

A ^1H NMR Investigation of Rotational Isomerism and Hydrogen Bonding in 1,2-Diarylethanols

RAYMOND J. ABRAHAM^a and JAN M. BAKKE^b

^aThe Robert Robinson Laboratories, The University of Liverpool, Liverpool, England and ^bChemistry Department, The University of Trondheim, NLHT, N-7000 Trondheim, Norway*

Conformational analyses of 1,2-diarylethanols in CCl_4 and DMSO solutions have been performed by ^1H NMR spectroscopy. 2J (HCH), 3J (CH,CH), 3J (CH,OH) couplings and the OH chemical shifts were used as conformational probes. Two conformers have been identified, both having the two aryl groups *trans* (*anti*), with the 2-aryl ring at an angle of *ca.* 50° to the carbon chain. The conformer giving rise to the OH frequency at 3610 cm^{-1} has the hydroxyl proton pointing away from the 2-aryl ring. The conformer giving rise to the OH frequency at 3550 cm^{-1} , which is the major band for the di-*o*-nitro and di-*o*-methoxy compounds, has the hydroxyl in proximity to both the *ortho* substituents. In neither conformer is there any indication of hydrogen bonding involving the π -electrons of the aromatic ring.

Previous investigations into hydrogen bonding in 2-arylethanols have been mainly by IR spectroscopy. Generally, the appearance of two OH bands in dilute CCl_4 solution has been accepted as evidence for an intramolecular hydrogen bond to the π -electrons of the 2-aryl ring.^{1–3} We have used FT NMR to study rotational isomerism in benzyl alcohol⁴ and showed that the two bands present in the IR spectrum were due to the two rotamers about the CH_2OH bond, as in ethanol and that hydrogen bonding to the π -electron cloud was not an important factor in determining the molecular conformation. We have now used this technique to study the conformations of 1,2-diarylethanols (*I*) and the extent of internal hydrogen bonding in these substances.

* *Present address:* Organic Chemistry Laboratories, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim, Norway.

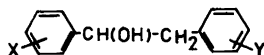
The conformation of 1,2-diphenylethanol (*Ia*) is determined by the dihedral angles $\text{C}_2\text{C}_1\text{C}'_1\text{C}'_2$ (ω_1), $\text{C}'_1\text{C}_2\text{C}_1\text{C}'_1$ (ω_2), $\text{C}_1\text{C}_2\text{C}'_1\text{C}'_2$ (ω_3) and $\text{C}'_1\text{C}_1\text{OH}_M$ (ω_4), where the ω 's are taken as positive for a clockwise rotation from the eclipsed ($\omega=0$) position (Fig. 1).

There are three possible conformations around the C_1-C_2 bond (X, Y and Z), each of which has three possible conformations of the OH around the C_1-O bond. In addition, in each of these conformations the dihedral angles of the phenyl groups (ω_1 and ω_3) need to be defined. All this makes the 1,2-diarylethanols rather complex molecules and NMR studies alone cannot be expected to give exact information about the conformational composition. It was hoped, however, that the NMR results could resolve ambiguities in the IR studies, *e.g.* the extent of internal hydrogen bonding.

From ^1H NMR, four types of information are available. J_{AB} is dependent on the dihedral angle ω_3 ; J_{AX} and J_{BX} on the relative proportions of X, Y and Z; J_{MX} on the relative proportions of the rotamers of the OH group (A, B and C) and δ_{OH} will depend (among other things) on the degree of internal hydrogen bonding.

RESULTS AND DISCUSSION

The NMR spectra were measured in CCl_4 at two different concentrations, both $<10^{-2}\text{ M}$ (Table 1) and in d_6 -DMSO solution (Table 2). No concentration dependence of the spectrum was observed except for the OH chemical shift, and the ∞ dilution value is given in Table 1. In such conditions, intermolecular hydrogen bonding may

Table 1. Proton chemical shifts (δ , ppm) and coupling constants (J , Hz) for 1,2-diarylethanols in CCl_4 , $C < 10^{-2}$ M.

