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Ring Current and Anisotropy Effects on OH Chemical Shifts in Resonance-Assisted Intramolecular H-Bonds.

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A B S T R A C T

Ring current effects on resonance-assisted and intramolecularly bridged hydrogen bond protons for 10-hydroxybenzo[*h*]quinoline **1** and a number of related compounds were calculated and the through-space NMR shieldings (TSNMRS) obtained hereby visualized as iso-chemical-shielding surfaces (ICSS) of various size and direction. These calculations revealed that this through-space effect is comparably large (up to 2 ppm) dependent on the position of the intramolecularely bridged OH proton, and, therefore, contribute considerably to the chemical shift of the latter making it questionable to use δ(OH)/ppm in the estimation of intramolecularly hydrogen bond strength without taking this into account. Furthermore, the *anisotropy effects* of additional groups on the aromatic moiety (*e.g.* the carbonyl group in salicylaldehyde or in *o*-hydroxyacetophenone of *ca.* 0.6 ppm deshielding) should also be considered. These through-space effects need to be taken into account when using OH chemical shifts to estimate hydrogen bond strength.

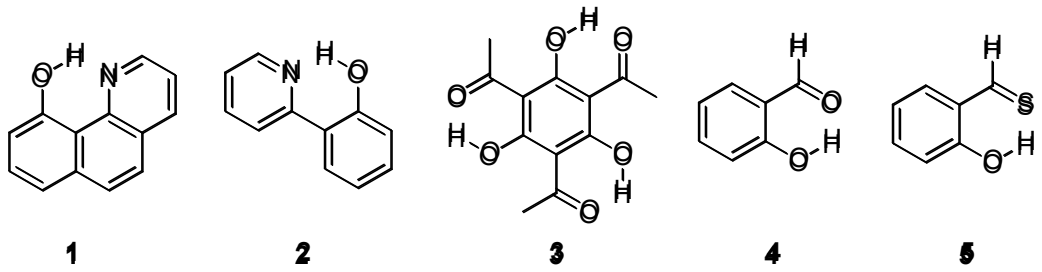
Keywords: RA-intramolecular hydrogen bond; Through-space NMR shieldings (TSNMRS); Iso-chemical-shielding surfaces (ICSS); Ring current effect; Anisotropy effect

1. Introduction

^{1}H NMR chemical shifts have often been used to characterize hydrogen bonds and hydrogen bond strengths since OH bond elongation will lead to low field shifts of δ(OH)/ppm. In the hydrogen bonds, studied in this paper, the OH group is the donor and either C=O, C=S or a heterocyclic nitrogen is the corresponding acceptor group. Taking 10-hydroxybenzo[*h*]quinoline **1** as an example, an OH chemical shift of 14.90 ppm is found; taking this shift at face value could suggest a strong hydrogen bond. However, this strong hydrogen bond, suggested by Martinez and co-workers,[1] was questioned based on studies of isotope effects on ^{13}C chemical shifts.[2] A similar system is that of 2-(2′-pyridyl)phenol **2** with δ(OH) = 12 ppm.

Moreover, for 1,3,5-triacetyl-2,4,6-trihydroxybenzene **3** a very high OH chemical shift of 17.09 ppm was found.[3] The hydrogen bond geometry of the latter system shows a very short O…O distance as proved by both X-ray diffraction[4] and computational studies;[3] the reason for this is that intramolecular hydrogen bonding keeps the acetyl groups in the ring plane resulting in considerable steric strain. Recently, Perrin and co-workers claimed that steric strain does not lead to strong hydrogen bonds.[5] Given this debate, it is therefore of interest to elucidate the various contributions to the chemical shifts in this type of compounds.

In compounds such as *o*-hydroxythioacetophenones the OH chemical shifts are approximately 1 ppm larger than in the corresponding *o*-hydroxyacetophenones.[6] While in structures **1-3** the contribution of the aromatic ring current effect to δ(OH)/ppm is unknown, the corresponding contribution of the anisotropy effects of C=O and C=S functional groups (and the ring current effect of the aromatic moieties) to δ(OH)/ppm in **4** and **5** is also not clear. To clarify this topic, and to quantify and visualize the spatial magnetic effects and their contributions to δ(OH)/ppm in compounds **1-5** is the subject of this paper.



