Acta Chemica Scandinavica B 38 (1984) 547–554

An NMR study of OH···π Electron Interaction. The Conformations of Aryl Alcohols

RAYMOND J. ABRAHAM,[a] JAN M. BAKKE[b] and TORE SKJETNE[c]

[a] The Robert Robinsons Laboratories, University of Liverpool, P.O.Box 147, Liverpool L69 3BX, England, [b] Organic Chemistry Laboratories, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway and [c] Department of Chemistry, University of Trondheim, NLHT, N-7000 Trondheim, Norway

The conformations of *o*-chloro-, *o*-methyl- and 2,6-dimethylbenzyl alcohol (*1*), 9-fluorenol (*2*), diphenylmethanol (*3*) and 1-indanol (*4*) have been investigated by NMR and IR spectroscopy. The conformational equilibrium in the substituted benzyl alcohols is satisfactorily explained in terms of the competing steric and electrostatic interactions the effects being too small to obtain a single conformation. In 9-fluorenol the *trans* conformer is dominant, whereas in diphenylmethanol the *gauche* orientation is preferred. In 1-indanol all three possible conformers of the CH.OH fragment are populated with a preference towards a benzyl alcohol type of conformers. The full analysis of the NMR spectrum of the aliphatic and OH protons of 1-indanol is given indicating the existence of two interconverting envelope-type conformations (angle of pucker *ca.* 35°).

The results provide strong support for the hypothesis that the conformational equilibrium in aryl alcohols is determined as much by oxygen lone-pair–π electron repulsions as by OH···π electron hydrogen bonding.

The nature and strength of the hydrogen bond presumed to occur between an alcoholic hydroxy group and the π-electrons of an aryl ring has been the subject of debate for some time.[1–3] IR spectroscopy has been the primary investigating technique, but although this technique shows clearly and unequivocally the existence of the various conformers it does not provide clear-cut evidence as to the precise geometry of the conformers. Recently we have shown, using FT NMR, that in substituted benzyl alcohols[4] and 1,2-diarylethanols[5] contrary to the popularly held belief, there is no evidence for an attractive OH···π intramolecular hydrogen bond.

These, and other results,[6] lead to the further suggestion that the location of the hydroxyl hydrogen in these conformationally mobile molecules is the result not of an attractive OH···π interaction, but of a repulsive oxygen lone-pair---π electron interaction. In order to examine this hypothesis in more detail we present here the results of a similar NMR investigation of some less conformationally mobile molecules.

In substituted benzyl alcohols the value of the ^3J (CH·OH) coupling shows clearly that the predominant conformation has the hydroxyl proton *endo* to the phenyl group. However, the extra conformational mobility of the phenyl ring about the C·CH_2 bond makes the determination of the precise conformation of these molecules in solution less certain, both a freely rotating model and one with an O·C·C·C. dihedral of *ca.* 60° being consistent with the NMR data.[4]

This extraneous conformational flexibility can be in principle removed either by introducing steric effects, such as abutting *ortho* methyl groups, which should force the oxygen out of the aromatic ring plane, or by examining cyclic systems. Thus here we present an NMR and IR analysis of 2,6-dimethylbenzyl alcohol (*1*), 9-fluorenol (*2*), diphenylmethanol (*3*) and 1-indanol (*4*). A variable temperature NMR study of 9-fluorenol has been the subject of a preliminary communication.[6]

0302-4369/84 $2.50

RESULTS AND DISCUSSION

The NMR spectra of the compounds studied have been obtained in dilute DMSO and CCl_4 or $CFCl_3$ solutions, the latter at two different concentrations, both $<10^{-2}$ M. The relevant data for the CH·OH protons for (*1*)–(*4*) and for the *o*-chloro- and *o*-methylbenzyl alcohols is given in Table 1, the hydroxyl chemical shifts in CCl_4/$CFCl_3$ recorded being obtained by extrapolation to ∞ dilution. For convenience, the data for benzyl alcohol from Ref. 4 is also included.

The use of $CFCl_3$ as a non-polar solvent is more convenient than CCl_4 for low temperature studies (m.p. −111 °C vs −23 °C for CCl_4), and it appears to be entirely equivalent to CCl_4 in our studies. This is best illustrated by the IR data in Table 2. The two compounds measured in both solvents show small shifts (*ca.* 5 cm^{-1}) to high frequencies in $CFCl_3$ compared to CCl_4, whereas any hydrogen bonding to the solvent would be expected to result in shifts to low frequencies.