Substance	J_{AB}	J_{AX}	J_{BX}	J_{CHOH}	δ_A	δ_B	δ_X	$\delta_{\text{OH}\infty}$
1a, X=Y=H	-13.58	4.64	8.40	2.3 ^a	2.943	2.900	4.79	1.531
1b, X=H, Y=o-OCH ₃	-13.53	4.05	8.30	3.0	3.043	2.839	4.85	1.881
1c, X=p-OCH ₃ , Y=o-OCH ₃	-13.50	4.48	8.12	3.0	3.002	2.844	4.80	1.784
1d, X=Y=o-OCH ₃	-13.50	4.41	8.00	5.0	3.036	2.896	5.04	2.305
1e, X=H, Y=o-Cl	-13.58	4.25	8.71	3.0	3.144	2.982	4.92	1.527
1f, X=o-Cl, Y=H	-13.60	2.86	9.25	3.2	3.156	2.658	5.22	1.660
1g, X=Y=o-Cl	-13.70	3.84	8.86	3.5	3.260	2.971	5.38	1.677
1h, X=H, Y=o-NO ₂	-13.50 ^c	3.58 ^c	8.82	3.7 ^b	3.328	3.082	4.95	1.725
1i, X=o-CH ₃ , Y=o-NO ₂	-13.45	3.86	9.05	3.9	3.271	3.133	5.20	1.614
1l, X=Y=o-NO ₂	-13.71	3.15	9.10	-	3.357	3.427	5.48	1.963

^aBroad signals, OH still exchanging. ^bLong-range coupling, 0.8 Hz. ^c $\Delta\nu_{\frac{1}{2}A} = 2.0$ Hz, $\Delta\nu_{\frac{1}{2}B} = 1.4$ Hz.

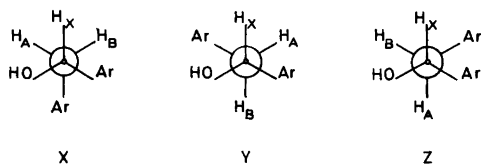
Table 2. Proton chemical shifts (δ , ppm) and coupling constants (J , Hz) for 1,2-diarylethanols in DMSO ca. 5% solutions. Formula, see Table 1.

Substance	J_{AB}	J_{AX}	J_{BX}	J_{CHOH}	δ_A	δ_B	δ_X	δ_{OH}
a, X=Y=H	-13.53	4.70	8.45	4.86	2.863	2.898	4.751	5.249
b, X=H, Y=o-OCH ₃ ^a		6.7		4.80	2.855	2.855	4.764	5.156
c, X=p-OCH ₃ , Y=o-OCH ₃ ^a		6.8		4.88	2.843	2.843	4.680	5.064
d, X=Y=o-OCH ₃	-13.54	4.60	8.13	5.12	2.851	2.806	5.220	4.889
e, X=H, Y=o-Cl ^a		6.6		4.88	2.995	2.995	4.831	5.371
f, X=o-Cl, Y=H ^a		6.83		4.88	2.990	2.990	4.819	5.383
g, X=Y=o-Cl	-13.86	4.75	8.82	4.76	3.040	2.973	5.255	5.431
h, X=H, Y=o-NO ₂ ^a		6.3		4.50	3.164	3.164	4.736	5.392
i, X=o-CH ₃ , Y=o-NO ₂	-13.54	5.12	8.34	4.80	3.174	3.157	4.922	5.283
j, X=p-NO ₂ , Y=H ^a		6.5		4.78	2.931	2.931	4.950	5.646
k, X=Y=p-NO ₂	-13.57	4.90	8.22	4.75	3.144	3.036	5.068	5.799

^aA₂X spectrum observed giving one averaged coupling.

be assumed to be absent.³ Conversely, in DMSO solution strong hydrogen bonds to the solvent are the only form of hydrogen bonding present.⁴

For all spectra, both in DMSO and CCl_4 , J_{AB} is close to -13.5 Hz (13.5–13.7 Hz). Use of the equation given in Ref. 5 relating J_{gem} to the



orientation of the phenyl ring, gave a value of 50° for ω_3 . However, the calculated value of J_{AB} for a freely rotating phenyl group is -14.2 Hz.⁵

Thus it is not possible to unambiguously distinguish between these two models. Electron diffraction and other NMR studies of benzyl derivatives have shown these consistently to have ω of ca. 60°,⁶ and this may be typical for benzyl derivatives.

