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Spectroscopic and theoretical studies on intramolecular OH–π hydrogen bonding in 4-substituted 2-allylphenols†‡

Paul Rademacher,* Levan Khelashvili and Klaus Kowski

Institut für Organische Chemie, Universität Duisburg-Essen, 45117, Essen, Germany. E-mail: paul.rademacher@uni-essen.de; Fax: +49-201-1834252; Tel: +49-201-1832404

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2-Allylphenol (**1**) constitutes a mixture of conformers, in which an OH–π hydrogen bonded closed (**1a**) and open form (**1b**) can be distinguished. 4-Substituted 2-allyphenols (**2–9**) have been synthesised and investigated by theoretical and spectroscopic methods. In **1–9**, the energy and the structure of the hydrogen bonds show distinct variation with substituents. In the PE spectra of most compounds, two ionisations can be distinguished which are related to the allylic π(C=C) orbitals of the two conformers **a** and **b** and differ in energy by ΔIP(C=C). Alternatively, ΔIP(C=C) can be determined indirectly from comparison of the PE spectra of the respective phenols and anisoles with the same substituents. ΔIP(C=C) values between 0.3 and 1.1 eV were found. Frequency shifts Δν(OH) of the O–H vibration in $CHCl_3$ solution were measured by IR spectroscopy. By means of correlation analysis of the relationship between the strength of the intramolecular hydrogen bond, ΔIP(C=C), Δν(OH) values and substituent constants it is established how substituents in 4-position affect the intramolecular OH–π hydrogen bond. The investigations demonstrate that the ΔIP(C=C) data can be used as descriptors for this intramolecular interaction.

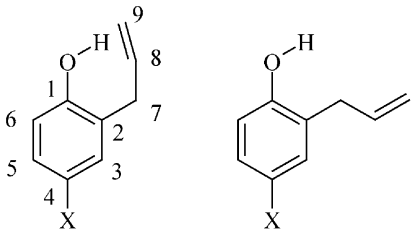
Introduction

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

Photoelectron spectroscopy (PES) has proved to be a valuable aid to the elucidation of the electronic structure of molecules. Brown was the first to prove the existence of intramolecular OH–π hydrogen bonds in *syn*-7-norbornenol[5,6] and similar compounds by PES. In *syn*-7-norbornenol the π(C=C) ionisation shows a value approximately 0.2 eV higher than in the *anti*-isomer. The energy difference is ascribed to the stabilisation of the π(C=C) MO by the hydrogen bond. On the other hand, the hydrogen bond causes a decrease in the n_π(O) ionisation by approx. 0.3 eV.

We have recently investigated intramolecular hydrogen bonds in various alkenols including 2-allylphenol (**1**) by PES.[7] In contrast to the compounds studied by Brown,[5,6] 2-allylphenol shows conformational mobility, so that along with the H-bonded closed conformer **1a** an open form **1b** was found (Scheme 1). A strong ionisation band (10.01 eV) is assigned to the allylic carbon–carbon double bond in the closed conformer, and a weak band (9.72 eV) to that in the open conformer. A ratio of about 2 : 1 has been estimated from the relative intensities of these bands.[7]

The properties of 2-allylphenol (**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 hydrogen bond by experimental and theoretical methods. We have synthesised a series of 4-substituted 2-allylphenols by Claisen rearrangement from the corresponding allylphenylethers[8–10] and investigated these compounds by means of PES and IR spectroscopy as well as by quantum-chemical calculations. As substituents the following groups have been chosen: CH_3, Br, Cl, OCH_3, OC_2H_5, CN, $COCH_3$, and NO_2 (Scheme 1). Along with the phenols (**1–9**), their methyl ethers (anisoles) have been prepared as reference compounds without hydrogen bonds. PE spectra of the latter compounds were measured and their IP(C=C) values relate to the allylic C=C bonds undisturbed by hydrogen bonding.[11]



X	H	CH_3	OCH_3	OC_2H_5	Cl	Br	CN	$COCH_3$	NO_2
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

Scheme 1 Structures of compounds **1–9**, conformers with (**a**) and without (**b**) intramolecular hydrogen bond.