The hydroxyl proton chemical shift, the CH.OH coupling and when measurable the $^2J_{HH}$ coupling all can provide conformational information in these molecules, and it is convenient to consider the general pattern before discussing each molecule individually.

Following the previous treatment,[4] we use values of J_g and J_t for the CH_2·OH fragment of 2.2 and 11.0 Hz., which gives couplings for the *exo* and *endo* conformations (Fig. 1) of 2.2 and 6.6 Hz.

For the CH·OH fragment in (*2*), (*3*) and (*4*) we

Table 1. OH Proton chemical shifts (δ) and CH.OH couplings (Hz) for benzyl alcohols and related compounds.

Substance	δ(OH) DMSO	$CCl_4(\infty)$[b]	^3J(CH.OH) DMSO	CCl_4/$CFCl_3$	$\Delta\delta$[c]	% *endo* or *gauche*[d]
Benzyl alcohol[a]	5.14	1.09	5.66	5.79	4.05	90
o-Chlorobenzyl alcohol	5.41	1.43	5.7	(5.1)[e]	3.98	—
o-Methylbenzyl alcohol	5.03	0.77	5.45	5.6	4.26	77
2,6-Dimethylbenzyl alcohol	4.73	0.60	5.32	5.54	4.13	76
9-Fluorenol (*2*)	5.82	1.27	5.5	11.23	4.55	0
di-Phenylmethanol (*3*)	5.89	1.62	4.15	3.32	4.27	87
1-Indanol (*4*)	5.20	1.08	5.86	7.33	4.12	42

[a] Ref. 4. [b] ∞ dilution, by extrapolation. [c] $\Delta\delta=\delta$(DMSO)$-\delta(CCl_4)$. [d] From the CH.OH coupling (CCl_4/$CFCl_3$ sol). See text, Fig. 1. [e] Exchanging, see text.

Table 2. Hydroxyl absorption (ν_{max}) in aromatic alcohols in $CFCl_3$/CCl_4 solutions.

Substance	Solvent	Conc., mM	λ_{max}
Benzyl alcohol	$CFCl_3$	5.2	3622 3638 (sh)
Benzyl alcohol	CCl_4	3.7	3615 3635 (sh)
2,6-Dimethylbenzyl alcohol	$CFCl_3$	7.0	3628
1-Indanol	$CFCl_3$	6.9	3608 3620 (sh) 3633 (sh)
1-Indanol	CCl_4	3.4	3603 3613 (sh) 3633 (sh)
9-Fluorenol	CCl_4	2.7	3602 3625 (sh)
Diphenylmethanol	$CFCl_3$	5.4	3613

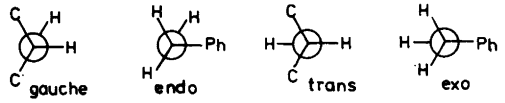

Fig. 1. Orientations of the CH_2OH and CH·OH fragments.

assume similar values of J_g and J_t, though the replacement of hydrogen by carbon could in principle affect the rotamer couplings. These values together with the observed couplings give immediately the percentage *exo* and *endo* conformations in the molecules studies, and these percentages are given in Table 1. Discussion of these will be deferred until the hydroxyl chemical shifts can also be considered.

We have shown previously[4,7] that there is a close correspondence between the hydroxyl chemical shifts in CCl_4 and DMSO, both sets of data correlation well with the Hammett σ values of the substituents. These S.C.S. have been discussed elsewhere;[7] what is of relevance to the present investigation is that the correspondence between the OH shifts in the two solvents implies no solvation dependent specific effects of the substituents, in particular no intramolecular hydrogen bonding between the OH and the substituent in CCl_4 solution. The chemical shifts of all the *meta* and *para* substituted benzyl alcohols measured (eleven compounds)[7] give a constant solvation shift $\Delta\delta$ (δ (DMSO)$-\delta$ (CCl_4)) equal 4.09 p.p.m. with a range of error of $\pm$0.03 p.p.m., essentially within the combined experimental error of the measured values. This solvation shift can be used as a test for any specific hydrogen bonding and conformational effects in $CCl_4/CFCl_3$ solution arising both from *ortho* substituents and also from the less conformationally mobile molecules studied here. We note that the largest deviation from this constant solvation shift occurs with the *ortho* methoxy and *ortho* nitro substituents,[4] which give $\Delta\delta$ values of 3.33 and 3.47 p.p.m. respectively, due to intramolecular hydrogen bonding between the OH and the *ortho* substituent in CCl_4 solution, which is broken down by the solvent in DMSO solution. The solvation shifts for the molecules studied here are given in Table 1 and can now be considered together with the CH·OH couplings.

