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Intramolecular Hydrogen Bonding in Aryl Substituted Aliphatic Alcohols

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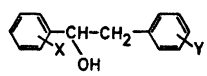
The internal hydrogen bonding in *ortho* substituted benzyl alcohols and in *ortho* and *para* substituted 1,2-diarylethanols (1-X-phenyl-2-Y-phenylethanol) (*1*) has been studied by IR spectroscopy and with chloro, methoxy, and nitro groups as substituents. The hydrogen bonds to these *ortho* groups in benzyl alcohols or in 1-(*o*-X-phenyl)-2-phenylethanols are non-existent or very weak, with the strongest bond to the nitro group. With the Y groups in *ortho* position in 1,2-diarylethanols (*1*), relatively strong hydrogen bonds to the *ortho* substituents (Y) are indicated. The results may be explained by steric relations in the molecule.

Intramolecular hydrogen bonding in *ortho* substituted phenols is well documented.[1,2] Many of these internal hydrogen bonds are particularly strong, *e.g.* in *o*-nitrophenol, and broad and strong absorptions are recorded in the OH region of the infrared spectra; a large frequency shift occurs as compared to the absorption found with nonbonded phenols.

In contrast to the *ortho* substituted phenols, no systematic study seems to have been carried out on *ortho* substituted benzylic alcohols or 2-arylethanols with the *ortho* substituent as hydrogen bond acceptor. Both these classes of substances have, however, been thoroughly studied from the point of view of internal hydrogen bonding to the π-bond system.[3–5]

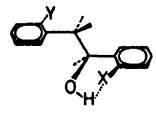
It was thus considered of interest to study some *ortho* substituted benzyl alcohols and arylethanols where the *ortho* group might serve as hydrogen bond acceptor. The aim of the study was to see if the *ortho* substituents would serve as acceptors and whether there existed a preference in acceptor site for the hydrogen bond, *i.e.* if the π-bond system or the *ortho* substituent would dominate as acceptor site.

It was considered of particular interest to study the 1,2-diaryl substituted ethanols of type *1* where competition between four acceptor sites for the hydrogen bonds is possible (*i.e.* the conformers I – IV) in addition to conformer V which has the hydroxyl group non-bonded.

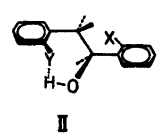


1

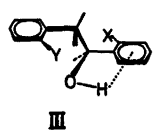
1a. X=H, Y=H
b. X=o-OCH_3, Y=H
c. X=H, Y=o-OCH_3
d. X=p-OCH_3, Y=o-OCH_3
e. X=Y=o-OCH_3
f. X=o-NO_2, Y=H
g. X=H, Y=o-NO_2
h. X=o-NO_2, Y=p-NO_2
i. X=p-NO_2, Y=o-NO_2
j. X=Y=o-NO_2
k. X=Y=p-NO_2
l. X=o-Cl, Y=H
m. X=H, Y=o-Cl
n. X=Y=o-Cl



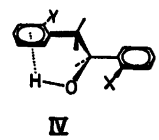
I



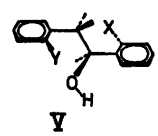
II



III



IV



V

Table 1. Hydroxyl stretching frequencies of benzyl alcohols, in cm^{-1}. Absorbance (A) as log I_0/I.

X	a_1	a_2	A_1/A_2
H[a]	3634	3614	–
H[b]	3635(sh)	3615	1:15
o-OCH_3 [a]	3636(sh)	3610	–
o-OCH_3 [b]	3630(sh)	3615	1:0.8
m-OCH_3 [12]	3636.2	3616.9	1:1.7
p-OCH_3 [12]	3636.0	3617.1	1:2.5
p-OCH_3 [b]	3635(sh)	3615	1:3
o-NO_2 [a]	3640	3597	–
o-NO_2 [b]	3634.0	3600	1:0.7
m-NO_2 [a]	3632	3617.2	–
m-NO_2 [b]	3635	3615	1:1
p-NO_2 [a]	3635	3619	–
p-NO_2 [b]	3635	3615(sh)	1:0.3
o-Cl [a]	3635.7	3615.3	–
m-Cl [a]	3632.4	3615.3	–
m-Cl [12]	3636.4	3617.0	1:1.3
p-Cl [a]	3632.1	3616.4	–
p-Cl [12]	3635.3	3617.1	1:1.4

[a] Private communication from v. R. Schleyer, P. [b] This work.