Results and discussion

Molecular structures and energies

Conformational analysis of 2-allylphenol (**1**) has been carried out by means of different spectroscopic and theoretical methods by Baker and Shulgin,[12,13] Oki and Iwamura,[14] Schaefer *et al.*,[15] Kim *et al.*,[16] as well as by Bosch-Montalvá *et al.*[17] According to these investigations, the most stable conformer has a closed structure (**1a**) with a significant stabilisation by intramolecular

† Electronic supplementary information (ESI) available: Spectroscopic and theoretical studies on intramolecular OH–π hydrogen bonding in 4-substituted 2-allylphenols. See http://www.rsc.org/suppdata/ob/b5/b504765j/

‡ Dedicated to Professor Wolfgang Lüttke, Göttingen, on the occasion of his 85th birthday.

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Table 1 Selected bond lengths (in pm) and angles (in °) for three conformers of compound **1** (B3LYP/6-31+G** results)

	1a	1b	1c
O–H	97.0	96.6	96.9
(C-1)–O	137.1	137.6	137.3
(C-2)–(C-7)	152.0	151.8	151.4
(C-7)–(C-8)	151.2	151.1	151.6
(C-8)–(C-9)	133.9	133.6	133.8
OH–(C-8)	231.6	417.2	243.3
OH–(C-9)	249.6	549.5	258.2
O–(C-8)	309.7	327.3	321.4
O–(C-9)	345.1	460.7	331.7
(C-1)–O–H	110.3	109.8	109.9
φ^a	20.6	178.6	25.3
η^b	−60.3	79.1	−66.3
τ^c	126.3	121.5	−9.5
γ^d	69.3		63.2
θ^d	153.5		137.0
E^e	−424.048002	−424.046638	−424.046595
$E_{rel}{}^f$	0.00	3.58	3.69

[a] (C-2)–(C-1)–O–H. [b] (C-1)–(C-2)–(C-7)–(C-8). [c] (C-2)–(C-7)–(C-8)–(C-9). [d] See text [e] Total energy [au] including zero-point corrections [f] Relative energy [kJ mol^{-1}].

interaction between the allylic carbon–carbon double bond and the hydroxy group.

We have investigated the conformational properties of **1** by using the density functional theory (DFT) hybrid method B3LYP[18,19] with the basis set 6-31+G**. Of the many possible conformers the most stable three (**1a–1c**) are depicted in Fig. 1. Some relevant structure and energy parameters of these conformers are summarised in Table 1. Their relative energies, including zero-point corrections, are **1a**: 0.00, **1b**: 3.58, **1c**: 3.69 kJ mol^{-1}. The most significant differences between **1a** and **1b** are the torsions of the hydroxy group and the allyl group relative to the benzene ring. While in **1a** both parameters adopt values for favourable OH–π interaction, in **1b** the opposite is true. This is expressed by the torsional angles φ = (C-2)–(C-1)–O–H and η = (C-1)–(C-2)–(C-7)–(C-8); **1a**: $\varphi = 20.6°$, $\eta = -60.3°$; **1b**: $\varphi = 178.6°$, $\eta = 79.1°$. For **1a** this leads to 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.[20] However, in **1a** there are some deviations from the "ideal" geometry of the OH–π hydrogen bond which can be expressed by the angles γ and θ.[20] 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 ($\gamma = 90°$ refers to an orthogonal orientation), and the latter angle defines the deviation from a straight line ($\theta = 180°$) between the centre of the double bond and the hydroxy group. γ and θ are close to 90 and 180°, respectively, in the methanol–ethene complex. In **1a** less favourable values $\gamma = 69.3°$ and $\theta = 153.5°$ are enforced by the molecular skeleton. X-Ray structure analyses of compounds **5**, **6** and **9** indicate that in the crystalline state the molecules adopt conformations corresponding to **b**, and the molecules are associated mainly by intermolecular O–H ⋯ O hydrogen bonds.[21]

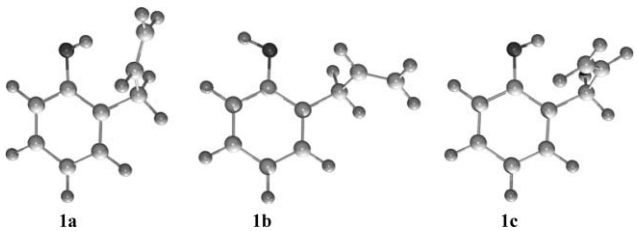

Fig. 1 Conformers **1a–1c** of 2-allylphenol (**1**), B3LYP results.

