 1.92 (1D) kcals mole^{-1} respectively.[12] These were performed with standard geometries without including any geometrical relaxation, which could appreciably alter the relative energies. Molecular mechanics calculations using the MODELS 2 programme[15] showed that 1D was preferentially stabilised by approximately 0.8 kcals mole merely by allowing the C.C.O. angle to deform. Thus the only conclusion from these calculations is that there is no large energy difference between the conformers.

RESULTS AND DISCUSSION

The CH.OH *coupling*. The CH.OH coupling has been used to obtain conformational information for many

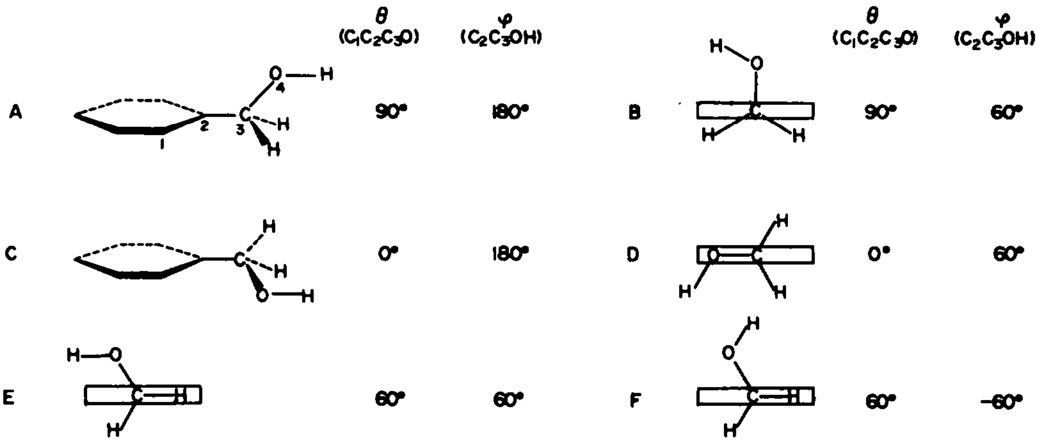


Fig. 1. Possible conformations of benzyl alcohol.

years.[16–19] However, it has an intrinsic solvent dependence, which can be observed in methanol, in which conformational isomerism is absent. Our results (Table 1) taken together with those of Rader[18] in other solvents (e.g. 5.58 (C_6H_{12}); 5.53 (C_6H_6); 5.08 (p. liqd.)) suggest that the solvent dependence of the methanol coupling is due to the presence (or absence) of an H-bond. In accord with this Rader observed the coupling to be independent of concentration in DMSO (from 0.10 to 3.0 M)[18] and therefore we have measured the alcohol couplings in dilute CCl_4 solution (~0.02M), but in more concentrated DMSO solution (0.2M).

The couplings in alcohols of fixed conformation, together with the observed (averaged) coupling of 5.1 Hz in a series of primary alcohols lead Rader to suggest values of J_g (J_{gauche}) and J_t (J_{trans}) of 2.6 and 10.4 Hz.[18] Fraser *et al.* fitted the two observed couplings in a hindered $C.CH_2OH$ fragment to a "Karplus" type curve, to give values of J_g and J_t of 2.0 and 12.0 Hz respectively.[17] Zahra *et al.*[19] report values of J_g and J_t of 2–3 Hz and 10.5–11.5 Hz for a number of cyclic alcohols in fixed conformations. Using J_{AV} as 5.1 Hz and taking all the above results into consideration suggests that values of J_g and J_t of 2.2 and 11.0 Hz are reasonable and we shall use these henceforth.

These values can now be used together with the observed coupling in the benzyl alcohols (Table 1) to provide information on the rotamer populations in the CCH_2OH fragment.

As the coupling is independent of the phenyl ring orientation there are only two conformations to consider which may be termed the *endo* (1B, D, E, F) and *exo* (1A, C) orientations respectively (Fig. 2).

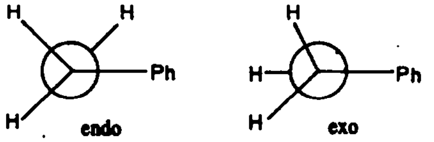


Fig. 2. Endo and exo orientations of the CCH_2OH fragment.

The rotamer couplings are then J_g (2.2 Hz) for the *exo* and $1/2(J_t + J_g)$ i.e. 6.6 Hz for the *endo*.