SUBSTITUTED BENZYL ALCOHOLS

These molecules were studied to further examine the competing effects of steric and hydrogen bonding interactions of the *ortho* substituents with the hydroxyl group. The solvation shifts for the *o*-chloro-, *o*-methyl- and 2,6-dimethylbenzyl alcohols are all not very different from the standard value (4.09 p.p.m.) somewhat surprisingly that of the *ortho* methyl showing the largest deviation. The value for the *o*-chlorobenzyl alcohol is particularly illustrative in demonstrating the very weak (if any) hydrogen bond between the hydroxyl and the chlorine atom, a result in complete agreement with previous IR investigations.[8] The low value of the CH·OH coupling is extraneous and caused by exchange broadening, due to the exchange of the OH proton even at the lowest dilutions examined.

The *ortho* methyl group would be expected to have little affect on the solvation shift, as is observed, but in both the *ortho*-methyl and 2,6-dimethyl compounds there is a significant decrease in the population of the *endo* conformer. Note that the decrease in the *endo* population from 90 % in benzyl alcohol to 76 % in (*1*) corresponds to a significant change in the energy difference (*exo-endo*) from 0.9 kcal mol^{-1} in benzyl alcohol to 0.3 kcal mol^{-1} in (*1*). In (*1*) we may safely disregard, on steric grounds, those conformers with the alcohol oxygen in the plane of the aromatic ring. This leaves, in the nomenclature of Ref. 4, conformers A, B, E and F (Fig. 2). The increase in the percentage of the *exo* form reflects the decreased relative energies of conformers similar to A w.r.t. E and F.

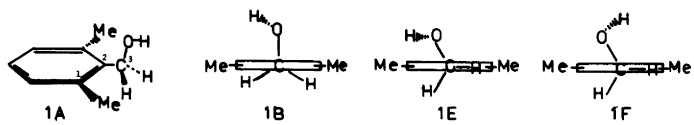

Fig. 2. Possible conformations of 2,6-dimethylbenzyl alcohol (*1*). ϕ (C_2C_3OH)=180° (A), 60° (B and E) and −60° (F).

This is perfectly explicable in terms of the steric interactions with the *ortho* methyl groups, as here steric interactions will be smaller compared to those in E and F. The precise orientation of the C·O bond in *1* is not certain, as it could be orthogonal (A and B) to the benzene ring or equilibrating between two non-planar structures such as F. The measured geminal H·C·H coupling of 11.23 (±.06) Hz (obtained from the $^2J_{DCH}$ coupling of 1.72±.01 Hz in the mono-deutero compound, see Experimental) is numerically less than that of benzyl alcohol (−12.4 Hz), again in agreement with a more orthogonal conformation of the hydroxyl group in this molecule. Thus, the results for the substituted benzyl alcohols are very much in line with what would be anticipated on steric and electrostatic grounds. The only discordant note arises from the failure to detect two hydroxyl bands in the IR spectrum of (*1*) (Table 2), which would be anticipated from the above analysis of the NMR data. It is of note that the observed IR frequency of 3628 cm^{-1} occurs almost exactly at the average of the two benzyl alcohol bands in the same solvent and it may be that in *1* small frequency changes in the *exo* and *endo* components have resulted in a single unresolved band rather than two separate bands.