From J_{AX} and J_{BX} , the population of X, Y and Z can be estimated if one assumes Y (with the phenyl groups *trans*) to be the most abundant conformer. In this case H_B can be identified as the proton *trans* to

H_X in this conformer, as J_{BX} will be the largest of J_{AX} and J_{BX} . The rotamer populations can now be calculated in the normal manner, once the couplings in the individual rotamers can be estimated.

We use as a model for Y, 1-*tert*-butyl-2-phenylethanol in which J_{AX} and J_{BX} are 2.5 and 10.6 Hz, respectively,⁷ and the large steric interactions between *gauche* phenyl and *t*-butyl groups precludes any amount of the rotamers corresponding to X and Z. The *trans* coupling may be safely transferred to J_{BX} (Y). The remaining *gauche* couplings will vary with the orientation of the electronegative substituents and were calculated using the equations of Ref. 9. These couplings are given below the rotamers. (Note that the equations of Ref. 9 give J_g for Y equal 2.6 Hz, in excellent agreement with the observed value in 1-*tert*-butyl-2-phenylethanol).

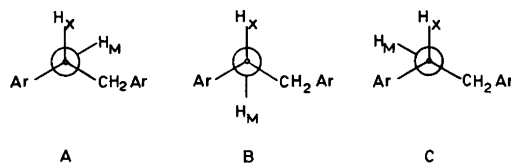
$$J_{AX}^{\text{obs}} = \sum_i n_i J_{AX}^i \quad (1)$$

$$J_{BX}^{\text{obs}} = \sum_i n_i J_{BX}^i \quad (2)$$

$$\sum_i n_i = 1 \quad (3)$$

From eqns. (1)–(3), where J_{AX}^i and J_{BX}^i , and n_i are the coupling constants and mol fractions of the *i*th rotamer, the values of n_i can be calculated (Table 3). For all investigated alcohols, the Y conformer was present in 70 to 80% and X in only a minor amount (less than 13%).

Three rotamer forms, A, B and C are possible for the hydroxyl group.



From the observed ${}^3J_{CH-OH}$ the percentage of rotamers B and (A+C) can be estimated, if the values of J_g and J_t are known. We use, as before⁴ values of 2.2 and 11.0 Hz.

In all eight ethanols investigated in dilute CCl_4 solution the *gauche* forms (A+C) are dominant (Table 3).

From the IR study it was concluded that *1b*, *1c*, *1d* and *1h* were partly hydrogen bonded to the *ortho* substituent in the 2-aryl ring (ν_{OH} at ca. 3550 cm^{-1}). The other four alcohols, *1a*, *1e*, *1f* and *1g* showed only one band at ca. 3610 cm^{-1} which was also present in the other four.³

We will first discuss the possibility of a hydrogen bond to the π -electron system of the 2-aryl ring, which was assumed to give rise to an IR band at ca. 3610 cm^{-1} .¹⁻³ For four of our alcohols, *1a*, *1e*, *1f* and *1g* this was the only band in the OH region. From our results (Table 3) such a hydrogen bonded species would have to consist mainly of conformer Y with rotamer A for the OH group. This would make free rotation of the 2-aryl group impossible (for steric reasons) and ω_3 would be -50 or -130° (from J_{AB}). Iwamura has studied the OH frequencies

Table 3. Conformational composition of 1,2-diarylethanols (*1a*–*1l*) in CCl_4 ($C < 10^{-2}\text{ M}$) from NMR data (Table 1). Formula, see Table 1.

Substance	Isomerism around the C_1-C_2 bond			Isomerism around the C_1-O bond	
	X	Y	Z	A+C (<i>gauche</i>)	B (<i>trans</i>)
<i>1a</i> , X=Y=H ^a	8	67	25	99	1
<i>1b</i> , X=H, Y= <i>o</i> -OCH ₃	14	69	17	91	9
<i>1c</i> , X= <i>p</i> -OCH ₃ , Y= <i>o</i> -OCH ₃	12	65	23	91	9
<i>1d</i> , X=Y= <i>o</i> -OCH ₃	15	64	21	68	32
<i>1e</i> , X=H, Y= <i>o</i> -Cl	7	72	21	91	9
<i>1f</i> , X= <i>o</i> -Cl, Y=H	14	84	2	89	11
<i>1g</i> , X=Y= <i>o</i> -Cl	9	76	15	85	15
<i>1h</i> , X=H, Y= <i>o</i> -NO ₂	12	76	12	83	17
<i>1i</i> , X= <i>o</i> -CH ₃ , Y= <i>o</i> -NO ₂	7	77	16	90	10
<i>1l</i> , X=Y= <i>o</i> -NO ₂	13	81	6	—	—