The observed coupling in benzyl alcohol in CCl_4 solution of 5.8 Hz implies a preponderance of the *endo* conformation. With the above coupling data, we obtain 90% *endo*. This conformation has a statistical weight of 2, compared with the *exo* form and thus the energy difference in favour of the *endo* form from this coupling is approximately 0.9 kcal/mole. The relative proportions of the two forms (approximately 1:10 in CCl_4 solution) are in excellent agreement with the IR data (approximately 1:15), when one considers the uncertainties in both sets of data and allow an unambiguous assignment of the IR bands at 3615 and 3634 cm^{-1} to the OH frequency in the *endo* and *exo* rotamers respectively.

Table 1. CHOH couplings in alcohols

Compound	J(CH–OH) Hz CCl_4	 DMSO-d_6
Methanol	5.46[a], 5.37[b]	5.19[a], 5.21[b]
Ethanol	5.1[c]	5.07[a], 5.07[b], 5.0[c], 5.08[e]
iso-Propanol	—	4.13[a], 4.20[b]
Benzyl alcohol	5.79[a], 5.9[c], 5.95[g]	5.66[a], 5.6[c], 5.7[d]
o-NO_2 Benzyl alcohol	6.35	5.35
p-NO_2 Benzyl alcohol	5.42	5.59
o-MeO Benzyl alcohol	5.86	5.70
p-MeO Benzyl alcohol	5.44	5.67
o-F Benzyl alcohol	6.06[f]	—

[a] This work, conc., 0.02M (CCl_4); 0.2M (DMSO); ±0.05 Hz.
[b] Ref. 18, ±0.05 Hz.
[c] Ref. 20, ±0.1 Hz.
[d] 1:1 acetone, ±0.02 Hz, Ref. 21.
[e] 1:1 acetone, ±0.05 Hz, Ref. 16.
[f] 0.1 M in CS_2, Ref. 10.
[g] 1 M in CS_2, Ref. 11.

In DMSO solution the coupling decreases, implying an increase in the proportion of the *exo* form to approximately 20%.

In the *para* substituted alcohols, the coupling in DMSO solution is identical within the experimental limits of error to that in the parent alcohol, showing that, as would be expected, there is no intrinsic substituent effect in this solvent on the coupling. The consistently low values for the *para* substituted alcohols in CCl_4 solution have no obvious explanation.

In contrast the *o*-nitro substituent causes a considerable increase in the coupling due to stabilisation of the *endo* conformers. Although they cannot be distinguished from the coupling, clearly 1D is energetically unfavourable as the only reason for the increased stability is H-bonding to the nitro group which cannot occur in 1D. Thus the results indicate very clearly that 1B (or 1E) is the dominant conformer in *o*-nitro benzyl alcohol, and this is chemically very reasonable as the OH group is situated in approximately the optimum position for H-bonding to the nitro substituent.

In DMSO solution in contrast the CHOH coupling is less than in the parent alcohol. Competition with the much stronger donor of the solvent molecules has removed the intra-molecular H-bond and in consequence the *o*-nitro group is now merely an added steric hindrance to the CH_2OH group. This would clearly stabilise 1C (and possibly 1A) in which the OH group is in the preferred *exo* position for inter-molecular H-bonding.

The *ortho*-OMe substituent has a similar but much weaker effect. In CCl_4 the coupling is increased, but only by an amount similar to the experimental error and the coupling in DMSO is unchanged. This is entirely consistent with the much weaker interaction of the OH with the *o*-OMe group.[7] The coupling in *o*-fluoro benzyl alcohol again suggests a stabilisation of (1B, E) and indeed 1E was calculated to be the most stable form.[10]

In conclusion the CH.OH coupling and the IR data show clearly that the dominant conformer of benzyl alcohol (and the *ortho* substituted benzyl alcohols) has the OH group *endo* (i.e. *anti* to a CH proton). The central question remaining is the orientation of the phenyl group in this dominant conformer. In considering this with regard to the other NMR parameters observed, it is simpler to neglect henceforth the contributions of the minor *exo* conformation (1A and 1C).