9-FLUORENOL AND DIPHENYLMETHANOL

It is convenient to consider these molecules together, as they both have apparently similar constitutions (Ar.CH.OH.Ar) though in fact very different structures and results. The value of the CH.OH coupling in 9-fluorenol is dilute CCl_4 or $CFCl_3$ solution of 11.2Hz unequivocally establishes the sole conformer to be that in which the CH.OH fragment is *anti* oriented, *i.e.*, the hydroxyl proton bisects the two aromatic rings. Even in 5 % $CDCl_3$ solution the coupling is still resolved (*ca.* 9.3 Hz), and the OH not exchanging. Only in DMSO solution is the average coupling of 5.5Hz observed, illustrating the much more powerful hydrogen bonding capabilities of this solvent. Variable temperature studies of the CH.OH coupling in dilute ($CFCl_3$ solutions provided an estimate of the enthalpy difference between the stable *trans* conformer and the possible *gauche* conformer, a value in excess of 3 kcal $mole^{-1}$ being found.[6] The solvation shift of the hydroxyl proton is higher than for the substituted benzyl alcohols, but this cannot be used diagnostically as now there is the ring current of both aromatic rings to consider. However, all the NMR data is consistent with the existence of a strongly preferred conformation which could be explained on the basis of a strong intramolecular OH···π hydrogen bond.

However the IR spectrum does not give any indication of a strong intramolecular hydrogen bond (Table 2), the major peak observed at high dilution in non-polar solvents comes at 3602 cm^{-1}, only 10−20 cm^{-1} below that of a series of saturated aliphatic alcohols without any possibility of intramolecular hydrogen bonds.[1] Furthermore, the frequency separation between the major and minor components of the hydroxyl band (*ca.* 23 cm^{-1}) is also consistent with what would be expected between two conformers differing merely in the orientation of the H·O·C·C bonds (Fig. 1), as in benzyl alcohol.

Our explanation for this apparent anomaly between the results for the two techniques is that the interaction between the hydroxyl and the π-electron system is not an attraction caused by a hydrogen bond but a repulsion between the π-electrons and the lone pair electrons on the hydroxyl oxygen. The stable *trans* conformer in 9-fluorenol is due to a repulsion between the π-electrons on both sides of the hydroxyl group and the lone-pair electrons on the hydroxyl oxygen. This results in only one stable conformer in which this repulsion is minimised by the hydroxyl proton orientation, as in any other conformer the lone-pair π-electron repulsion will be considerable.

In complete contrast the CH·OH coupling in diphenylmethanol is characteristic of a predominantly *gauche* orientation. The application of the J_g and J_t values given previously gives 87 % *gauche* conformation, corresponding to an energy difference in favour of the *gauche* form of *ca.* 0.7 kcal mol^{-1} though in view of the disimilar coupling fragment considered these values must be considered with care. Intriguingly, in view of the presence of two aromatic rings, the solvation shift is almost the normal value (4.27 *cf.* 4.09 p.p.m.), suggesting that the ring current shifts of at least one of the phenyl rings at the hydroxyl proton is quite small. Again the IR data (Table 2) does not unambiguously confirm the NMR results, in that only one band at 3613 cm^{-1} is

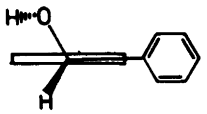

Fig. 3. Proposed conformation of diphenylmethanol (*3*).

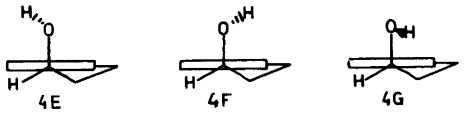

Fig. 4. Conformations of 1-indanol (*4*) about the CH·OH bond.

observed. The frequency of this band is the mean of the two bands observed in 9-fluorenol, and again it is possible that the two conformers have very similar IR frequencies.

The important difference between diphenylmethanol and 9-fluorenol is that in the latter the aromatic rings are co-planar, whereas they are certainly not co-planar in the former, and indeed could be orthogonal to each other. A possible conformation which is consistent with the experimental data and the steric considerations is as shown in Fig. 3., which is analogous to conformation *1E* of benzyl alcohol. In this conformation, one of the oxygen lone-pairs points towards the edge of the orthogonal phenyl ring, which is the area of the smallest electron density. It should be noted, however, that there is no direct evidence for this particular conformation (apart from the *gauche* position of the hydroxyl proton), though the low-field value of the hydroxyl proton chemical shift is very suggestive of an orientation in which the OH lies almost on one aromatic ring plane. The difference between the OH chemical shifts of diphenylmethanol (δ 1.62) and benzyl alcohol (δ 1.09, Table 1), is nicely explained on this basis, the calculated value being 0.50 p.p.m.[4] However, the probable occurrence of large amplitude molecular motions in this rather "floppy" molecule suggests that the results of such calculations must be applied with some caution.