The third conformer (**1c**) is a second closed form with OH–π interaction. The main difference with respect to **1a** is the torsion around the (C-7)–(C-8) bond in the allyl group. The corresponding dihedral angle τ = (C-2)–(C-7)–(C-8)–(C-9) has the values 126.3° (**1a**) and −9.5° (**1c**), indicating that in **1a** the allyl group adopts the anticlinal (+*ac*) form while in **1c** it is in the energetically less favourable synperiplanar (*sp*) form. The structural data of **1c** characterizing the OH–π hydrogen bond are comparable to those of **1a**, however, a closer inspection indicates that OH–π interaction in **1c** is somewhat less favourable than in **1a**.

Bosch-Montalvá *et al.*[17] have estimated the strength of the hydrogen bond OH–π in 2-allylphenol (**1a**) and related compounds by calculating the energy of the closed forms and comparing it with the result of a single point calculation for a structure with the O–H bond in opposite orientation to the OH–π interaction. On the HF/6-31G** level of theory they obtained a value of 16.38 kJ mol^{-1}. This value is essentially confirmed by the B3LYP method which in the same way gave 18.75 kJ mol^{-1} for **1a** and 15.25 kJ mol^{-1} for **1c**. Recently, Korth *et al.*[22] have criticised this approach. Their results demonstrate that the genuine strength of the intramolecular hydrogen bond of a phenolic compound cannot be unequivocally derived by simple rotation of the OH group into the "away" orientation, because additional steric and/or electronic 1,2 interactions may take place which are difficult or even impossible to separate from the sole H-donor/acceptor interaction.

Since for the investigated compounds **1–9** only minor structural differences are to be expected, in the present investigation we have used the energy difference of the closed conformer **a** and the open conformer **b** as an energetic measure of hydrogen bonding. We have only included these two most important conformers (analogous to **1a** and **1b**). The third (**1c**) can be considered as rather similar to **1a** in its electronic properties, and accordingly it would be very difficult if not impossible to determine individual spectroscopic properties of this conformer that might be present in small amounts besides the other two.

For compounds **1a–9a**, it has been found that substitution in 4-position of the aromatic ring only slightly perturbs the structure parameters of the OH–π hydrogen bond.[23] For all compounds the closed conformers **a** are more stable than the open forms **b**. The energy differences are summarised in Table 2. They vary between 3.27 kJ mol^{-1} (**2**) and 5.69 kJ mol^{-1} (**9**), indicating a small but significant influence of the substituent on the strength of the hydrogen bond. Donor substituents weaken and acceptor substituents strengthen the OH–π interaction. This is indicated also by the distances between the hydroxy group and the allylic carbon–carbon double bond [OH–(C-8)/C(−9) and O–(C-8)/(C-9)] which is increased by the former and decreased by the latter type of substituents.[23] 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° (**9a**) and 25.7° (**3a**). As a general trend it can be stated that the acceptor groups enforce a more coplanar orientation of OH group and phenyl ring and as such strengthen the hydrogen bond, while donor substituents have the opposite effect.

Table 2 Total energy, E, including zero-point corrections of the closed conformer **a** of compounds **2–9** and relative energy, E_{rel}, with reference to the less stable, open conformer **b** (B3LYP/6-31+G** results)

	E/au	E_{rel}/kJ mol^{-1}
1a	−424.0480	3.58
2a	−463.3408	3.27
3a	−538.5420	3.59
4a	−577.8366	3.57
5a	−883.6514	4.11
6a	−2995.1844	4.33
7a	−516.2960	5.05
8a	−576.6689	5.25
9a	−628.5579	5.69