The OH *chemical shift*. We now wish to obtain the ∞ dilution OH chemical shifts of the benzyl alcohols and to compare them with the shifts of the simple aliphatic alcohols. The errors involved in the analysis of OH-dilution curves, from *moderately concentrated solutions*, are well known[22,23] and give large errors in the extrapolated ∞ dilution values (e.g. MeOH 0.4–0.98).[22] However, measurements at very low concentrations largely eliminates these errors as the slope of the OH/dilution curve *decreases* at low alcohol concentrations (see refs 23 and 24 for a detailed discussion). At the concentrations used here ($<10^{-2}$ M) the concentration dependence of the OH chemical shifts was small (*ca* 0.15 ppm per 0.05 M change in conc.) allowing simple linear interpolation to give the ∞ dilution values to ±0.05 ppm (Table 2).

The results in Table 2, taken with the ∞ dilution shift of t-butanol (0.70),[24] show that apart from methanol, the OH chemical shift in aliphatic alcohols is constant at 0.70 (±0.05) δ. This is well within the range of values previously reported (0.3–1.1).[22] The benzyl alcohol ∞ dilution shift (1.09δ) differs substantially from the only reported value (0.28δ), of some very early work[25] and more significantly is deshielded by 0.39 ppm compared to the simple aliphatic alcohols. The obvious explanation of this is the ring current effect of the phenyl ring.

This may be calculated precisely for each of the possible conformers 1A...1D (Fig. 1) using either the Johnson and Bovey tables[26] or the simple equivalent dipole formula recently proposed by Abraham *et al.*[27] The calculations give ring current shifts at the OH proton (equivalent dipole in parenthesis) of 0.21 (0.22), 0.15 (0.15), 0.30 (0.29) and 0.50 (0.49) ppm for 1A, B, C and D respectively. It is pleasing to see that the equivalent dipole approximation, which was intended for intermolecular calculations, gives identical results to the current loop calculations for this intramolecular situation.

For the *endo* isomer with $\theta \neq 0, 90°$ the different values of φ (±60°) result in non-identical conformations. The equivalent dipole calculated ring current shifts for (1F) and (1E) are 0.08 and 0.39 ppm respectively. Finally the calculated shift for the "hydrogen-bonded" conformer (90°, 0°) is −0.1 ppm, i.e. a small upfield shift.

The observed ∞ dilution shift is the weighted mean of the shifts of the different conformers, but using the results of the preceding section we may neglect the contribution of the *exo* conformer (1A, C) and consider only the possible *endo* forms.

The observed shift is in exact, though perhaps fortuitous agreement with the calculated shift for 1E. However, the calculated shift for free rotation of the phenyl group, which is *ca* the mean of 1B and 1D is 0.33 ppm, again very close to the observed value.

Thus the ∞ dilution OH shift, whilst supporting the dominance of the *endo* conformer and removing any possibility of a "H-bonded conformer" with the OH over the aromatic ring, cannot differentiate between the alternatives of one stable conformer (1E) and free rotation of the phenyl ring.

The OH shifts in DMSO may be considered to be of the fully solvated species and confirming this the complexation shift ($\Delta\delta = \delta_{DMSO} - \delta_{CCl_4}$) is constant for methanol (3.75), ethanol (3.70) and iso-propanol (3.59). For benzyl alcohol $\Delta\delta$ (4.05 ppm) is significantly larger. This increase is too large to be due to ring current effects and is probably due to small differences in the structure of the benzyl alcohol–DMSO solvation shell compared to that of the aliphatic alcohols.

The OH shifts in the substituted benzyl alcohols are of interest. The effect of the *para* substituent can be clearly seen in the OH shift, both in CCl_4 and DMSO. In the series *p*-MeO, *p*-H, *p*-NO_2 the shifts are 0.98, 1.09, 1.48 (CCl_4) and 5.03, 5.14, 5.53 (DMSO). The essentially constant difference $\Delta(\delta_{DMSO} - \delta_{CCl_4})$ shows that these

Table 2. OH chemical shifts (δ) for alcohols

Compound	CCl_4 (m.l.$^{-1}$ × 10^{-2})	OH Chemical shift CCl_4 (∞ dil^n)	DMSO-d_6
MeOH	0.497(4.9); 0.446(2.5); 0.377(1.3)	0.34	4.09
EtOH	0.777(3.4); 0.734(2.8); 0.70(1.4)	0.65	4.35
iPrOH	0.786(2.7); 0.760(0.9)	0.75	4.34
benzyl alcohol	1.192(2.0); 1.138(1.0)	1.09	5.14
o-nitro benzyl alcohol	2.168(2.6); 2.123(1.3)	2.08	5.55
p-nitro benzyl alcohol	1.603(3.3); 1.511(1.0)	1.48	5.53
o-methoxy benzyl alcohol	1.678(2.8); 1.650(1.4)	1.63	4.96
p-methoxy benzyl alcohol	1.159(2.8); 1.030(0.9)	0.98	5.03

shifts are simply substituent chemical shifts (S.C.S.) and not due to differences in conformation. The S.C.S. of the methylene protons are generally smaller, e.g. p-MeO- 0.092; p-NO_2 0.182 reflecting the greater sensitivity of the OH proton to electric field effects than the methylene protons.

