

EFFECT OF THE π -ELECTRON RING CURRENT ON THE ¹H NMR SPECTRA OF 1,1'-BINAPHTHOL DERIVATIVES

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High resolution ¹H NMR spectra of two 1,1'-binaphthols (*I*, *II*), two 1,1'-binaphthalenediols (*III*, *IV*) and four 1,1'-binaphthalenediol acetates (*IIIa* – *VIa*) were obtained and analyzed. The effect of the ring current was evaluated by comparing the chemical shifts of the compounds, assigned through H–H COSY NMR experiments, to those of the corresponding monomers. All experimental chemical shifts are in close agreement with the theoretical values obtained via the Bovey model for the ring current effect of a benzene moiety.

The ¹H NMR chemical shifts of the hydrogens located in the proximity of a benzene ring are greatly affected by their orientation with respect to the molecular plane of the aromatic moiety. The expected shifts for such hydrogens have been calculated by application of the free electron theory¹ and other models². However no such study has been reported for 1,1'-binaphthalenediol derivatives whose angular geometries have been established both in the solid³ and liquid phases⁴. In all cases of either phase, the naphthalene rings of the most stable conformer are oriented in such an angle that the hydrogens of one ring are affected by the π -electron system of the other ring. Studies using Corey–Pauling–Koltum (CPK) models predict a considerable effect for H-8, assuming a π -electron ring current magnitude similar to that of a benzene ring. Similarly, for the corresponding acetyl derivatives, the hydrogens of the acetyl groups that are located in the neighborhood of the 1,1'-linkage are greatly affected.

In order to study this effect, the high-resolution ¹H NMR spectra of α -binaphthol (*I*), β -binaphthol (*II*), 2,2',3,3'-tetrahydroxy-1,1'-binaphthalene (*III*) and 4,4',6,6'-tetra-

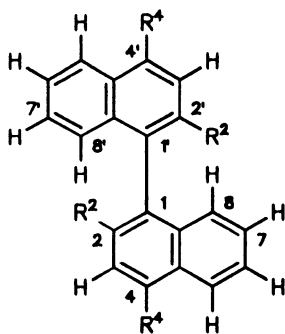
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hydroxy-1,1'-binaphthalene (*IV*) were obtained. To further support the findings, the tetraacetate derivatives of *III* and *IV*, as well as 1,1'-binaphthyl-2,2',6,6'-tetraacetate (*Va*) and 1,1'-binaphthyl-4,4',8,8'-tetraacetate (*VIa*) were also obtained and analyzed. All signals were assigned through COSY NMR experiments and the effect of the ring current was evaluated by comparing the chemical shifts of the hydrogens in these compounds with the analogous chemical shifts of the corresponding monomers.

EXPERIMENTAL

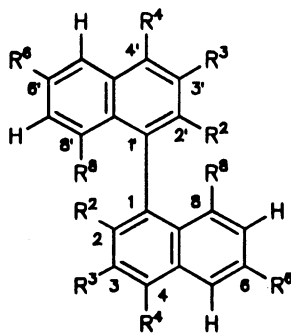
The naphthalenediols (Aldrich) were recrystallized from toluene or ethanol–water mixtures before the spectra were taken. The dimers were prepared by oxidation of the corresponding monomers with one-equivalent quantities of FeCl_3 or $\text{FeNH}_4(\text{SO}_4)_2$ and purified by repetitive water–ethanol recrystallizations⁵. The general acetylation procedure involved refluxing (45 min) of the phenolic compound (2 g) acetic anhydride (15 ml) and anhydrous sodium acetate (1 g). The reaction mixture was poured and stirred 2 h in an ice–water mixture and the isolated crystals were recrystallized from ethanol–water.