1-INDANOL

The previous analysis of the benzyl alcohol conformation was consistent with an oxygen-ring dihedral angle of *ca.* 60°, a result supported by electron diffraction measurements, but due to the rapid rotation on the NMR time scale about the C·C single bond the methylene protons are equivalent and consequently it was not possible to unequivocally distinguish between the two *endo* conformers with this orientation (*1E* and *1F*) (Fig. 2). This study of 1-indanol was prompted by the realization that if the alcohol CH_2 is incorporated into a ring system this equivalence is removed. In 1-indanol there are three non-equivalent conformations as shown in Fig. 2, where we retain for comparison the E and F labels. (The conformation of the five membered ring will be considered subsequently). The presumably favoured conformations *4E* and *4F* can be distinguished immediately by the CH·OH coupling, as the protons are *gauche* oriented in *4E* (and *4G*) and *trans* oriented in *4F* (Fig. 4).

The value of this coupling in dilute non-polar solvents (7.3 Hz, Table 1), does indeed favour conformer *4F*, with a percentage population of 58 %. Both the ∞ dilution chemical shift of the hydroxyl proton and the solvation shift (Table 1) are virtually identical to benzyl alcohol, confirming the absence of any large perturbations due to the five membered ring, though as the five membered ring is certainly non-planar (see later) the precise agreement in Table 1 may be fortuitous. If the results of the benzyl alcohol analysis can be carried over to 1-indanol, we would expect a relatively small amount of conformer *G* (10 % in benzyl alcohol), giving an estimate of the rotamer population of *ca.* 30:60:10 for *4E*, *F* and *G*. This analysis is supported by the IR data (Table 2), in which three hydroxyl bands are observed, two of them as shoulders, presumably arising from the three different rotamers. Unfortunately, it was not possible to obtain any estimate of the relative intensity (peak area) of these bands, which would have given a better estimate of the conformer populations. Further discussion on these results will be deferred until the conformational analysis of the five membered ring can be considered.

The five membered ring of 1-indanol may be safely assumed to adopt the envelope or C_S conformation found in cyclopentene and related systems, as the aromatic ring will enforce the planarity of C_1 and C_3 with the ring (Fig. 5). Cyclopentene has a pucker equivalent to a dihedral angle of *ca.* 25°[9,10] and the use of this value was also consistent with an NMR and

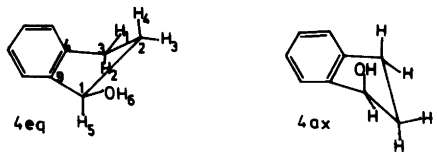

Fig. 5. The skeletal conformers of 1-indanol (*4*).

dipole moment investigation of some 1,2-dihalogenoindans.[11] The two interconverting conformers of 1-indanol are energetically non-equivalent with a pseudo-axial hydroxyl in *4ax* and pseudo-equatorial in *4eq*, thus a detailed analysis must evaluate not only the angle of pucker (α between C_3,C_4, C_9, C_1 and C_1, C_2, C_3) of the conformers, but also the relative populations of 4_{eq} and 4_{ax}. We will assume henceforth that the angles of pucker of the two conformers are identical. They would certainly not be very different, as the hydroxyl group does not constitute a major perturbation of the cyclopentene ring, and as we shall see this assumption is consistent with our analysis.

There is sufficient information in the analysis of the NMR spectrum of indanol (Table 3) to obtain both the angle of pucker and the conformer populations from the vicinal HH couplings. The determination of conformational information from these couplings is *via* the application of the various modifications of the well-known Karplus equation relating these to the H·C·C·H dihedral angles. The most recent comprehensive treatment of this angular dependence is due to Haasnoot,[12,13] who has applied this general equation to the analysis of the observed coupling constants in a number of bio-organic molecules, including substituted prolines and derivatives.[14] In these molecules a comparable situation to the 1-indanol case exists in that the couplings were analysed on the basis of two interconverting non-equivalent *ca.* envelope type conformations of the proline ring with different angles of pucker (equivalent to ϕ of 30–40°).