The substituents used in the study of the alcohols of type *1* may be classified according to their electronic properties. Two of the substituents utilized, the nitro and methoxy groups, would be expected to have opposite electronic effects on the aryl rings, but to function as good hydrogen bond acceptors.[6,7] The chloro substituent would be expected to give rise to only weak hydrogen bonds and to have electronic properties intermediate between those of the nitro and methoxy group.[1,2]

By using these substituents it was hoped to obtain some information concerning the preferred conformer or conformers I – V, both as the acceptor sites and the electron density in the π-bond systems varied. The study was carried out by IR spectroscopy.

RESULTS

The IR absorptions in the OH-region (*i.e.* 3300 – 3700 cm^{-1}) of benzyl alcohols are given in Table 1 and those of 1,2-diarylethanols in Tables 2a – 2c.

All spectra were recorded in dilute CCl_4 solution with concentrations below 10^{-2} M and for compounds *1h*, *1i*, and *1k* below 10^{-4} M. Continued dilution did not change the ratio between the various absorption bands. These concentrations are so low that intermolecular hydrogen bonds are usually broken.[7]

Some of the bands given in Tables 1 and 2 were only partly resolved. In such cases the exact frequencies of the absorptions making up

Table 2. Hydroxyl stretching frequencies in 1,2-diarylethanols (*1*), in cm^{-1}. Absorbance (A) as log I_0/I.

Substance	X	Y	ν_1	ν_2	A_1/A_2
(a) With methoxy substituents					
1a	H	H	–	3620	–
1b	o-OCH_3	H	3620	3590(sh)	1:0.2
1c	H	o-OCH_3	3620	3550(bd)	1:0.6
1d	p-OCH_3	o-OCH_3	3620	3550(bd)	1:0.4
1e	o-OCH_3	o-OCH_3	3615	3560(bd)	1:2.5
(b) With nitro substituents					
1f	o-NO_2	H	3610(bd)	–	–
1g	H	o-NO_2	3615	3560(bd)	1:0.14
1h	o-NO_2	p-NO_2	3625	3600(sh)	1:0.05
1i	p-NO_2	o-NO_2	3625	3560(bd)	1:0.12
1j	o-NO_2	o-NO_2	3615	3540(bd)	1:1.1
1k	p-NO_2	p-NO_2	3620	–	–
(c) With chloro substituents					
1l	o-Cl	H	3610	–	–
1m	H	o-Cl	3615	–	–
1n	o-Cl	o-Cl	3615	–	–

the registered band, and furthermore the absorbance (A) of each absorption, is uncertain [8] and must be used with caution. No "Curve Resolver" was available.

DISCUSSION

The IR absorption in the O–H stretching region of benzyl alcohol in dilute solution is usually interpreted as being contributed to by two conformers of the alcohol: one with a free hydroxyl group and one with a hydrogen bond to the π-bond system.[3-5] The spectrum (Table 1) shows the OH band of the hydrogen bonded conformer to be 20 cm^{-1} below that of the free conformer. This is a shift of the same magnitude as that between the two rotamers A and B of ethanol [8-9] (9 – 17 cm^{-1}) and it has been questioned if the band at 3615 cm^{-1} in benzyl alcohol is really due to a hydrogen bonded species.[10]

A B

From Table 1 it is evident that there are no strong internal hydrogen bonds in any of the studied benzyl alcohols. Of the three *ortho* substituted benzyl alcohols, *o*-methoxy-, *o*-nitro-, and *o*-chlorobenzyl alcohol; the methoxy and chloro compounds have ν_2 in the same position as in the corresponding *m*- or *p*-compounds. The *o*-nitrobenzyl alcohol has a rather strong band at 3600 cm^{-1}, 15 cm^{-1} lower than that of *m*-nitrobenzyl alcohol. From these frequencies, it seems probable that there is no or only a very weak hydrogen bond to the *ortho* substituents in *o*-methoxybenzyl alcohol and *o*-chlorobenzyl alcohol. For *o*-nitrobenzyl alcohol there appears to be a possibility of a hydrogen bond to the *o*-nitro group as judged from ν_2.