All NMR spectra were registered at 22 °C with an AM-300 spectrometer (Bruker), using tetramethylsilane as the internal standard. The spectra of the phenolic and acetyl derivatives were obtained in CD_3SOCD_3 and CDCl_3 , respectively. The hydrogen signals were assigned by 2D COSY experiments using the software provided by Bruker. Molecular dimensions for all compounds were estimated using ChemDraft II software (C-Graph Software, Inc.), using X-ray crystallographic data for 1,1'-binaphthol³.



I, $\text{R}^2 = \text{H}$; $\text{R}^4 = \text{OH}$

II, $\text{R}^2 = \text{OH}$; $\text{R}^4 = \text{H}$



	R^2	R^3	R^4	R^6	R^8
<i>III</i>	OH	OH	H	H	H
<i>IIIa</i>	OAc	OAc	H	H	H
<i>IV</i>	H	H	OH	OH	H
<i>IVa</i>	H	H	OAc	OAc	H
<i>Va</i>	OAc	H	H	OAc	H
<i>VIa</i>	H	H	OAc	H	OAc

RESULTS AND DISCUSSION

All ¹H NMR chemical shifts obtained for the phenolic and acetyl derivatives are listed in Table I and Table II, respectively, together with the deviations of the dimer hydrogens from the corresponding monomeric compounds.

The data of Table I indicate that in all binaphthol derivatives the signals corresponding to H-8 and H-7 are shifted upfield when compared to the corresponding monomeric ones. The deviation is more significant for H-8 (range 0.74 – 0.59 ppm) than for H-7 (range 0.20 – 0.16 ppm). The chemical shifts are practically identical for H-6 while there is an inconsistent variation (upfield or downfield) for H-2, H-3, H-4, and H-5.

The above data suggest that the closer the hydrogen is to the ring current the greater the effect. Thus, H-6 which is located the furthest away, shows no deviation, while H-8 (primarily) and H-7 (to a lesser degree) are practically engulfed in the ring current and, therefore, display a much greater shift. The same effect is observed with the acetyl protons in the acetyl derivatives that are attached to C-2 (range 0.47 – 0.38). On the other hand the acetyl hydrogens located further away from the ring current (acetyl hydrogens at C-3 in *IIIa*, C-6 in *IVa* and C-6 in *Va*) are practically unaffected (shift range 0.01 – 0.00).

To test if the magnitude of the upfield shifts measured for H-8 and H-7 for 1,1'-binaphthol are consistent with the values expected due to the ring current theory, the Bovey model for benzene was applied. The dihedral angle between the two naphthalene

TABLE I

¹H NMR chemical shifts (ppm, δ-scale) for monomers and dimers of naphthols (*I*, *II*) and naphthalene diols (*III*, *IV*) in CD₃SOCD₃; chemical shifts are relative to tetramethylsilane. Δδ = (δ_{dimer}) – (δ_{monomer})

Compound	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8
<i>I</i>	–	7.24	6.99	–	8.24	7.42	7.29	7.16
Monomer	–	7.32	6.90	–	8.16	7.45	7.45	7.81
Δδ	–	–0.08	0.09	–	0.08	–0.03	–0.16	–0.65
<i>II</i>	–	–	7.33	7.66	7.65	7.23	7.17	6.95
Monomer	7.13	–	7.09	7.75	7.76	7.25	7.36	7.64
Δδ	–	–	0.24	–0.09	–0.11	–0.02	–0.19	–0.69
<i>III</i>	–	–	–	7.75	8.17	7.67	7.48	7.33
Monomer	7.62	–	–	7.62	8.07	7.68	7.68	8.07
Δδ	–	–	–	0.13	0.10	–0.01	–0.20	–0.74
<i>IV</i>	–	6.97	6.87	–	7.47	–	6.87	7.06
Monomer	7.20	7.04	6.76	–	7.37	–	7.03	7.65
Δδ	–	–0.07	–0.11	–	0.10	–	–0.16	–0.59

rings of the most stable conformer is found to be close to 90° in the solid phase³ and slightly less in the liquid phase⁴.