Table 3. Proton chemical shifts (δ; ppm) and coupling constants (Hz; ±0.02 Hz) for 1-indanol.[a,b]

δ_1 3.0584	J_{12}	−15.71
δ_2 2.8174	J_{13}	4.82
δ_3 2.4710	J_{14}	8.42
δ_4 1.9306	J_{23}	8.27
δ_5 5.1009	J_{24}	6.73
δ_6 1.0850	J_{34}	−13.16
	J_{35}	6.76
	J_{45}	5.26
	J_{56}	7.32

[a] In $CFCl_3$ solution, conc. 8.9 mM. [b] Aromatic protons at 7.11 (3H), 7.28 (1H).

The generalised equation used by these workers is somewhat complex, and it is sufficient for our purposes to make use of their general results in a less sophisticated analysis of the coupling data. The dihedral angles, and therefore couplings between the *cis* oriented protons are a function only of the angle of pucker of the conformers (and the electronegativity of the substituents etc.). If we consider only the C_2C_3 $CH_2.CH_2$ fragment and make the additional assumption of equal angles of pucker in the two interconverting conformers 4_{eq} 4_{ax}, then the *cis*-couplings give directly the dihedral angles *via* the appropriate Karplus equation.

Garbisch and Griffiths[15] derived the equation $J=12.95\cos^2\phi$ from the low temperature couplings in cyclohexane-d_8; a somewhat better fit of this data is given by eqn. (1), and the application of

$$J=12.90\cos^2\phi-0.32\cos\phi \qquad (1)$$

eqn. (1) to the *cis*-oriented couplings (J_{14}, J_{23}) gives a value of the dihedral angle $\phi(H_4C_2C_3H_1)$ of 35.3° (±0.5°). This angle is equivalent to the dihedral angle $C_9H_1C_2C_3$ (from simple geometrical reasoning), which again is very close to the pucker angle α for angles of this magnitude. In contrast to the *cis*-couplings, the *trans*-couplings in this fragment (J_{13}, J_{24}) *are* dependent on the ratios of the conformers, J_{13} being *ca.* equatorial-equatorial in 4_{eq} and axial-axial in 4_{ax}. Eqn. (1) given with ϕ=35.0°, calculated values for these couplings of 10.9 Hz (ax-ax) and 0.08 Hz (eq-eq) and these together with the observed values of J_{13} and J_{24} give the percentage populations of the 4_{ax} conformer as 56 and 61 %, respectively. The agreement between the two values is good, giving 58 (±2) % of 4_{ax}, equivalent to stabilisation energy of 0.19 kcal mol^{-1}.

Our results from 1-indanol are again best interpreted by a model of repulsion between the hydroxyl group and the π-electron system and not one invoking intramolecular hydrogen bonds.

Table 4. Results from NOE experiments on 1-indanol (1 % in $CDCl_3$).

Irr. proton	Increase in intensity on proton No. (%)					
	1 (δ 3.058)	2 (δ 2.817)	3 (δ 2.471)	4 (δ 1.931)	5 (δ 5.101)	6 (δ 1.085)
3 (δ 2.471)	—	1	—	4	3	—
4 (δ 1.931)	2	1	4	—	—	—
5 (δ 5.101)	—	—	3	0.4	—	2

The only conformer with a possibility of such a bond is *4F*. However, this conformer is only slightly more populated than the sum of the other two, implying the stabilisation if any, to be very weak. Further, if one assumes the conformation *4G* to have 10 % of the population, (an assumption that appears reasonable from the identical δ_{OH} in benzyl alcohol and 1-indanol), the two major conformers are *4E* and *4F*, both with the lone-pair electrons of the hydroxyl oxygen pointing away from the π-electron cloud of the ring.

Conclusion. This investigation of the conformations of substituted benzyl alcohols, 9-fluorenol, diphenylmethanol and 1-indanol has not given any indications of intramolecular hydrogen bonds to the π-electron system. Instead, the data appear to support a model with repulsion between the hydroxyl oxygen lone-pair electrons and the π-electron cloud.