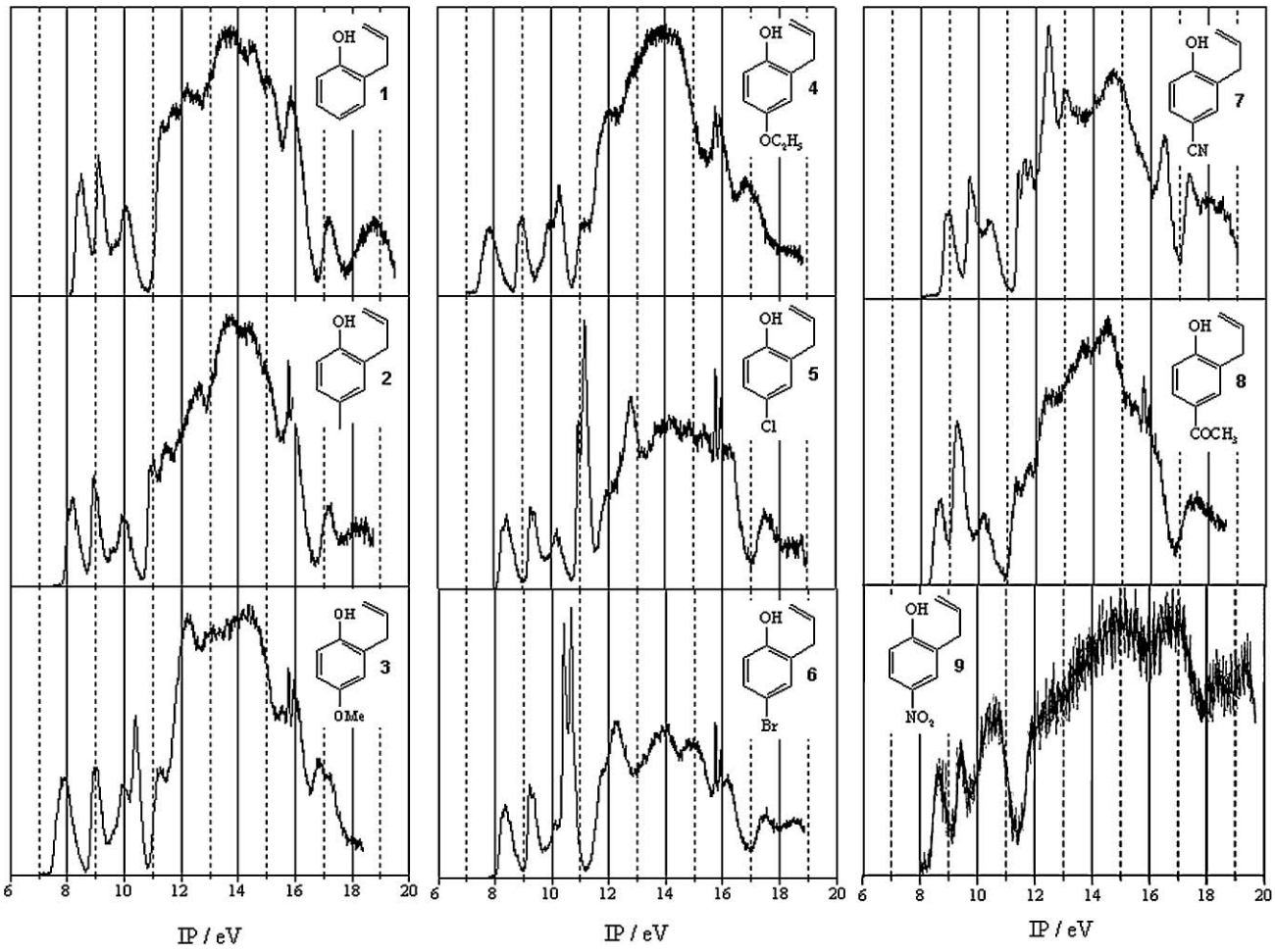

Fig. 2 PE spectra of 4-substituted 2-allylphenols **1–9**.

PE spectra

The measured PE spectra are depicted in Fig. 2. The observed ionisation potentials of the investigated compounds are summarised in Table 3. The assignments of the IPs are based on B3LYP calculations, which were performed for conformers **a** and **b**; the relevant results (orbital energies, calculated IPs, total energies of molecules and radical cations) are summarised in Tables 4 and 5. Assignments of the IPs can be achieved by using Koopmans' theorem,[24] $IP_i = -\varepsilon_i$, by which vertical ionisation energies and SCF MO energies are related. Although Kohn–Sham orbitals obtained by DFT methods[25] are not SCF MOs and their physical meaning is still debated, it has been shown that they can be used with high confidence for the interpretation of PE spectra (see, *e.g.*[26,27]).