^aOH protons were exchanging, estimate of *gauche* and *trans* not accurate.

of 2-arylethanol as a function of the angle of twist of the phenyl ring [note that in the conventions used θ (Ref. 1) = $-\omega_3$]. From his analysis, a ν_{OH} of 3610 cm^{-1} corresponds to ω_3 equal -60 to -70° , in good agreement with the value obtained from J_{AB} . However, inspection of molecular models shows that considerable steric repulsion between the *ortho* hydrogen of the 2-aryl ring and the hydroxyl hydrogen must occur in this case if rotamer A is dominant. If a hydrogen bond was formed, it would have to be strong enough to counteract this repulsion. For hydrogen bonds between phenols and dimethylacetamide, a $\Delta\nu$ of *ca.* 300 cm^{-1} corresponded to a ΔG° of *ca.* -2 kcal mol^{-1} .⁸ In our case, $\Delta\nu$ is not easily defined, but is most probably less than 50 cm^{-1} .³ Any hydrogen bond is therefore weak and cannot counteract the steric repulsion discussed above. This conclusion can only be fitted with the NMR data if one assumed the dominant rotamer of the hydroxyl group to be C and not A for conformer Y. The hydroxyl hydrogen thus points away from the 2-aryl group, with no possibility of a hydrogen bond to the π -electrons of this ring.

We believe that this is the reason for the lack of any hydrogen bonding in these molecules, rather than the explanation of Iwamura¹ that the hydroxyl hydrogen atom lies in the nodal plane of the aromatic π -electron cloud in a conformation equivalent to A. Our explanation finds strong support from the identity of the OH stretching frequency in this conformation (3610 cm^{-1}) with that of the "H-bonded conformer" of benzyl alcohol (3615 cm^{-1}). We have already shown that this conformer in benzyl alcohol (*If* in Ref. 4) has the OH- pointing side-on to the aromatic ring, which is precisely analogous to conformer C above.

One more observation fits in with this. For 1-phenyl-2-(*o*-nitrophenyl)ethanol (*1h*), which has *ca.* 90% of a conformer with $\nu_{\text{OH}} = 3615 \text{ cm}^{-1}$ (from IR data), a long-range coupling (0.8 Hz) was observed for the hydroxyl proton. This is explained by conformer Y with rotamer C being a dominant conformation, the hydroxyl proton would then be part of a W pattern⁹ with H_A . A slight broadening of the signals from H_A was observed.

Four of the investigated alcohols (*1b*, *1c*, *1d* and *1h*) showed an IR band at *ca.* 3560 cm^{-1} . These alcohols have an *ortho* nitro or methoxy group in the 2-aryl ring, and the relative low frequency of the IR band was explained by the existence of a hydrogen bond to that *ortho* substituent.³

The NMR parameters obtained for *1b*, *1c* and *1h*

in high dilution are not very different from those of *1a*, *1e*, *1f* and *1g* discussed above. Conformer Y and rotamers A or C are predominant also for these compounds.

This is, on reflection, not too surprising in view of the low relative intensity of the H-bonded species in these compounds, (from the IR data, the H bonded species were estimated 40, 30 and 10%, respectively, of the total OH intensity).³ The NMR parameters, being weighted averages over all conformations, are relatively insensitive to small amounts of minor conformations.

However, for compounds *1l* and particularly *1d* which both have two H-bonding acceptor groups as *ortho* substituents (NO_2 and OMe), the hydrogen bonded conformer is the major form, the IR studies giving 55 and 70% populations, respectively, and here the NMR data does differ significantly from the other alcohols in one important respect. The value of $J(\text{CH.OH})$ is considerably larger than in the other alcohols, leading to *ca.* 30% of the *trans* conformer B in *1d* (Table 3) (unfortunately due to solubility limitations this coupling could not be observed in *1l*). It is reasonable to suppose that this corresponds to the conformer giving rise to the OH band at 3550 cm^{-1} .