The OH shifts of the *ortho* substituted benzyl alcohols do not show such a simple relationship. Introduction of the o-NO_2 group produces the largest shift (1.0 ppm) which is decreased considerably in DMSO (0.41 ppm). This is in agreement with the IR results[7] in which a H bond to the *ortho* nitro group was observed. The decrease of the S.C.S. in DMSO is thus due to competition from the DMSO solvent, and in support of this we note that the OH shift is identical in DMSO for the *ortho* and *para* nitro compounds.

A similar analysis of the o-OMe data suggests here that possibly an intramolecular H bond is formed ($\Delta\delta$ 0.54 ppm in CCl_4 *cf* −0.18 ppm in DMSO). Again, the OH shift in DMSO is identical in the *ortho* and *para* compounds.

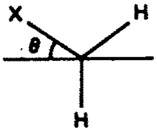
If the strength of the H-bond is reflected in the OH S.C.S., then the o-OMe group is only approximately half as effective in bonding to the OH as the o-nitro group. This is not inconsistent with the IR data[7] in that the much weaker bonding of the o-OMe group may not be resolved in the IR spectrum. The single result of the o-fluoro benzyl alcohol (δ_∞ equals 1.24 in CS_2 solution[10]) would suggest that there is virtually no H-bonding in this case and this would also agree with the IR data for o-halogenated benzyl alcohols.

The geminal H.C.H. *coupling*

The influence of hyperconjugative substituents on the value of the geminal H.C.H. coupling is well known.[28-31] We have recently proposed[30] that these couplings in benzyl or allyl fragments may be calculated from eqn (1).

$$^2J_{HH} = A + B\cos\theta + C\cos 2\theta \qquad (1)$$

where θ is the dihedral angle between the CH_2X substituent and the ring (or olefine) plane.



For X = H, C values of A, B and C of −15.8, 2.5 and −4.3 Hz were deduced. For simple electronegative substituents (F, Cl, Br) the appropriate values of the constants in eq^n 1 may be obtained by additive substituent effects.

For more complex substituents such as OH the hyperconjugative interactions of the oxygen lone-pairs give rise to an additional orientation dependence of the geminal coupling.[28,31]

In benzyl alcohol there are only two C.C.O.H. angles to consider, the *endo* and *exo* orientations (Fig. 2). For the *endo* orientation, an appropriate model is provided by the coupling in tetrahydropyran (−11.5 Hz) compared to cyclohexane (−12.5 Hz). Thus A in eqn (1) becomes −14.8 Hz.

For the *exo* orientation we use the observed (averaged) coupling in methanol (−10.8 Hz) with the above which gives the analogous coupling in methanol of −9.4 Hz compared to that in methane (−12.4 Hz) and thus the value of A in eqn (1) for this orientation is −12.8 Hz.

These values predict couplings of −8.4, −10.6, −14.5, −16.7 and −11.5 Hz for 1A, 1B, 1C, 1D and 1E respectively (Fig. 1). The rotationally averaged values (phenyl ring rotation) are then −11.5 (1A, C) and −13.7 (1B; D).

The $^2J_{HD}$ coupling in α-monodeuterobenzyl alcohol is 1.90 (±0.05) Hz in CCl_4 and DMSO, which corresponds to an HH coupling of 12.4 (±0.3) Hz, presumably negative. In benzyl methyl ether the corresponding couplings are 1.77 (±0.03) Hz (HD) and 11.5 (±0.2) Hz (HH).

It is again convenient to neglect the ~10% contribution of the *exo* conformers (1A + C) and consider the observed coupling in benzyl alcohol (−12.4 Hz) with the possible conformations of the *endo* form. It can be seen that the value of the coupling does not support the existence of either 1B (−10.6 Hz) or 1D (−16.7 Hz), however the values in 1E (−11.5 Hz) is in reasonable agreement as also is the coupling for free rotation of the phenyl group (−13.7 Hz). The uncertainties in the estimated rotamer couplings, combined with the possibility of appreciable vibrational corrections to the coupling, do not allow the differentiation of these two possibilities.