Scheme 1. Examined structures.

Aromaticity[7,8] is a multidimensional phenomenon[9] which is dependent on energetic,[10] geometric[11] and magnetic criteria.[12,13] The diamagnetic ring current can be used as the

magnetic criterion of aromaticity and is an experimentally available quantity which can be measured in the corresponding ^{1}H NMR spectra. The problem is finding relevant reference values to separate ring current effects from other contributions to the proton chemical shift δ(^{1}H)/ppm. However, NICS values[14] of a grid of ghost atoms placed around aryl structures (and functional groups), so called *spatial NICS*,[15] can be computed and visualized as Iso-Chemical-Shielding-Surfaces (*ICSS*). In this work, six ICSS have been employed to visualize and quantify the ring current/anisotropy effects in the ^{1}H NMR spectra of the studied molecules. From the NICS surfaces, the ring current/anisotropy effect becomes obvious. However, in order to obtain precise NICS values at a given position, a ghost atom must be placed there and the NICS value at the corresponding coordinates be computed. For example, this is necessary, when the stereochemical arrangement of a hydrogen atom proximal to the studied structure is to be clarified.[15-18] It was proven that experimentally measurable ring current/anisotropy effects Δδ/ppm in the ^{1}H NMR spectra of the studied molecules are the *molecular response property of spatial NICS*.[19,20]

Therefore we have an approach[15] in hand (for Computational Details, see Supplementary Material - ESI)) which precisely visualizes, qualifies and quantifies the ring current effect of aromatic species (and the anisotropy effect of functional groups).[15-20] As a benchmark, in Figure 1 the spatial NICS of 10-hydroxybenzo[*h*]quinoline **1** are visualized by ICSS of different size and direction (Fig. 1). This procedure has been employed to estimate both ring current effects of aromatic moieties and anisotropy effects of C=X (X = O, S) in compounds **1** − **5** and in a number of related compounds **6** − **12** to separate the latter effects from the experimentally determined δ(OH)/ppm values (Table 1).

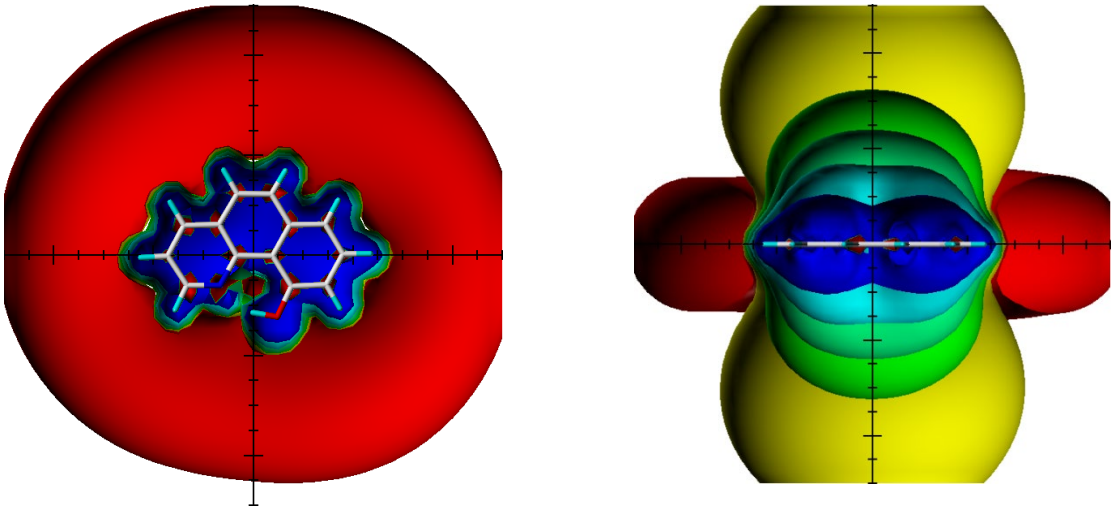


Figure 1. Visualization of the spatial magnetic properties (TSNMRS) of 10-hydroxybenzo[*h*]quinoline **1** as ICSS of different direction and size (blue represents 5 ppm shielding, cyan 2 ppm shielding, green/blue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding and red −0.1 ppm deshielding).