Judging from the spectral shifts of phenol or methanol in CCl_4 solutions containing nitrobenzene or anisole, the ether oxygen seems to give rise to stronger hydrogen bonds than the nitro group.[6] Further, a six membered ring would be formed by internal hydrogen bonding in *o*-methoxybenzyl alcohol and a seven membered ring in the *o*-nitrobenzyl alcohol. A six membered ring is usually favoured over a seven membered one both from enthalpy and entropy points of view. Both these circumstances would be expected to favour the formation of an internal hydrogen bond in *o*-methoxybenzyl alcohol as compared to *o*-nitrobenzyl alcohol.

There are, however, two other factors which would favour formation of the internal hydrogen bond in *o*-nitrobenzyl alcohol. One is the electron withdrawing property of the nitro group as opposed to the electron donating ability of the methoxy group. This would make the hydroxyl proton in *o*-nitrobenzyl alcohol more acidic than that in *o*-methoxybenzyl alcohol, and thus the nitrobenzyl alcohol a better hydrogen donor than the methoxybenzyl alcohol.

The other factor is of steric nature. The strength of some types of hydrogen bond is dependent on the angle O–H···O with maximum strength for an angle of 180°.[7] The angle O–H···O may be larger in the seven membered ring of *o*-nitrobenzyl alcohol than in the six membered one of *o*-methoxybenzyl alcohol, thus favouring the internal hydrogen bond in *o*-nitrobenzyl alcohol over the one in *o*-methoxybenzyl alcohol. These points will be further discussed in the following section on 1,2-diarylethanols.

The studied 1,2-diarylethanols (*1a – 1n*) can be divided into two groups, according to whether the *ortho* substituent is present in the 1-aryl or in the 2-aryl ring. The OH stretch absorptions of 1,2-diphenylethanol (*1a*) and of 1,2-di-*o*-substituted arylethanols (*i.e. 1e* and *1j*) are also reported in Table 2.

The substances with *o*-X-substituents (*i.e. 1b, f, h, l*) have IR absorption in the OH region (Table 2) similar to the corresponding *ortho* substituted benzyl alcohols (Table 1); *i.e.* *o*-methoxy-, *o*-nitro-, and *o*-chlorobenzyl alcohol, respectively. Some points are nevertheless worth of discussion.

No band at 3640 cm^{-1} could be detected for 1-(*o*-methoxy)-2-phenylethanol (*1b*), thus indicating a larger proportion of hydrogen bonded conformer than for *o*-methoxybenzyl alcohol. Replacing a hydrogen of *o*-methoxybenzyl alcohol with a benzyl group would slightly decrease the proton donor ability of the hydroxyl group. This electronic effect can therefore not be the reason for the decrease of the contribution of the free conformer.

In *1b* there is a possibility of hydrogen bonding to the 2-phenyl ring (*i.e.* IV) in addition to the 1-aryl ring (III). This may explain the apparent absence of the free conformer (V). However, the larger CH_2-Ph group placed on the hydroxyl bearing carbon may have severe consequences for the population of the various conformers, and may give increased importance to the one with hydrogen bonding to the 1-aryl ring (III) as compared to *o*-methoxybenzyl alcohol. This substitution at the hydroxyl bearing carbon may also result in a large portion of conformer I with a hydrogen bond to the *o*-methoxy group. The shoulder at 3590 cm^{-1} may be interpreted as a band of this species.