Much better agreement between experimental and theoretical values can be expected for the first vertical IP (IP_{1V}) when the energies of the molecule M and the radical cation $M^{\bullet+}$ are calculated. Since a vertical IP corresponds to the transition with the highest Franck–Condon factor without any structural change, a single point calculation is performed for $M^{\bullet+}$ using the molecule's geometry in order to obtain IP_{1V}. The corresponding energy values, which do not include any zero-point corrections, are given in Table 5. We can now correct the other ε^{B3LYP} values by the difference between $-\varepsilon$(HOMO) and the calculated IP_{1V} in order to obtain higher IP_V values.[27] Whereas for the compounds studied here energy differences between IP_i and $-\varepsilon_l^{B3LYP}$ values are 2.0 to 2.5 eV, experimental and calculated IP_i values differ only by 0.0 to 0.7 eV (average 0.3 eV). Furthermore, both $-\varepsilon_l^{B3LYP}$ and calculated IP_i(calcd.) values are linearly correlated with the experimental IP_i(exp.) values with correlation coefficients (R^2 = 0.990 and 0.987) close to 1.000.

The IP values given in Table 3 have been assigned to ionisations of electrons from the MOs π_3 and π_2 of the aromatic ring,

Table 3 Experimental vertical ionisation potentials IP of 4-substituted 2-allylphenols (**1–9**)

	X	$IP_{(\pi_3)}$/eV	$IP_{(\pi_2)}$/eV	$IP_{(C=C)}$/eV	ΔIP(C=C)/eV	$IP_{(OH)}$/eV	$IP_{(X)}$eV
1	H	8.49	9.10	9.72, 10.01	0.29	11.37	—
2	CH_3	8.21	8.91	9.60, 9.99	0.39	11.04	—
3	OCH_3	7.90	9.06	9.61, 10.00	0.39	11.30	10.39
4	OC_2H_5	7.86	9.01	9.58, 10.00	0.42	11.20	10.28
5	Cl	8.42	9.27	9.74, 10.18	0.44	12.00	10.94, 11.18
6	Br	8.39	9.24	9.72, 10.13	0.41	11.80	10.43, 10.69
7	CN	8.92	9.66	10.40	0.78[a]	11.34	11.54, 12.45
8	$COCH_3$	8.67	9.40	10.21	1.05[a]	11.30	9.27
9	NO_2	(9.1)	(9.7)	(10.75)	1.10[a]		

[a] Determined relative to the analogous anisole[11] (see text).

Table 4 Orbital energies ε and total energy E_0 of 4-substituted 2-allylphenols (**1–9**, B3LYP/6-31 + G^{**} results)

	ε conformer **a**/eV						ε conformer **b**/eV					
	π_3	π_2	π(C=C)	n_π(O)	X	E_0	π_3	π_2	π(C=C)	n_π(O)	X	E_0/au
1	6.19	6.89	7.73	9.08	—	−424.214044	6.27	6.88	7.09	9.20	—	−424.212320
2	5.96	6.81	7.68	8.79	—	−463.534037	6.04	6.79	7.05	8.90	—	−463.532462
3	5.63	6.89	7.67	9.47	8.15, 9.00	−538.740432	5.67	6. 87	7.11	9.50	8.21, 9.04	−538.738589
4	5.59	6.86	7.65	9.35	8.09, 8.94	−578.063198	5.64	6.85	7.09	9.44	8.15, 8.97	−578.061385
5	6.26	7.26	7.92	9.71	8.57, 8.59	−883.807940	6.33	7.13	7.35	9.68	8.60, 8.66	−883.805923
6	6.23	7.27	7.90	9.66	7.95, 8.17	−2995.341037	6.30	7.14	7.35	9.63	7.96, 8.23	−2995.338997
7	6.76	7.62	8.15	9.07	9.13, 9.89, 10.08	−516.460772	6.85	7.69	7.36	9.14	9.17, 9.87, 9.96	−516.458422
8	6.55	7.24	7.92	9.20	6.92	−576.872254	6.62	7.40	7.22	9.25	6.94	−576.869881
9	7.08	7.72	8.22	9.95	8.10, 8.61, 8.63	−628.726624	7.14	7.79	7.44	9.82	8.14, 8.65, 8.67	−628.724072

Table 5 Calculated ionisation potentials IP_c and total energy E_0 [au] of 4-substituted 2-allylphenols (**1–9**, B3LYP/6-31+G** results)