2. Results and Discussion

2.1 ^{1}H Chemical shifts and structure of the studied compounds

The ^{1}H Chemical shifts of readily exchangeable protons at oxygen (also partly at nitrogen; less at sulfur) are not easy to compute. In Table 1, δ(^{1}H)/ppm values of the hydroxyl protons in **1-5** are aligned to the corresponding computed values. The agreement is satisfying, thus, experimental values are adequately reproduced. From this follows that the structures and the spatial magnetic properties (TSNMRS)[15] both computed at the MP2/6-311G(d,p) level of theory are sufficiently correct.

2.2 Ring current effect of aromatic moieties and anisotropy effects - the method

Ring current effects of the aromatic part of the studied compounds was determined using our TSNMRS approach.[15] The calculated spatial NICS values are visualized by various ICSS of different size and direction (*cf.* Fig. 1). 10-Hydroxybenzo[*h*]quinoline **1** is completely planar due to intramolecular H-bonding, and the OH proton is found, as expected, within the deshielding area of the present ring current effect [ICSS (−0.1 ppm deshielding − red].
As the iso chemical shielding surface corresponding to a deshielding of -0.1 ppm [ICSS (−0.1 ppm)] in **1** extends more than 10 Å away from the center of the aromatic ring (ICSS(-0.1)>10A), and the hydroxyl proton being situated much closer, that is at a distance of ca. 2.5 Å from the center of the ring, it will experience a significantly stronger ring current effect corresponding to a TSNMRS value >> than -0.1 ppm. However, the exact value cannot be extracted from the general view in Fig. 1 but would require calculations involving ghost atoms that should also take into account multiple conformational states of *e.g.* hydroxyl protons.

In order to proceed further, the corresponding molecule without the hydroxyl group in the molecule (hydrogen at this position), benzo[*h*]quinoline **1a**, was computed at the identical level of theory (*cf.* Fig. 2). This is necessary because in **1** (*cf.* Fig. 1) with the intramolecular H-bonded hydroxyl group the corresponding spatial magnetic properties at the position of the

OH proton would be distorted by the H proton electrons. In benzo[*h*]quinoline **1a**, however, at the same position (pink dot) the space is free of nuclei and the TSNMRS value at the same position of the hydroxyl proton as in **1** can be determined free of any distortions; the spatial NICS value, obtained at the coordinates of the OH proton in **1**, is −1.91 ppm deshielding, which proves to be the ring current effect of the benzo[*h*]quinoline moiety on the hydroxyl proton in 10-hydroxy-benzo[*h*]quinoline **1**.