The result from the 2-aryl-1-(*o*-nitrophenyl)-ethanols (*1f*, *h*) have some bearing on these problems. 1-(*o*-Nitrophenyl)-2-phenylethanol (*1f*) has a relatively broad absorption centered at 3610 cm^{-1}, and no observable band at 3640 cm^{-1}. The IR absorption thus gives no indication of a free hydroxyl group (*i.e.* no V). The same possibilities exist for hydrogen bonding in *1f* as in *1b: i.e.*, to the aryl rings and to the *ortho* substituent. From the discussion above on the methoxy case and from the results from substances *1f* and *1h*, some indications of the preferred acceptor site of the hydrogen bond may be obtained. Both in *1f* and *1h* there may exist a hydrogen bond to the *o*-nitro group. However, the IR spectra (Table 2b) indicate that such bonds are not stronger and do not account for a larger proportion of the conformers than in *o*-nitrobenzyl alcohol. This type of hydrogen bond therefore seems not to be predominant in substances with *o*-X-substituents, at least not with $X=NO_2$. Further, the frequency of the main peak in *1f* is at 3610 cm^{-1} and that of *1h*, where a *p*-nitro group has been substituted in the 2-phenyl ring, is at 3625 cm^{-1}. This is the expected direction of the frequency shift if an important conformer of *1f* was one with hydrogen bonding to the 2-phenyl ring (*i.e.* IV). By substituting a *p*-nitro group into the 2-ring, a weaker bond to this ring may be expected,[6] resulting in an IR absorption at a higher frequency. The proportion of this conformer is probably determined largely by steric effects, as a hydrogen bond giving rise to an absorption near 3600 cm^{-1} in any case is rather weak. The results from the substances with *o*-X-substituents thus indicate the conformer IV with hydrogen bonding to the 2-aryl ring to be of importance in this group. This conclusion is in accordance with the one of v. R. Schleyer *et al.* on the hydrogen bonding in 2-arylethanols,[5] and is confirmed by the spectrum of 1,2-di(*p*-nitrophenyl)ethanol (*1k*) (Table 2b) which shows a single band at 3620 cm^{-1}. The band at 3635 cm^{-1} in the spectrum of *p*-nitrobenzyl alcohol indicates a large fraction of non-bonded conformer. The absence of such a band in the spectrum of 1,2-di(*p*-nitrophenyl)ethanol shows the importance of hydrogen bonding to the 2-aryl ring.

The substances with *o*-Y-substituents (*1c*, *d*, *g*, *i*) give a different IR absorption pattern from the ones discussed above, as all four substances have a rather broad band in the region 3550–3560 cm^{-1}.

This is a larger frequency shift than those discussed above and indicates stronger hydrogen bonds than those found with the compounds with *o*-X-substituents and for the benzyl alcohols in Table 1.

The only possible reason for these relatively strong hydrogen bonds must be that the *ortho* substituent (Y) in the 2-aryl ring is acting as a hydrogen bond acceptor (conformer II). From the discussions above on benzyl alcohols and diarylethanols with *o*-X-substituents no such strong hydrogen bonds could be expected to the 1-or 2-aryl rings (*i.e.* conformers III and IV).

The reason for the stronger hydrogen bond to the *o*-Y-substituents as compared with the *o*-X-substituents must be a more favourable geometry for the hydrogen bond in conformer II than in I. For 1-aryl-2-(*o*-methoxyphenyl)ethanols (*1c*, *d*) this conformer results in a seven-membered ring, and for 1-aryl-2-(*o*-nitrophenyl)-ethanols (*1g*, *i*,) in an eight-membered ring. In both cases one would expect a larger $O-H\cdots O$ angle (closer to 180°) than for the corresponding 1-*o*-substituted arylethanols or *o*-substituted benzyl alcohols, where six- and seven-membered rings, respectively, results from hydrogen bonding to the *o*-substituents.