Benzyl methyl ether gives a significantly more positive coupling (−11.5 Hz) than benzyl alcohol and this is exactly what would be predicted on steric grounds, 1D being the most hindered conformation with the most negative coupling. Note that the percentage of the *exo* conformers may also be increased here and this would also increase the coupling.

It would be of interest to determine the geminal coupling in, e.g. *ortho* nitrobenzyl alcohol, in which the free rotation model is no longer possible, giving a more precisely defined check on the model couplings obtained here.

CONCLUSION

The separate investigations into the OH chemical shift, CHOH coupling and geminal HH coupling together give a reasonably coherent picture. In the case where the CHOH rotation was specifically studied (via the CHOH coupling) the results are unambiguous, favouring the endo conformation by at least 1 kcal/mole over the *exo* conformation.

The OH chemical shift and geminal HH coupling are in accord with this picture, but in both cases averaging over all orientations of the phenyl group gives results which are very similar to those predicted by the single conformer (1E). Thus whilst the results do not support the existence of one extreme conformer (1B or 1D) they do not differentiate between the two proposed alternatives.

We note that all the investigations made provide no support for the existence of a "hydrogen bonded conformer" in which the OH points towards the benzene ring. We conclude that there is no intramolecular H-bonding in the generally accepted sense of the term in benzyl alcohol.

EXPERIMENTAL

The compounds used were either commercially available or their preparation had been reported previously. The α-D-benzyl alcohol was prepared by reducing benzaldehyde with LAD and the corresponding α-D benzyl chloride by reaction of α-D-benzyl alcohol with $SOCl_2$. No impurity signals were observed in the NMR spectra.

The proton spectra were obtained on a JEOL FX-100 spectrometer in CCl_4 and DMSO solns, probe temp. 23°, using inter-

Table 3. Proton chemical shifts (δ) in alcohols

Compound	Solvent[a]	Chemical Shift (δ) $C\underline{H}OH$	 Others
MeOH	CCl_4	3.399	—
	DMSO-d_6	3.168	—
EtOH	CCl_4	3.621	1.188(Me)
	DMSO-d_6	3.440	1.054(Me)
iPrOH	CCl_4		1.148(Me)
	DMSO-d_6	3.772	1.038(Me)
Benzyl alcohol	CCl_4	4.598	7.252(Ph)
	DMSO-d_6	4.457	7.299(Ph)
o-NO_2 Benzyl alcohol	CCl_4	4.929	8.067(H_3)
	DMSO-d_6	4.827	8.031(H_3)
p-NO_2 Benzyl alcohol	CCl_4	4.780	8.191($H_{3,5}$), 7.483($H_{2,6}$)
	DMSO-d_6	4.636	8.194($H_{3,5}$), 7.578($H_{2,6}$)
o-Methoxy Benzyl alcohol	CCl_4	4.550	3.854(OMe)
	DMSO-d_6	4.484	3.762(OMe)
p-Methoxy Benzyl alcohol	CCl_4	4.502	3.765(OMe), 6.760($H_{3,5}$), 7.179($H_{2,6}$)
	DMSO-d_6	4.410	3.728(OMe), 6.870($H_{3,5}$), 7.229($H_{2,6}$)
α-D Benzyl chloride	CCl_4	4.491(CHD)	7.285(Ph)
α-D Benzyl methyl ether	CCl_4	4.344(CHD)	3.280(OMe)

[a] Concs. $\leq$0.02M (CCl_4), 0.2M (DMSO-d_6).

nal ^{2}D lock for the DMSO solns and external ^{7}Li lock for the CCl_4 solns. A typical run would be 100–200 transients with S.W. 1000 Hz, P.W. 40 μs and A.T. 4 sec (with 8K storage), giving a digitisation accuracy of 0.1 Hz (0.001 ppm). Expanded sweeps were used with 16K storage to measure the coupling constants. Repeated measurements gave a reproducibility of 0.05 Hz.

To stop the exchange of the OH proton in CCl_4 solns, the solns were stored over Na_2CO_3 or molecular sieves overnight before measuring. In most cases this was sufficient to allow resolution of the CHOH coupling, but in EtOH and PrOH repeated attempts failed to stop the OH protons exchanging.