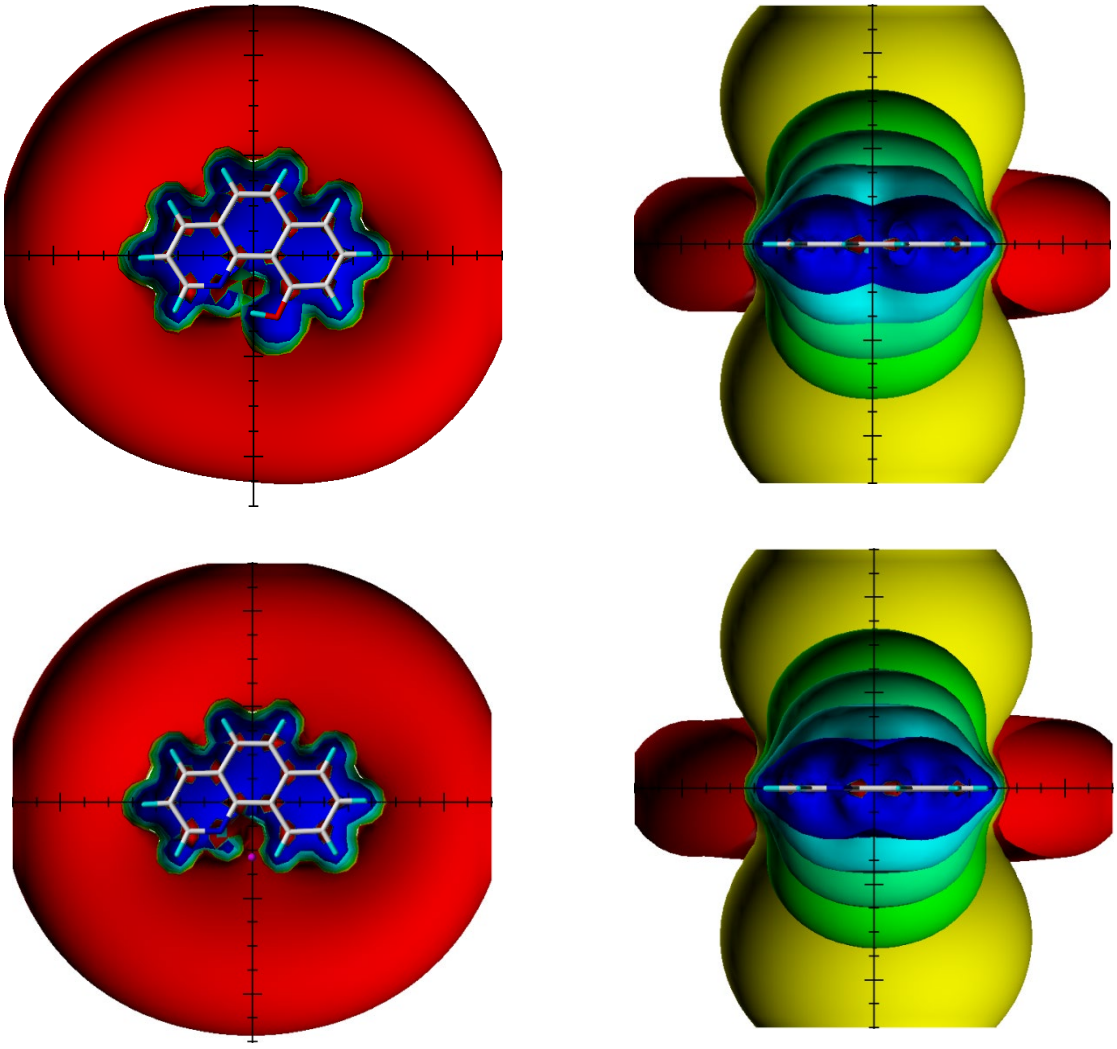
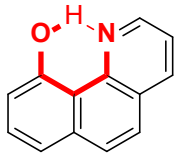


Figure 2. Visualization of the spatial magnetic properties (TSNMRS) of 10-hydroxybenzo[*h*]quinoline **1** (above) and benzo[*h*]quinoline **1a** (below) as ICSS of different direction and size (blue represents 5 ppm shielding, cyan 2 ppm shielding, greenblue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding and red −0.1 ppm deshielding). The pink dot in the top view of benzo[*h*]quinoline **1a** shows the position of the OH atom in 10-hydroxybenzo[*h*]quinoline **1**.

When discussing the TSNMRS values of 10-hydroxybenzo[*h*]quinoline **1** it should be noted that the six-membered ring fragment of resonance-assisted intramolecular hydrogen bonding (RAHB - *cf.* Scheme 2), which contains six delocalized π-electrons and which was assigned to partially adopt the role of a typical aromatic ring[21,22] can be precluded. In the

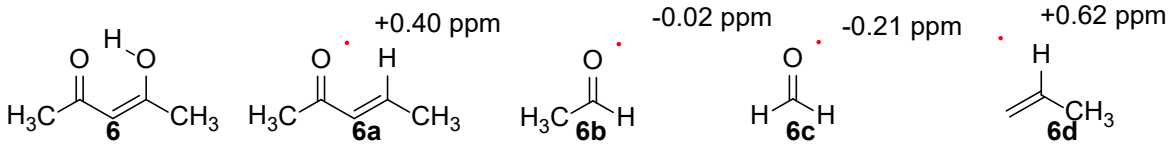
centre of this moiety there is clearly deshielding (red) and not shielding as above/below aromatic ring systems (*cf.* Fig. 1).[23]



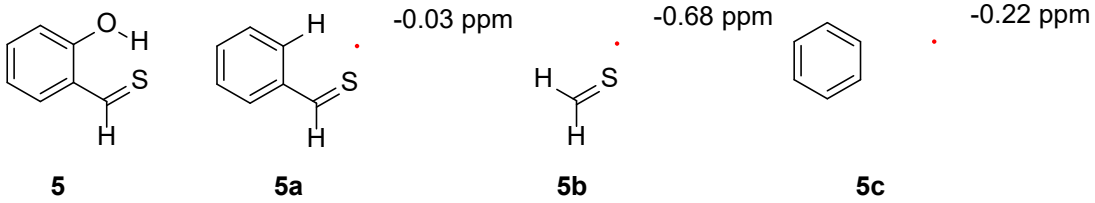
Scheme 2. RAHB fragment in 10-hydroxybenzo[*h*]quinoline **1**.