This conformer in *1d* could either have a hydrogen bond to the 2-phenyl *ortho* methoxy group or the interaction between the two *ortho* methoxy groups may force the 2-phenyl group into the $\omega_3 = 120^\circ$ orientation (which would, from Iwamura's plot, give $\nu(\text{OH})$ equal to *ca.* 3575 cm^{-1}) and thus facilitate a hydrogen bond to the π -electron system of the 2-aryl ring.

The former explanation fits the observed data, whereas the latter is untenable for the following reasons.

(a) *ortho*-chloro substituents (*1g*) did not produce this effect, yet on steric grounds they would be similar to methoxy.

(b) The similarity between *1l* and *1d* shows that the effect is not caused by the electronic effects of the methoxy groups, but is common to those molecules with two *ortho* H-bonding acceptor groups.

(c) The necessity for two *ortho* H-bonding acceptor groups is illustrated by *1i*, in which the steric effect of the 1-phenyl *ortho* methyl group should be comparable to a nitro group. However, IR studies of *1i* at high dilution in CCl_4 showed that the OH band at 3560 cm^{-1} was only *ca.* 10% of the free OH bond at 3610 cm^{-1} .

(d) The OH frequency of this conformer (3540

-3560 cm^{-1}) is significantly different from the lowest frequency possible on Iwamura's scale (3575 cm^{-1}). This is now explained as due to a quite different hydrogen bond, between the OH and neighbouring oxygen atoms, not the π -cloud.

(e) The *trans* orientation of the OH proton (conformer B), when considered with the unaltered values of J_{gem} (J_{AB}) and J_{vic} (J_{AX} and J_{BX}), leads to a conformation (conformer Y and rotamer B) in which the OH is pointing towards the *o*-methoxy and not the 2-phenyl ring.

All the above evidence points to a preferred conformation (Fig. 1) in which there is a hydrogen bond between the hydroxyl and the two *ortho* methoxy (or nitro) substituents. The increased stabilisation provided by the 1-*ortho* phenyl substituent is now seen as the reason for the increased percentage of the H-bonded conformer in *1d* and *1l*. Analogous H-bonding in the *o*-methoxy and *o*-nitrobenzyl alcohols was detected by NMR⁴ and IR³ investigations.

CONCLUSIONS

The detailed NMR studies reported here when considered with the previous IR data, lead to new conclusions on the conformations of the 1,2-diarylethanols in solution. Two major conformers are identified, which are responsible for the OH stretching bands at 3610 and 3550 cm^{-1} . Both conformers have a planar CCCC chain with the C_2 phenyl ring tilted at *ca.* 60° to this. In the non H-

bonding conformer (giving $\nu(\text{OH})\ 3610\text{ cm}^{-1}$) the OH points away from the 2-phenyl ring (Fig. 1a). In the H-bonded conformer ($\nu(\text{OH})\approx 3550\text{ cm}^{-1}$), in the two compounds with two *ortho* H-bonding acceptor groups (OMe, NO_2) it is possible to deduce the preferred conformation which involves a three-centre hydrogen bond and a *trans* arrangement of the OH proton (Fig. 1b).

It is tempting to speculate that the H-bonded conformer in the other compounds has a similar conformation, but we have no direct evidence on this, save for the similar value of $\nu(\text{OH})$, as the percentage of this conformation is too small to be detected by time-averaged NMR experiments.

What is, however, clear from these studies is that a similar situation exists in the 1,2-diarylethanols as in the benzyl alcohols, in that intramolecular H-bonding to the aromatic ring (if there is any) plays no part in determining the conformer energies and thus populations of the major conformers.