	IP_c conformer **a**/eV						IP_c conformer **b**/eV					
	π_3	π_2	π(C=C)	n_π(O)	X	$E_0{}^a$/au	π_3	π_2	π(C=C)	n_π(O)	X	$E_0{}^a$/au
1	8.16	8.86	9.70	11.05	—	−423.914230	8.18	8.79	8.91	11.11	—	−423.912081
2	7.85	8.70	9.57	10.68	—	−463.245307	7.90	8.65	8.91	10.76	—	−463.241979
3	7.49	8.75	9.53	11.33	10.01, 10.86	−538.465071	7.59	8. 74	9.03	11.42	10.14, 10.96	−538.460813
4	7.42	8.69	9.48	11.18	9.92, 10.77	−577.790248	7.38	8.59	8.83	11.18	9.89, 10.71	−577.786021
5	8.13	9.13	9.79	11.58	10.44, 10.46	−883.509053	8.14	8.94	9.35	11.49	10.41, 10.47	−883.505656
6	8.06	9.10	9.73	11.49	9.78, 10.00	−2995.341030	8.09	8.93	9.11	11.42	9.75, 10.02	−2995.041294
7	8.59	9.45	9.98	10.90	10.96, 11.72, 11.91	−516.140741	8.66	9.50	9.17	10.95	10.98, 11.68. 11.77	−516.139641
8	8.37	9.06	9.74	11.02	8.74	−576.564813	8.37	9.15	8.97	11.00	8.69	−576.562307
9	9.02	9.66	10.16	11.89	10.04, 10.55, 10.57	−628.398672	8.90	9.55	9.20	11.58	9.90, 10.41, 10.43	−628.398883

[a] Radical cation with the molecule's geometry.

to ionisations from the π(C=C) orbital of the allyl group and from an n orbital of the hydroxy group and finally to ionisations from orbitals mainly localised on the substituent X. Such a classification is only approximate, since most orbitals are delocalised over the entire molecule. For compounds **1–6**, individual IPs related to the allylic π(C=C) orbital could be identified in the spectra for conformers **a** (higher value) and **b**. The two IPs differ by about 0.3–0.4 eV. This energy difference is explained by the intramolecular OH–π hydrogen bond. For the remaining phenols **7–9**, because of band overlap the second (weak) IP could not be determined. Since the difference ΔIP(C=C) of the IP(C=C) values of the two conformers of compounds **1–9** is of essential importance for the present investigation (see below), we have estimated these values from the corresponding IP(C=C) of the respective anisoles[11] when direct measurement is not possible or inaccurate. For compounds **1–6**, the exact position of the weak peak related to the "free" allylic carbon–carbon double bond (conformer **b**) was determined in several independent measurements, in some cases even at different temperatures, so that the accuracy of ΔIP(C=C) is about ±0.05 eV. Some of these spectra are supplied as electronic supplementary information (ESI)†. In correlation analysis (see below) similar results are obtained, when ΔIP(C=C) is also determined for **1–6** with the aid of the corresponding anisoles.

IR spectra

From the band shape and frequency of the O–H stretching vibration measured by IR spectroscopy inter- and intramolecular hydrogen bonds can be distinguished by using a dilution series in non-polar solvents.[2,28,29] Hydrogen bonds are characterised by a frequency shift $\Delta\nu_{OH}$ between the free and the associated hydroxy group. Baker and Shulgin[12] have measured $\Delta\nu_{OH}$ values for several 2-alkenylphenols including the parent compound **1** in CCl_4 solution. The $\Delta\nu_{OH}$ shifts were shown to depend on the basicity of the π bond and on the geometrical configuration around the bonding groups. For 2-allylphenol (**1**), a gas phase IR spectrum displays two bands in the OH stretching region.[17] The free ν_{OH} appears at 3650 cm^{-1}, while the intramolecularly associated ν_{OH} gives rise to a band at 3590 cm^{-1}. These two values indicate a frequency shift characterizing the hydrogen bond of $\Delta\nu_{OH} = 60$ cm^{-1}.

Our measurements on compounds **1–9** were carried out in $CDCl_3$ solution with concentrations of 0.7, 0.07 and 0.007 mol. The observed frequencies ν_{OH} and frequency shifts $\Delta\nu_{OH}$ are summarised in Table 6 together with the corresponding calculated data. As expected,[25] the calculated values are larger than the experimental. Comparison of the data leads to a scale factor of about 0.94 for the calculated values. The experimental and calculated frequencies of the associated hydroxy groups are linearly correlated ($R^2 = 0.931$), and the same holds for the $\Delta\nu_{OH}$ values ($R^2 = 0.967$).