1

The same procedure for extracting the ring current effect on the hydroxyl proton in 10-hydroxy-benzo[*h*]quinoline **1** was employed to determine the anisotropy effects of the carbonyl and thiocarbonyl moiety, and of the C=C double bond as well. A representative example of the corresponding anisotropy effects of the fragments on the position of the intramolecularely bridged OH proton in the *enol form* of acetylacetone **6** (the dots at the position of the hydroxyl in **6a** to **6d**) and on the OH proton in thiosalicylaldehyde **5** are given in Scheme 3 and 4.



Scheme 3. Calculated anisotropy effect of fragment **6a**, of the acetyl (**6b**), of the carbonyl (**6c**) and of the propenyl group (**6d**) on the OH proton in **6**; the dot in **6a-d** indicates the position of the OH proton in **6**.



Scheme 4. Calculated anisotropy/ring current effects of the fragments **5b-c** on the OH proton in **5**; the dot in **5a-c** indicates the position of the OH proton in **5**.

Ring current effects obtained by this approach for 10-hydroxy-benzo[h]quinoline **1** represented as TSNMRS value at the hydroxyl proton position in **1a** (*cf.* Fig. 2), for *the enol tautomer* of acetylacetone **6** (*cf.* Scheme 2) and for thiosalicylaldehye **5** (*cf.* Scheme 3) are given in Table 1; in addition and using the same procedure the corresponding ring current/anisotropy effects for **2** − **4** and **7** − **12** (*cf.* Table 1) were determined.

When studying 10-hydroxy-benzo[h]quinoline **1**, the ring current effect of the aromatic moiety on the position of the OH proton in compound **1** proved to be −1.91 ppm deshielding. This deshielding effect of nearly 2 ppm must be considered and subtracted from

the experimentally determined δ(OH) value of 14.90 ppm. This proves to be important if δ(OH)/ppm should be a (at least approximate) measure of the H-bond strength.

In 7,9-dinitro-10-hydroxy-benzo[*h*]quinoline **9**, the corresponding ring current effect is only slightly diminished to −1.71 ppm (compared with **1**, *cf.* Table 1), the chemical shift of the hydroxyl proton [δ(OH) = 19.45 ppm],[32] however, proves to be ca. 4.5 ppm lowfield shifted compared with 10-hydroxy-benzo[*h*]quinoline **1** [δ(OH) = 14.90 ppm].[3]

Table 1. TSNMRS values of the position of the hydroxyl proton in **1-12** as an estimate of the contribution of ring current/anisotropy effects on δ(OH/ppm values. In addition, calculated and known experimental δ(OH)/ppm are given.