EXPERIMENTAL

The spectra were run in CCl_4 (dried over molecular sieves) or DMSO on either a Varian XL 100 or a Perkin Elmer R 34 NMR. The spectra of *1i* and *1l* were run on a Nicolet 200 MHz NMR. To stop exchange of the hydroxyl protons it was essential to dry the NMR tubes for at least 4 h at *ca.* 100°C . The ABX spectra were calculated by a LAOCOON III¹¹ or NEMEN program.¹² The obtained parameters were accurate at $\pm 0.05\text{ Hz}$. The syntheses of substances *1a*–*1h* and *1j*–*1l* have been described.³ 1-(*o*-Methylphenyl)-2-(*o*-nitrophenyl)ethanol (*1i*) was prepared by addition of *o*-nitrotoluene to *o*-tolualdehyde in DMSO.¹³ It had m.p. 63 – 64°C . IR (KBr): $3550, 3300, 3020, 2940, 2860, 1610, 1550, 1525, 1350, 1040, 785, 760, 740, 730\text{ cm}^{-1}$. IR (10 mg/150 ml CCl_4 , 10 cm path length): 3610 cm^{-1} ($A=0.30$), 3560 ($A=0.03$). Fig. 1 was prepared from a computer plot (the program was a modified version of ORTEP¹⁴ employing standard bond lengths and angles).

Acknowledgements. R.J.A. acknowledges a Senior CIBA-GEIGY Fellowship (July to December, 1979) and J.M.B. support from Norges Almenvitenskapelige Forskningsråd and Norges Teknisk-Naturvitenskapelige Forskningsråd. A NATO Science Research Grant (No. 1315) is also acknowledged. The preparation of the computer plot for Fig. 1 by Dr. Frode Mo is gratefully acknowledged.

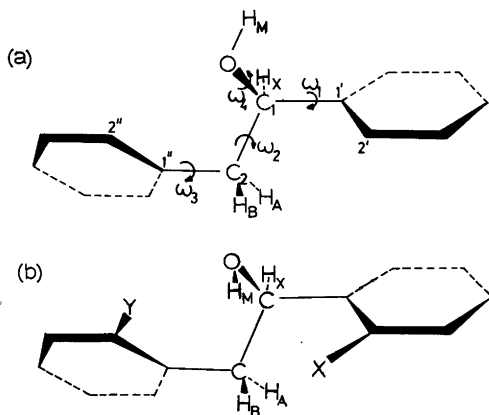


Fig. 1. The two proposed conformations of 1,2-diphenylethanols. (a) gives $\nu(\text{OH})\ 3610\text{ cm}^{-1}$; (b) gives $\nu(\text{OH})\approx 3550\text{ cm}^{-1}$.

REFERENCES

1. Iwamura, H. *Tetrahedron Lett.* 26 (1970) 2227.
2. v. R. Schleyer, P., Winter, C., Trifan, D. S. and Baeskai, R. *Tetrahedron Lett.* 14 (1959) 1.
3. Bakke, J. M. and Lorentzen, G. B. *Acta Chem. Scand. B* 28 (1974) 650.
4. Abraham, R. J. and Bakke, J. M. *Tetrahedron* 34 (1978) 2947.
5. Abraham, R. J. and Bakke, J. M. *Org. Magn. Reson.* 11 (1978) 373.
6. a. Abraham, R. J., Hearmon, R. A., Trætteberg, M. and Bakken, P. *J. Mol. Struct.* 57 (1979) 149;
b. Trætteberg, M., Østensen, H. and Seip, R. *Acta Chem. Scand. B* 34 (1980) 449.
7. Abraham, R. J. *Unpublished results.*
8. Stymne, B., Stymne, H. and Wettermark, G. *J. Am. Chem. Soc.* 95 (1973) 3490.
9. Abraham, R. J. and Loftus, P. *Proton and Carbon-13 NMR Spectroscopy*, Heyden, London 1978.
10. Abraham, R. J. and Bakke, J. M. *Org. Magn. Reson.* 14 (1980) 312.
11. Abraham, R. J. *The Analysis of High Resolution NMR Spectra*, Elsevier, Amsterdam 1971.
12. NEMEN is based on S. Castellano and A. A. Bothner-By's program LAOCOON 3 modified by W. Larson, University of California, Los Angeles.
13. Bakke, J. M. *Acta Chem. Scand.* 21 (1967) 1967.
14. Johnson, C. K. *ORTEP II*; Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge 1976.

Received January 29, 1981.