Correlation analysis

In order to evaluate whether the ΔIP(C=C) values determined by PE spectroscopy (Table 3) can be used as an indicator of the strength of the hydrogen bond in a similar way as $\Delta\nu_{OH}$ values, we have performed various linear correlation analyses. It has been found that indeed there is a fair linear correlation ($R^2 = 0.867$) between ΔIP(C=C) and the energy of the hydrogen bond as expressed by the E_{rel} values (Table 2). In Fig. 3 the data points are depicted together with the correlation line and error limits (±0.05 eV). For comparison, it is mentioned that between E_{rel} and $\Delta\nu_{OH}$(exp.) as well as $\Delta\nu_{OH}$(calcd.) (Table 6) there is a satisfactory linear correlation ($R^2 = 0.975$ for both). Furthermore, fair linear correlations[30] are observed between ΔIP(C=C) and the pK_a values[31] of phenols **1–9** ($R^2 = 0.836$) and with the Hammett substituent constants σ_p[32] of the substituents in 4-position ($R^2 = 0.803$). Again, these correlation coefficients are somewhat worse than for the $\Delta\nu_{OH}$ values. $\Delta\nu_{OH}$(exp.) and ΔIP(C=C) are also linearly correlated ($R^2 = 0.860$). Thus, both can be used as a measure for the strength of the OH–π hydrogen bond in phenols. That ΔIP(C=C) performs somewhat worse than $\Delta\nu_{OH}$, is probably caused by the rather small values and little variation of the former parameter.

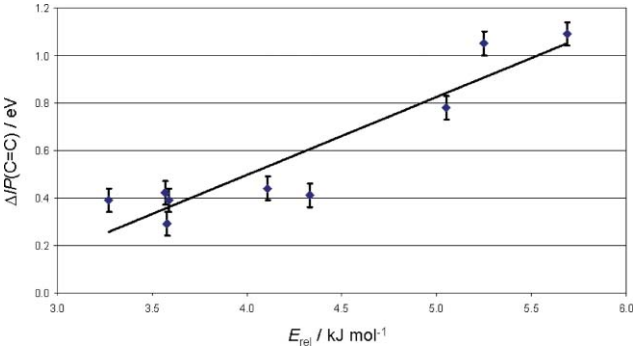

Fig. 3 Correlation of relative energy E_{rel} and ΔIP(C=C) of 4-substituted 2-allylphenols **1–9**.

Further correlations characterizing the hydrogen bond, in particular those between its energy and stereochemistry, have been published.[23]

Conclusion

The weak intramolecular OH–π hydrogen bond in 4-substituted 2-allylphenols is modified by the substituents in 4-position. Acceptor groups clearly strengthen this interaction whereas donor substituents weaken it slightly. The strength of the hydrogen bond increases in the following order of substituents: $CH_3 < OC_2H_5 \approx H \approx OCH_3 < Cl < Br < CN < COCH_3 < NO_2$. In a similar way as IR frequency shifts $\Delta\nu_{OH}$, ΔIP(C=C) values that are determined by PE spectroscopy from the ionisation potentials of the allylic carbon–carbon double bond in the free and in the associated conformer, can be used as indicators for the strength of the hydrogen bond.

Table 6 Experimental and calculated ν_{OH} absorptions of 4-substituted 2-allylphenols **1–9** for free and intramolecularly associated hydroxy groups

R		$\nu_{OH_{free},exp}$/cm^{-1}	$\nu_{OH_{free},calcd}$/cm^{-1}	$\nu_{OH_{ass},exp}$/cm^{-1}	$\nu_{OH_{ass},calcd}$/cm^{-1}	$\Delta\nu_{OH,exp}$/cm^{-1}	$\Delta\nu_{OH,calcd}$/cm^{-1}
H	**1**	3598	3832.04	3529	3738.14	69	93.9
CH_3	**2**	3597	3833.31	3527	3743.03	70	90.2
OCH_3	**3**	3600	3838.33	3528	3743.93	72	94.4
OC_2H_5	**4**	3599	3838.52	3528	3744.83	71	93.6
Cl	**5**	3597	3832.72	3523	3731.54	74	101.1
Br	**6**	3595	3832.08	3521	3729.79	74	102.2
CN	**7**	3585	3826.06	3505	3712.18	80	111.3
$COCH_3$	**8**	3584	3825.77	3505	3714.72	79	111.0
NO_2	**9**	3580	3823.98	3498	3701.02	82	122.9