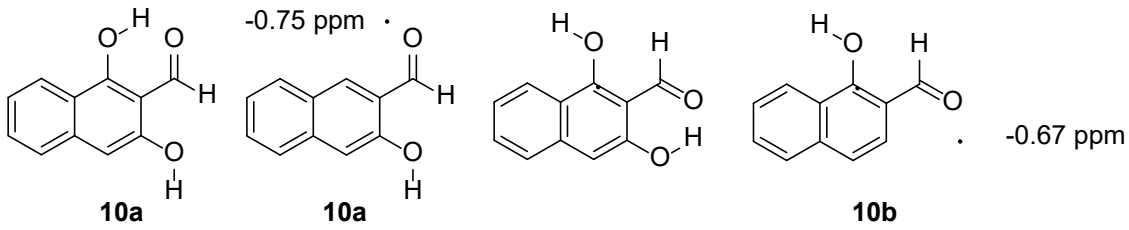
No.	Compound	TSNMRS value δ(OH)/ppm	δ(OH)/ppm calculated[a]	Experimental	Ref.
1	10-Hydroxy-benzo[*h*]quinoline	−1.91	13.64[b]	14.90	2
2	2-(2′)Pyridyl)-phenol	−1.00	13.31	12.00	24
3	1,3,5-Triacetyl-2,4,6-Trihydoxybenzene [c]	0.17	16.52	17.09	3
4	Salicylaldehyde	−0.67	11.80	11.01	25
5	Thiosalicylaldehyde	−0.03	12.42	-	
6	*Enol* form of acetylacetone	0.40	16.82	15.51	26
7	*o*-Hydroxyaceto-phenone	−0.65	12.11	12.26	25
8	*o*-Hydroxythio-actophenone	0.08	13.18	13.35	6, 27
9	7,9-Dinitro-10-hydroxy-benzo[*h*]quinoline	−1.71	15.61[d]	19.45	2
10	1,3-Dihydroxy-naphthyl-2-aldehyde	−0.67[e] and −0.74[f]	13.16[e] 11.35[f]	12.61[g] 10.32[h]	25 27
11	1-Hydroxy-2-acetyl-6-nitro-benzene	−0.46	12.64	12.82	28
12	1-Hydroxy-2-acetyl-4-nitro-benzene	−0.59	12.49	12.87	28

[a] ^{1}H chemical shifts (δ/ppm) with reference to the TMS values computed at the same level of theory.
[b] δ(OH) = 13.71 ppm ($CDCl_3$) and 13.73 ppm (DMF). An open form gave 4.61 ppm (vacuum), 5.77 ppm ($CDCl_3$) and 5.32 ppm (DMF).
[c]. The effect of the aromatic ring alone was calculated to be -0.35 ppm in 1,3-diacetyl-2,4-dihydroxybenzene.
[d] δ(OH) = 15.88 ppm ($CDCl_3$) and 15.92 ppm (DMF).
[e] RAHB to 3-hydroxyl.
[f] RAHB to 1-hydroyl (*cf.* Scheme 5).
[g] Estimated from 1-hydroxy-2-naphthaldehyde.
[h] Estimated from 3-hydroxy-2-naphthaldehyde.

A common feature for the systems discussed and collected in Table 1 is clearly the ring current effect of the aromatic moieties and the anisotropy effects of the C=C, C=O and C=S double bonds. Ring current effects have been discussed in detail and the NICS analysis clearly changed the traditional view[7] and was recently reviewed.[15c] In the past no focus has been given to the ring current effects on the extreme OH chemical shifts, especially in resonance assisted intramolecular hydrogen bonds. As seen above, the ring current effect at the OH chemical shifts of 10-hydroxybenzo[h]quinoline **1** is quite large and if subtracted from the OH chemical shift of 14.9 ppm leads to a chemical shift due to hydrogen bonding of around 12.9 ppm. By the same estimates, both the ring current effect of the benzene moiety and the anisotropy effects in salicylaldehyde and thiosalicylaldehyde caused by the C=O and the C=S double bonds, respectively, are calculated as −0.67 ppm and −0.03 ppm, respectively; the anisotropy effects of C=O (−0.21 ppm) and C=S (−0.68 ppm) are visualized in Figure 3 (see also Scheme 4). The calculations are performed on these simple molecular systems to avoid further anisotropy effects. The green dot indicates the position of the OH proton taken from the corresponding salicylaldehyde and thiosalicylaldehyde, respectively. The total effect (together with benzene moiety ring current effect) at the OH position is −0.67 and −0.03 ppm, respectively. It should be noted that minus refers to deshielding, a low field shift. For *o*-hydroxy-acetophenone the effect of −0.65 is similar to that of salicylaldehyde (−0.67 ppm). For *o*-hydroxythioacetophenone a total ring current/anisotropy effect of 0.08 ppm shielding is calculated, which is very similar to that of thiosalicylaldehyde (−0.03 ppm). The anisotropy effect is therefore not the reason for the higher chemical shift of the OH group in *o*-hydroxythioacetophenones lending support to the finding that hydrogen bonding to C=S is stronger than to C=O.

Figure 3. Visualization of the spatial magnetic properties (TSNMRS) of formaldehyde (left) and thioformaldehyde (right) as ICSS (blue represents 5 ppm shielding, cyan 2 ppm shielding, greenblue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding and red −0.1 ppm deshielding).