These results may thus explain in part, why *o*-nitrobenzyl alcohol and not *o*-methoxybenzyl alcohol has a hydrogen bond to the *ortho* substituent (see above). When the methoxy group is part of a seven membered ring system (*e.g. 1c*) it becomes part of an even stronger hydrogen bond than the nitro group in *o*-nitrobenzyl

alcohol does. When the nitro group is involved in an eight-membered ring system, (*e.g. 1g*) a stronger hydrogen bond results than for the seven-membered ring system. The results thus stress the importance of the ability of the angle O – H···O to approach 180°.

From the intensity ratios A_1/A_2 it is nevertheless indicated that the conformer II may not be of great percentage for the species discussed so far.

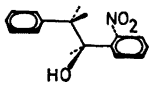
A different picture emerges when one inspects the spectra of 1,2-di(*o*-methoxyphenyl)-and 1,2-di(*o*-nitrophenyl)ethanol (*1e* and *1j*). These two compounds provide a relatively broad band in the region 3540 – 3560 cm^{-1} of the spectra, indicating a hydrogen bond to the *ortho* substituent in the 2-aryl ring. However, for these two compounds, the band in this region has a larger intensity than those discussed above, indicating a relatively larger proportion of the conformer II.

The reason for this might be the changed electron density in the 1-aryl ring as compared to the substances discussed above. In *1j* with a nitro substituent in the 1-aryl ring, this might give conformer III diminished importance, thus increasing the relative importance of conformer II. However, in substance *1i*, there is a *p*-nitro group in the *1*-phenyl ring which would give approximately the same electron density in this ring as in substance *1j* with two *o*-nitro groups. Nevertheless, the spectrum of *1i* indicates a far smaller proportion of conformer II than that of compound *1j*.

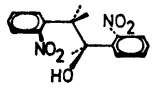
Changes in the electron density of the 1-ring can thus not be invoked to explain the increase of conformer II in compound *1j* as compared to *1g* and *1i*. For 1,2-di-(*o*-methoxyphenyl)ethanol the change in electron density in the 1-aryl ring cannot be the explanation for the increase in importance of conformer II. In this case, the 1-aryl ring was made a better hydrogen acceptor by the introduction of the *o*-methoxy group, and should thus have decreased the importance of conformer II as compared to *1c* and *1e*.

An explanation of the apparently increased importance of conformer II for the di-*o*-substituted compounds *1e* and *1j* therefore has to be sought in the changed steric conditions.

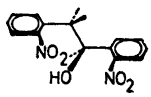
In the solid state, X-ray studies by Sivertsen [12] showed that for compounds *1f* and *1j* the hydroxyl group is placed *transoid* to the *o*-nitro group at the 1-aryl ring.



1f



1j



1j

Further, in *1j*, the nitro-group in the 2-aryl ring is placed *cisoid* to the hydroxyl group.

Inspection of models suggests that these conformations are important even in dilute solution. Except for a small hydrogen bonded portion, the *o*-nitro group of the 1-aryl ring in both *1f* and *1j* will probably be *transoid* to the hydroxyl group. For *1j*, this has consequences for the conformation of the 2-aryl group as there will be repulsion between the two nitro groups if these are in the *cisoid* conformation. The conformation with the nitro groups *transoid* to each other will therefore probably be preferred in solution as well as in the solid state. This means that the hydroxyl group and the nitro group in the 2-aryl ring will be *cisoid* to each other, favourable for hydrogen bonding, and resulting in an increase in conformation II for substance *1j* as compared to compound *1g*. The same type of argument may be used to explain the increased portion of conformer II in 1,2-di(*o*-methoxyphenyl)ethanol (*1e*) as compared to 1-phenyl-2-(*o*-methoxyphenyl)ethanol (*1c*).

This reasoning is based on the assumption that the proportion of various conformers is determined by the steric relations in the molecule and not by the presence of the hydrogen bond. This assumption is not unreasonable when one remembers that a hydroxyl group stretch frequency of 3540 cm^{-1} probably corresponds to an enthalpy of the hydrogen bond of only a few kcal/mol.[7]

The chlorosubstituted 1,2-diarylethanols did not give any indications of hydrogen bonding to the chlorine atoms as shown by the IR data (Table 2c), although a hydrogen bond to the

2-aryl group probably is as important for these alcohols as for those discussed above.