EXPERIMENTAL

The investigated compounds, except for 2,6-dimethylbenzyl alcohol and 2,6-dimethyl-α-^{2}H-benzyl alcohol, were all commercially available. They were recrystallised before use. The solvents used were distilled and stored over molecular sieves (3A, activated at 400 °C for 4 h). The procedures for obtaining the IR and NMR spectra have been reported.[6] The high dilution NMR spectra were run on a Bruker WM 400 spectrometer, the others on a JEOL FX 100 MHz spectrometer. The 6 spin part of the 1-indanol NMR (Table 3) spectrum was analysed by the PANIC program on the BRUKER instrument. The assignements of the 1-indanol spectrum (Table 3) were supported by NOE experiments (Table 4).

The NOE measurements were obtained by preirradiation of the different proton chemical shift frequencies for 8 s. Eight scans, preceeded by 2 dummy scans, were collected at the selected irradiation frequency, the FID was stored, and the irradiation frequency changed. A reference FID with irradiation at an off resonance frequency was acquired. The entire frequency list was repeated 100 times under computer control with addition of the new data to those already stored. The accumulated FID's were processed with same line broadening and phase corrections.

2,6-Dimethylbenzyl alcohol- (1) and 2,6-dimethyl-α-^{2}H-benzyl alcohol (α-^{2}H-*1*) were prepared by $LiAlH_4$ or $LiAl^2H_4$ reduction of 2,4-dimethylbenzaldehyde in diethyl ether.[17] The two compounds had almost identical IR. *1* had NMR (5.0 mM, $CFCl_3$): δ 5.9–6.05 (3H, m), 4.653 (2H, d, *J* 5.54 Hz), 2.402 (6H, s), 0.661 (1H, t, *J* 5.54 Hz), α-^{2}H-*1* had NMR (5.9 mM, $CFCl_3$, O*H* irradiated): δ 5.9–6.05 (3H, m), 4.618 (1H, t, *J*=1.65 Hz), 2.388 (6H, s). *1* had MS (IP 70 eV; *m/e* (% rel.int.)): 136 (55, M^+), 118 (100), 91 (37), 77 (25), α-^{2}H-*1* had MS (IP 70 eV; *m/e* (% rel.int.)): 137 (53, M^+), 119 (100), 92 (22), 78 (14), 77 (15).

Acknowledgements. The use of BRUKER WM 400 at the Norwegian National NMR Laboratorium at the University of Trondheim is gratefully acknowledged.

REFERENCES

1. Bellany, L. J. *The I.R. Spectra of Complex Molecules,* Chapman & Hall, London 1975.
2. Schuster, P., Zundel, G. and Sanderfy, C. *The Hydrogen Bond,* North-Holland, Amsterdam 1976, Vol. 2.
3. Schleyer, P. R., Trifan, D. S. and Baeskai, R. *J. Am. Chem. Soc. 80* (1958) 6691.
4. Abraham, R. J. and Bakke, J. M. *Tetrahedron 34* (1978) 2947.
5. Abraham, R. J. and Bakke, J. M. *Acta Chem. Scand. B 35* (1981) 367.
6. Abraham, R. J. and Bakke, J. M. *Acta Chem. Scand. B 37* (1983) 865.
7. Abraham, R. J. and Bakke, J. M. *Org. Magn. Reson. 14* (1980) 312.
8. Bakke, J. M. and Lorentzen, G. B. *Acta Chem. Scand. B 28* (1974) 650.

9. Davis, M. I. and Muecke, T. W. *J. Phys. Chem. 74* (1970) 1104.
10. Usher, D. A., Dennis, E. A. and Westheimer, F. H. *J. Am. Chem. Soc. 87* (1965) 2320.
11. Buys, H. R. and Harvinger, E. *Tetrahedron 24* (1968) 4967.
12. Haasnoot, C. A. G. *Thesis,* State University, Gorlaeus Lab., Leiden, Netherlands 1979.
13. Haasnoot, C. A. G., Leeuw, F. A. A. M. and Altona, C. *Tetrahedron 36* (1980) 2783.
14. Haasnoot, C. A. G., Leeuw, F. A. A. M., Leeuw, H. P. M. and Altona, C. *Biopolymers 20* (1981) 1211.
15. Carbisch, E. W. and Griffiths, M. C. *J. Am. Chem. Soc. 90* (1968) 6543.
16. Trætteberg, M. *Private communication.*
17. Nauta, W. T., Ernsting, M. J. E. and Faber, A. C. *Recl. Trav. Chim. Pays - Bas 60* (1941) 915.

Received September 26, 1983.