Similar effects were computed for the naphthyl analog **10** of salicylaldehyde **4** (*cf.* Table 1 and Scheme 5), and for the *ortho*- and *para*-nitro substituted *o*-hydroxyacetophenone derivatives **11** and **12** (*cf.* Table 1); comparable ring current/anisotropy effects on the proton chemical shift of the hydroxyl protons in **10** (as found in **4**) and in **11** and **12** (as found in **7**) can be concluded.



Scheme 5. Calculated ring current/anisotropy effects.

An interesting case is that of 1,3,5-triacetyl-2,4,6-trihydroxybenzene. Hydrogen bonding keeps the acetyl groups into the ring plane and results in steric strain reducing the O….O distances. Considering the resonance assistance interactions this will lead to a reduction of the π-electron density for the central aromatic ring; quasi- aromaticity has been discussed.[21,22] The present calculations show that the effect of the ring is only very smallt, −0.17 ppm shielding compared to that of salicylaldehyde (−0.67 ppm). The comparison of salicylaldehyde, *o*-hydroxyacetophenone and 1,3,5-triacetyl-2,4,6-trihydroxybenzene clearly shows that it is necessary to correct the OH chemical shift if these are to be used as measures of hydrogen bond strength.

However quasi-aromaticity of the six-membered ring fragments of resonance-assisted intramolecular hydrogen bonding (RAHB) in 1,3,5-triacetyl-2,4,6-trihydroxybenzene **3**,[21,22] could not be confirmed:[23] centres of the three RAHB moieties in **3** are again (*vide supra*) deshielding (red) and not shielding as above/below aromatic ring systems (*cf.* Fig. 3).

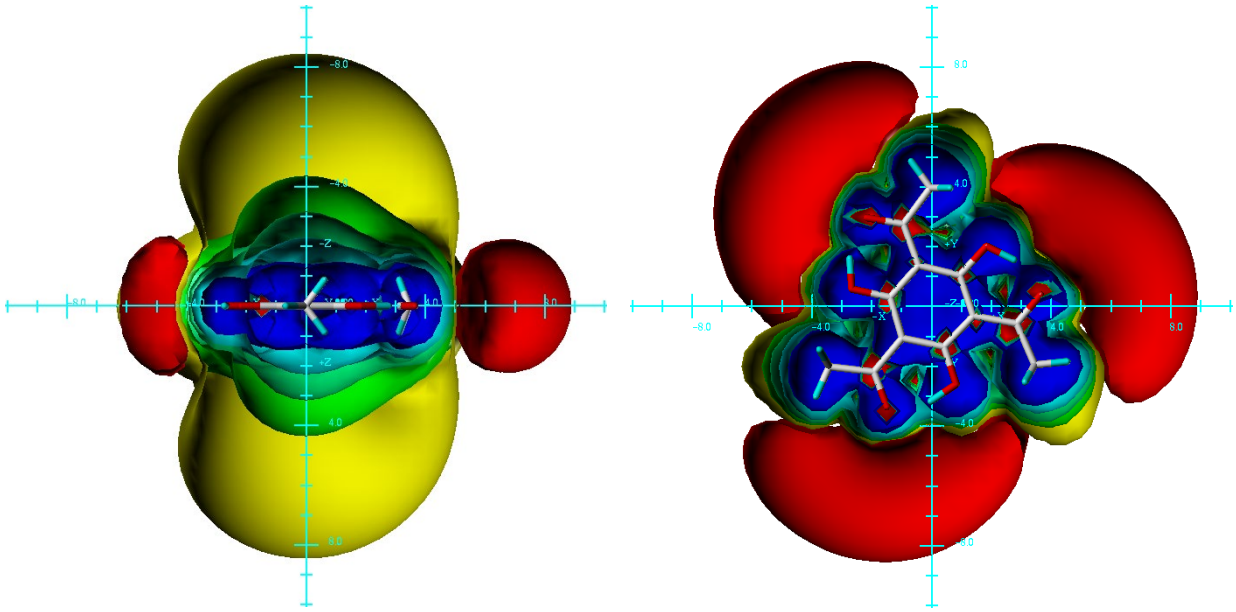


Figure 4. Visualization of the spatial magnetic properties (TSNMRS) of 1,3,5-*tris*-acetyl-2,4,6-*tris*-hydroxybenzene **3** at various ICSS (blue 5 ppm, cyan 2 ppm, greenblue 1 ppm, green 0.5 ppm and yellow 0.1 ppm shielding; red, −0.1 ppm deshielding).[31]