In conclusion, the hydrogen bonds to the *ortho* substituent in *o*-chlorobenzylalcohol and *o*-methoxybenzylalcohol are either non-existent, or of the same strength as those to the π-bond system. In *o*-nitrobenzyl alcohol on the other hand such a hydrogen bond is not excluded. The same is the case with the corresponding 1-(*o*-X-phenyl)-2-arylethanols (*1*). With 1-aryl-2-(*o*-Y-phenyl)ethanols, there exists a relatively strong hydrogen bond to the *o* substituent (Y) in the 2-aryl ring when the substituent is nitro or methoxy. The populations of the various conformers seem to be mainly determined by steric effects and not by the presence or absence of a hydrogen bond.

EXPERIMENTAL

The infrared spectra were recorded in dilute CCl_4 solution. The CCl_4 was dried by refluxing over P_2O_5 and pipetted on to the sample. The spectra were run in 1 cm quartz cells or a 10 cm cell equipped with NaCl windows. The spectra were recorded on a Perkin-Elmer infrared spectrophotometer, Model 457. The resolution of the instrument is 4 cm^{-1} in the OH stretch region. The spectra were recorded in the slow scanning mode, with a minimum slit opening. The various benzyl alcohols studied were all available commercially. The synthesis of the substances *1g*, *1j*, and *1k* have been reported earlier.[13,14]

1-(o-Nitrophenyl)-2-phenylethanol (1f). This substance was made from *o*-nitrostilbeneoxide by refluxing with *p*-toluenesulfonic acid followed by $NaBH_4$ reduction of the resulting ketone. This procedure is analogous to the one used for the synthesis of 1-(*p*-nitrophenyl)-2-phenylethanol.[15] *1h* had m.p. 76–77 °C, IR (KBr): 3350 (broad), 1525, 1340, 1040, 750, 700, 545 cm^{-1}. NMR ($CDCl_3$): δ 7.2–8.2 (9 H, m, aromatic H), 5.3–5.6 (1 H, X part of ABX pattern, $-CHOH-CH_2-$), 2.5–3.4 (2 H, AB part of ABX pattern, $-CHOH-CH_2$), 2.3 (1 H, s, $-OH$).

The synthesis of 1-(*o*-nitrophenyl)-2-(*p*-nitrophenyl)ethanol (*1h*) and 1-(*p*-nitrophenyl)-2-(*o*-nitrophenyl)ethanol, (*1i*) will be described elsewhere.[16]

General procedure for the preparation of chloro and methoxy substituted 1,2-diarylethanols. All the chloro and methoxy derivatives of 1,2-diphenylethanol were prepared by Grignard reactions. The reaction mixture was poured onto a mixture of ice and acetic acid. The ether layer was separated and washed with 10 % sodium bicarbonate solution and water and dried over potassium carbonate. The solvent was removed under reduced pressure and the product was purified by various methods.

1,2-Di(o-methoxyphenyl)ethanol (1e) was synthesised by Grignard reaction of *o*-methoxybenzyl chloride and *o*-methoxybenzaldehyde. *1e* had m.p. 80–82 °C, IR (KBr): 3400, 1605, 1590, 1500, 1470, 1440, 1250, 1190, 1110, 1055, 1040, 755, 740 cm^{-1}. NMR ($CDCl_3$): δ 6.8–7.5 (8 H, m, aromatic H), 5.23 (1 H, t, J=6Hz, $-CHOH-CH_2-$), 3.84 (3 H, s, $-OCH_3$), 3.80 (3 H, s, $-OCH_3$), 3.14 (2 H, d, J=6Hz, $-CHOH-CH_2-$), 2.9 (1 H, s, $-OH$).