As a result H-8 and H-7 are mainly under the influence of the current of only one of the two rings of the neighboring naphthalene unit. Consequently one can adopt the approximation that the naphthalene moiety's ring current effect is virtually equal to that of a benzene ring. Thus, application of the theoretical Bovey model assuming the molecular dimensions reported for 1,1-binaphthol³, the origin in the center of the ring carrying the hydroxy groups and a 90° dihedral angle leads to upfield shifts for H-8 and H-7 of 0.78 ($\rho = 1.34$ radii units, ru , $z = 1.87$ ru) and 0.18 ppm ($\rho = 2.22$ ru , $z = 3.39$ ru), respectively. These values are in close agreement with the actual experimental upfield shifts found for H-8 (range 0.74 – 0.59 ppm) and H-7 (range 0.20 – 0.16 ppm).

The estimation of the upfield shifts for the acetyl hydrogens following the same approach was not attempted, because of the several possible conformations that this moiety can assume which affects many of the coordinates with respect to the origin. In the most extreme case, however, the acetyl group C-8 in *VIa* displays a very significant shift ($\Delta\delta = 1.35$), while a lesser effect is observed in the acetyl group of C-2 in *Va*. The CPK model would support this observation because it demonstrates that most of the possible conformations of the acetoxy group on C-8 of *VIa* reside much closer to the center of the neighboring naphthalene moiety.

TABLE II

¹H NMR chemical shifts (ppm, δ -scale) for the acetyl derivatives of naphthalene diol monomers and dimers (*IIIa* – *VIa*) in CDCl₃; chemical shifts are relative to tetramethylsilane. $\Delta\delta = (\delta_{\text{dimer}}) - (\delta_{\text{monomer}})$

Compound	H-2	H-3	H-4	H-5	H-6	H-7	H-8	Acetyl ^a	
<i>IIIa</i>	–	–	7.80	7.83	7.42	7.23	7.11	1.89(2)	2.28(3)
Monomer	–	–	7.62	7.73	7.42	7.42	7.73	2.27(2)	2.27(3)
$\Delta\delta$	–	–	0.18	0.10	0.00	–0.19	–0.62	–0.38(2)	0.01(3)
<i>IVa</i>	7.44	7.39	–	7.67	–	7.09	7.42	2.34(6)	2.51(4)
Monomer	7.45	7.28	–	7.58	–	7.27	7.88	2.35(6)	2.44(4)
$\Delta\delta$	0.01	0.11	–	0.09	–	–0.18	–0.46	–0.01(6)	0.07(4)
<i>Va</i>	–	7.43	7.94	7.68	–	7.04	7.17	1.88(2)	2.34(6)
Monomer	–	7.25	7.80	7.56	–	7.25	7.80	2.35(2)	2.35(6)
$\Delta\delta$	–	0.18	0.14	0.12	–	–0.21	–0.63	–0.47(2)	–0.01(6)
<i>VIa</i>	7.18	7.26	–	7.88	7.55	7.13	–	2.50(4)	1.05(8)
Monomer	7.40	7.27	–	7.76	7.47	7.27	–	2.40(4)	2.40(8)
$\Delta\delta$	–0.22	–0.01	–	0.12	0.08	–0.14	–	0.10(4)	–1.35(8)

^a Number in parentheses indicates the position of the acetyl group.

According to the Bovey model, changes in the dihedral angle of 1,1'-binaphthols affect only the *z* coordinates of H-8, while ρ remains constant. Therefore, by fitting *z* with the experimental upfield shift observed for H-8, an estimate of the dihedral angle of the most stable conformations of such compounds can be obtained. Such calculations, however, would require further work to validate quantitative measurements.

The observation that the upfield shifts found for the internal acetyl hydrogens differ considerably with the shifts observed in the extreme positions, suggests that the correct assignment of the peaks in the ¹H NMR spectrum would serve as a powerful tool in determining the structure of the oligomeric products formed during the oxidative coupling of naphthalenediols⁵⁻⁸.

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