The concentrations of the CCl_4 solutions were $\lesssim 10^{-2}$ M in order to obtain the spectrum of the "monomeric" species. In DMSO solns, the concentrations were approximately 0.2 M, but there was no sign of any concentration dependence in this solvent.

The remaining NMR data is given in Table 3. All the δ values, apart from the OH chemical shift, were independent of concentration in CCl_4.

Acknowledgements—We thank Profs. T. Schaefer and M. Traetteberg for communicating their results prior to publication and Dr. J. Krane for considerable assistance in operating the JEOL FX-100 spectrometer.

Financial support from the N.A.V.F. and the NATO Science Research Committee (Grant No. 1315) is gratefully acknowledged.

REFERENCES

[1] Part XXI. R. J. Abraham, P. Loftus and W. A. Thomas, *Tetrahedron* 33, 1227 (1977).

[2] L. J. Bellamy, *The IR Spectra of Complex Molecules*. Chapman & Hall, London (1975).

[3] P. Schuster, G. Zundel and C. Sandorfy, *The Hydrogen Bond* Vol. II. North-Holland, Amsterdam (1976).

[4] P. R. Schleyer, D. S. Trifan and R. Bacskai, *J. Am. Chem. Soc.* 80, 6691, (1958).

[5] W. A. P. Luck, *Chap.* 11 of Ref. 3.

[6] M. Oki, H. Iwamura and I. Urushibara, *Bull. Chem. Soc. Japan* 31, 796 (1958).

[7] J. M. Bakke and G. B. Lorentzen, *Acta. Chem. Scand.* B28. 650 (1974).

[8] T. Schaefer, J. B. Rowbotham, W. J. E. Parr, K. Marat and A. F. Janzen, *Can. J. Chem.* 54, 1322 (1976).

[9] T. Schaefer, L. J. Kruczynski and W. J. E. Parr, *Ibid.* 54, 3210 (1976).

[10] T. Schaefer and W. J. E. Parr, *J. Chem. Phys.* 65, 1197 (1976).

[11] T. Schaefer, W. Darchura, W. Niemczura and W. J. E. Parr, private communication.

[12] W. J. Hehre, L. Radom and J. A. Pople, *J. Am. Chem. Soc.* 94, 1496 (1971).

[13] M. Traetteberg, Private communication.

[14] R. H. Lees and H. J. G. Baker, *J. Chem. Phys.* 48, 5299 (1968).

[15] P. Loftus, Ph.D. Thesis, University of Liverpool (1971).

[16] R. J. Abraham, *Proc. XIth Colloque Ampere* 589 (1962).

[17] R. R. Fraser, M. Kaufman, P. Morand and G. Govil, *Can. J. Chem.* 47, 403 (1969).

[18] C. P. Rader, *J. Am. Chem. Soc.* 91, 3248 (1969).

[19] J. P. Zahra, B. Waegell and H. Bodot, *Bull. Soc. Chim. Fr.* 1107 (1974).

[20] W. B. Moniz, C. F. Poranski and T. N. Hall, *J. Am. Chem. Soc.*, 88, 190 (1966).

[21] P. L. Corio, R. L. Rutledge and J. R. Zimmerman, *J. Mol. Spec.*, 3, 592 (1959).

[22] J. C. Davis and K. K. Deb, *Adv. in Magnetic Res.* 4, 201 (1970).

[23] E. E. Tucker and E. Lippert, Chap. 17 of Ref. 3.

[24] E. E. Tucker and E. D. Becker, *J. Phys. Chem.* 77, 1783 (1973).

[25] T. M. Connor and C. Reid, *J. Mol. Spect.* 7, 32 (1961).

[26] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.* 29, 1012 (1958) reproduced in F. A. Bovey, *Nuclear Magnetic Resonance Spectroscopy*. Academic Press, New York (1969).

[27] R. J. Abraham, S. C. M. Fell and K. M. Smith, *Org. Mag. Res.* 9, 367 (1977).

[28] G. E. Maciel, J. W. McIver, N. S. Ostlund and J. A. Pople, *J. Am. Chem. Soc.* 92, 4151 (1970).

[29] R. Wasylishen and T. Schaefer, *Can. J. Chem.* 50, 1852 (1972).

[30] R. J. Abraham and J. M. Bakke, *Org. Mag. Res.* in press.

[31] R. C. Cookson, T. A. Crabb, J. J. Frankel and J. Hudec, *Tetrahedron Supplement* No. 7, 355 (1966).