2-(o-Methoxyphenyl)-1-phenylethanol (1c) was made by Grignard reaction from *o*-methoxybenzyl chloride and benzaldehyde and gave colourless prisms, m.p. 66–68 °C, on crystallization from ligroin/diethyl ether. NMR ($CDCl_3$): δ 2.53 (1 H, s, $-OH$, exchanged by D_2O), 2.9–3.15 (2 H, deformed d, $-CHOH-CH_2-$), 3.76 (3 H, s, $-OCH_3$), 4.75–5.1 (1 H, deformed t, $-CHOH-CH_2-$), 6.65–7.45 (9 H, broad m, aromatic H). Mass spectrum *m/e:* 228 (M^+), 122, 102, 91, 79.

1-(p-Methoxyphenyl)-2-(o-methoxyphenyl)-ethanol (1d) was made by Grignard reaction from *o*-methoxybenzyl chloride and *p*-methoxybenzaldehyde. 1-(*p*-Methoxyphenyl)-2-(*o*-methoxyphenyl)ethanol crystallized from ligroin/chloroform as tiny, white needles, m.p. 61–62 °C. NMR ($CDCl_3$): δ 2.45 (1 H, s, $-OH$, exchanged with D_2O), 2.9–3.1 (2 H, deformed d, $-CHOH-CH_2-$), 3.73 (3 H, s, $-OCH_3$, 3.76 (3 H, s, $-OCH_3$), 4.7–5.05 (1 H, deformed t, $-CHOH-CH_2-$), 6.7–7.35 (8 H, broad m, aromatic H).

1-(o-Chlorophenyl)-2-phenylethanol (1l) was prepared by Grignard reaction from benzyl chloride and *o*-chlorobenzaldehyde. Recrystallization from ligroin/chloroform gave 1-(*o*-chlorophenyl)-2-phenylethanol as colourless short prisms, m.p. 70–72 °C. NMR ($CDCl_3$): δ 2.62 (1 H, broad s, $-OH$, exchanged with D_2O), 2.8–3.0 (2 H, deformed d, $-CH(OH)-CH_2-$), 5.05–5.35 (1 H, m, $-CH(OH)-CH_2-$), 6.4–7.35 (9 H, m, aromatic H), IR (KBr): 3150–3500 (broad), 3015, 2950, 1600, 1590, 1500, 1040, 700–780 cm^{-1} (several bands).

2-(o-Chlorophenyl)-1-phenylethanol (1m) was prepared from *o*-chlorobenzyl chloride and benzaldehyde. Recrystallization of the product from ligroin/chloroform yielded 1-phenyl-2-(*o*-chlorophenyl)ethanol, m.p. 68–70 °C. NMR ($CDCl_3$): δ 2.48 (1 H, broad s, $-OH$, exchanged with D_2O), 2.9–3.15 (2 H, deformed d, $-CH(OH)-CH_2-$), 4.7–4.95 (1 H, deformed t, $-CH(OH)-CH_2-$), 6.95–7.35 (9 H, m, aromatic H). IR (KBr): 3200–3500 (broad, $-OH$), 3015, 2945, 1600, 1580, 1480 1030, 680–780 cm^{-1} (several bands).

1,2-Di-(o-chlorophenyl)ethanol (1n) was prepared from *o*-chlorobenzyl chloride and *o*-chlorobenzaldehyde. This yielded a pale yellow crystalline mass, which on recrystallization from ligroin/chloroform gave 1,2-di-(*o*-chlorophenyl)-ethanol as colourless cubes, m.p. 82–84 °C.

NMR ($CDCl_3$): δ 2.22 (1 H, broad s, $-OH$, exchanged with D_2O), 2.8–3.45 (2 H, AB-part of an ABX-system, $-CH(OH)-CH_2-$), 5.25–5.55 (1 H, X-part of an ABX-system, $-CH(OH)-CH_2-$), 7.05–7.6 (8 H, m, aromatic H). IR (KBr): 3500–3100 (broad), 3050, 2940, 1695, 1675, 1480, 1035, 765 cm^{-1}.

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