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Intramolecular OH···π hydrogen bonding in 4-substituted 2-allylphenols

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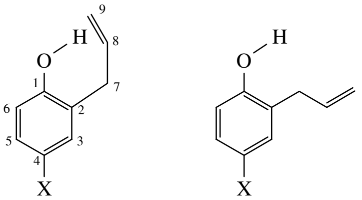
Conformational analysis of 4-substituted 2-allyphenols 1–10 by B3LYP calculations indicates that the energy and the structure of the intramolecular OH···π H-bond show a distinct variation with the substituent.

Hydrogen bonds are the most important intermolecular interactions. In biochemistry, pharmacy, crystallography and supramolecular chemistry, as well as in molecular recognition and self-organisation, this kind of bonding is playing a significant role. Weak H-bonds have recently received considerable interest.[1–3] Electron-rich π systems such as aromatic rings and CC double and triple bonds are the most important non-conventional acceptors in H-bonds. An OH···π H-bond was detected for the first time by IR spectroscopy in 2-phenylphenol in CCl_4 by Wulff *et al.*[4]



1a–10a **1b–10b**

1 X = H
2 X = Me
3 X = NH_2
4 X = OMe
5 X = OEt
6 X = Cl
7 X = Br
8 X = CN
9 X = COMe
10 X = NO_2

Scheme 1 Conformers of 2-allylphenol with (**1a**) and without (**1b**) intramolecular H-bond. Structures of compounds **1–10**.

We have recently investigated intramolecular H-bonds in various alkenols[5] and substituted 2-allylphenols[6] by gas-phase UV photoelectron spectroscopy. In contrast to compounds studied previously,[7,8] 2-allylphenol **1** shows conformational mobility, so that along with the H-bonded closed conformer **1a** an open form **1b** was found (Scheme 1). The properties of **1** can be varied widely by substituents in different positions, and such compounds offer excellent opportunities to study substituent effects on the intramolecular OH···π H-bond in a systematic way by experimental and theoretical methods. We have investigated parent compound **1** and a series of 4-substituted 2-allylphenols (**2–10**, Scheme 1) by means of quantum-chemical calculations.

Conformational analysis of 2-allylphenol **1** has been carried out by spectroscopic and theoretical methods.[9–14] According to these investigations, the most stable conformer has a closed structure **1a** with a significant stabilisation by intramolecular interaction between the double bond of the allyl group and the hydroxy group. We have studied the conformational properties of **1–10** using the density functional theory (DFT) hybrid method B3LYP[15,16] with the basis set 6–31+G**. Conformer **1a** was found to be 3.58 kJ mol^{-1} (including zero-point corrections) more stable than the open form **1b**. The OH···π H-bond in **1a** is characterised by the torsional angles $\varphi \equiv$ C(2)–C(1)–O–H = = 20.6° and η = C(1)–C(2)–C(7)–C(8) = –60.3° and by distances of 231.6 and 249.6 pm between the hydroxy hydrogen atom and C(8) and C(9), respectively, of the allyl group. The corresponding distances between the latter atoms and the oxygen atom are 309.7 and 345.1 pm, respectively. These data compare well with those calculated for the methanol–ethene complex.[17] However, in **1a**, there are some deviations from the 'ideal' geometry of the OH···π H-bond, which can be expressed by the angles γ and θ.[17] The former angle defines the twist of the plane of the ethylene group with respect to the line between the hydroxy proton and the centre of the double bond (γ = 90° refers to an orthogonal orientation), and the latter angle defines the deviation from a straight line (θ = 180°) between the centre of the double bond and the hydroxy group. Angles γ and θ are close to 90 and 180°, respectively, in the methanol–ethene complex. In **1a**, the less favourable values γ = 69.3° and θ = 153.5° are enforced by the molecular skeleton.

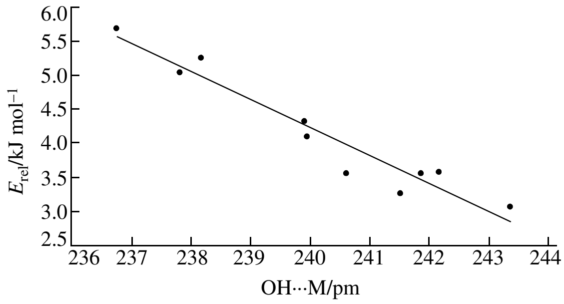


Figure 1 Correlation of E_{rel} and OH···M distances (R^2 = 0.931) for compounds **1–10**. M is the centre of the allylic C=C bond.