The enol form of acetyl acetone is a classic case of intramolecular hydrogen bonding and tautomerism. The analysis shows that the $CH_3CH{=}O$ fragment gave a shift of −0.02 ppm, the $CH_3CH{=}CH_2$ fragment a shift of +0.62 ppm and the $CH_3C(=O){-}CH{=}CH{-}CH_3$ fragment a shift of +0.40 ppm (*cf.* Scheme 3). These corrections do not change the picture of a relatively strong hydrogen bond, as also confirmed by measurements of deuterium isotope effects on ^{13}C chemical shifts.[29] The OH chemical shift of the corresponding thio-analogue thioacetylacetone, completely in the OH form, was estimated as 15.2 ppm.[30] Judging from the present results this does not need to be corrected to any large extent.

4. Conclusions

The fact that the ring current effects of aromatic ring systems must be taken into account when judging hydrogen bonds based on OH chemical shifts have emerged from the literature.[24] This topic has also been treated in a different manner by Scheiner and co-workers.[31] In simple compounds such as salicylaldehyde the effect is much smaller than −1 ppm deshielding. This is only increased slightly in the naphthalenes, whereas in the polycyclic aromatic systems such as 10-hydroxybenzo[*h*]quinolines **1** and **9** these effects can be large (up to 2 ppm deshielding). Nitro groups in the latter slightly diminish the effect due to their electron withdrawing properties. Ring current effects should therefore be calculated routinely. Anisotropy effects from C=C, C=O and C=C bonds should also be taken into account. With

respect to the ring current/anisotropy effect of C=S in thiosalicylaldehyde (−0.03 ppm) the effect is negligible.

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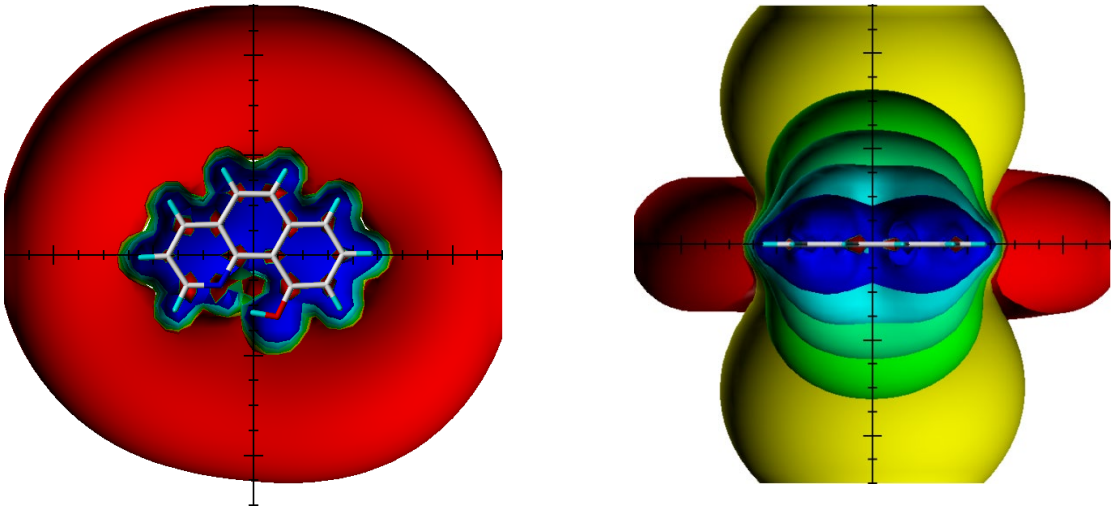
Graphical Abstract:



Ring current effect (***−1.91 ppm deshielding***) on the hydroxyl proton in 10-hydroxy-benzo[*h*]quinoline **1**.

Ring Current and Anisotropy Effects on OH Chemical Shifts in Resonance-Assisted Intramolecular H-Bonds.

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