For compounds **1–10**, some parameters characterising the intramolecular H-bond are presented in Table 1.[†] As indicated by the data given, substitution in the 4-position of the aromatic ring perturbs the structure parameters of the OH···π H-bond. For all 4-substituted 2-allylphenols the closed conformer **a** is more stable than the open form **b**. The energy difference varies between 3.07 (**3**) and 5.69 kJ mol^{-1} (**10**), indicating a small but significant effect of the substituent on the strength of the H-bond. Donor substituents such as Me and NH_2 weaken and acceptor substituents such as CN, COMe and NO_2 strengthen the OH···π interaction. On the other hand, alkoxy groups (OMe, OEt) leave the H-bond essentially unchanged, and the intramolecular interaction is somewhat strengthened by a halogen atom (Cl, Br). These energy changes are reflected by distances between the hydroxy group and the allylic CC double bond, measured by the interatomic distances OH···C(8)/C(9) and O···C(8)/C(9). These distances are increased by donor and decreased by acceptor groups (including the halogens). The torsional angle φ of the OH group with respect to the phenyl ring probably directly reflects the substituent effects: it varies between 16.7 (**10**) and 27.1° (**3**). As a general trend, it can be stated that acceptor groups enforce a more coplanar orientation of the OH group and the phenyl ring. By this they strengthen the H-bond, while donor substituents have an opposite effect.

The linear relationship between the energy of the H-bond E_{rel}, as expressed by the energy difference between conformers **a** and **b**, and the geometry of the H-bond becomes evident from Figure 1, which shows a plot of E_{rel} *versus* the OH···M distance, where M is the centre of the allylic CC double bond. The correlation coefficient R^2 = 0.931 indicates a quite satisfactory relationship.[18] An even slightly better linear correlation exists between E_{rel} and the O···M distance (R^2 = 0.956). Fair linear correlations are even found for E_{rel} and the angles C(1)–O–H (R^2 = 0.853) and φ (R^2 = 0.761). However, for the latter two

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[†] Density functional theory (DFT) B3LYP[15,16] calculations with the basis set 6-31+G** were performed using the program GAUSSIAN 98.[19]

Table 1 Selected bond lengths (pm) and angles (°) characterising the intramolecular H-bond for the closed conformers **a** of compounds **1–10** (B3LYP/6-31+G** results).

Compound	X	O–H	C(1)–O	OH···C(8)	OH···C(9)	O···C(8)	O···C(9)	C(1)–O–H	φ^a	E^b	E_{rel}^c
1	H	97.0	137.1	231.6	249.6	309.7	345.1	110.3	20.6	–424.048002	3.58
2	Me	97.0	137.3	232.8	250.2	310.6	345.6	110.2	22.0	–463.340789	3.27
3	NH_2	96.9	137.9	235.9	250.8	312.8	345.4	110.0	27.1	–479.571752	3.07
4	OMe	97.0	137.7	234.3	250.0	311.8	344.9	110.0	25.7	–538.542047	3.59
5	OEt	97.0	137.7	234.0	249.7	311.5	344.7	110.0	25.5	–577.836643	3.57
6	Cl	97.0	136.9	231.2	248.7	309.2	344.2	110.4	21.2	–883.651404	4.11
7	Br	97.0	136.9	231.3	248.5	309.3	344.0	110.5	20.8	–2995.184382	4.33
8	CN	97.2	136.2	228.3	247.3	306.7	343.2	110.7	17.8	–516.295976	5.05
9	COMe	97.1	136.3	228.7	247.6	307.2	343.5	110.6	17.5	–576.668878	5.25
10	NO_2	97.2	135.9	227.0	246.5	305.6	342.5	110.8	16.7	–628.557902	5.69

[a] Torsion angle C(2)–C(1)–O–H. [b] Total energy (a.u.) including zero-point corrections. [c] Relative energy (kJ mol^{-1}) with reference to the less stable open conformer **b**.

parameters hardly a better result can be expected, since the directionality of a weak OH···π H-bond is known to be less well established than that of strong H-bonds.[1–3] Further correlations characterising the H-bond have been observed for spectroscopic and physical properties of the compounds.[6]

In conclusion, we can state that the weak intramolecular OH···π H-bond in 4-substituted 2-allylphenols is modified by the substituents. This is apparent in the energy as well as in the stereochemistry: the distance between the OH group and the allylic CC double bond is linearly correlated with the strength of the interaction.

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