Experimental

Photoelectron (PE) spectra were recorded on a UPG200 spectrometer of Leybold-Heraeus equipped with a He(I) radiation source (21.21 eV). Samples were evaporated directly into the target chamber. In order to obtain sufficient vapour pressure temperatures between 25 and 150 °C were used. The energy scale was calibrated with the lines of xenon at 12.130 and 13.436 and of argon at 15.759 and 15.937 eV. The accuracy of the measurements was approximately ±0.03 eV for ionisation energies, for broad and overlapping signals it was only ±0.1 eV.

Infrared (IR) spectra were recorded at ambient temperature on a BIORAD FTIR spectrometer FTS135. The samples were dissolved in $CDCl_3$ in cells with a length of 0.1, 1.0, and 10 mm with concentrations of 0.7, 0.07 and 0.007 mol, respectively. The accuracy of the measurements is about ±1 cm^{-1}.

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer. The following frequencies were used: 500.13 MHZ (^1H), 125.76 MHz (^{13}C). The spectra were measured as solution in a 5 mm tube at 25 °C in the solvent $CDCl_3$.

Becke3LYP (B3LYP)[18,19] calculations were performed with the program GAUSSIAN 98.[33] The basis set 6-31+G** was used, if not stated otherwise. Prior to quantum chemical calculations, molecular geometries were pre-optimised by molecular mechanics calculations using the MMX[34] force field with the program PCMODEL.[35]

pK_a values of phenols **1–9** have been retrieved from Chemical Abstracts using SciFinder Scholar. The data have been calculated using ACD software.[31]

Materials

2-Allylphenol (**1**) and 4-acetyl-2-allylphenol (**8**) were purchased from Lancaster Synthesis GmbH, Mühlheim am Main, Germany. 4-Substituted 2-allylphenols have been prepared from the corresponding allyl-phenylethers by Claisen rearrangement.[8,9] Syntheses of compounds **2**,[9,36] **3**,[37] **5**,[36] **6**,[38] **7**,[39] and their spectroscopic characterisation have been described in the literature.

2-Allyl-4-ethoxyphenol (4). Bp 114 °C 2mbar^{-1} (lit.[40] 184–185 °C 67mbar^{-1}); ^1H-NMR (500 MHz, $CDCl_3$): δ 1.36 (t, J = 7.0 Hz, 3H, $ArOCH_2C\mathbf{H}_3$), 3.35 (dt, J = 6.4 Hz, 1.5 Hz, 2H; $ArC\mathbf{H}_2CH{=}CH_2$), 3.95 (q, J = 7.0 Hz, 2H; $ArOC\mathbf{H}_2CH_3$), 4.61 (s, 1H; Ar**OH**), 5.11–5.16 (m, 2H; $ArCH_2CH{=}C\mathbf{H}_2$), 5.98 (m, 1H, $ArCH_2C\mathbf{H}{=}CH_2$), 6.64 (d, J = 8.2 Hz, 1H, Ar**H**), 6.66 (s, 1H, Ar**H**), 6.71 (d, J = 8.2 Hz, 1H, Ar**H**); ^{13}C–NMR (126 MHz, $CDCl_3$): δ 14.93 (CH_3), 35.29 (–CH_2–), 63.97 (O–CH_2) 113.34 (C-5), 116.44 (C-3), 116.51 (C-6), 116.72 (=CH_2), 126.40 (C-2), 136.18 (allyl-CH), 147.88 (C-1), 153.10 (C-4); IR ($CDCl_3$): ν_{max}/cm^{-1} 3535 (OH_{ass}), 2982 (C–H), 1653 (C=C^{al}), 1505 (C=C^{ar}), 1203 (C–O).

2-Allyl-4-nitrophenol (9). Mp 77 °C (lit.[9] 79 °C); ^1H-NMR (500 MHz, $CDCl_3$): δ 3.45 (d, J = 6.4 Hz, 2H; $ArC\mathbf{H}_2CH{=}CH_2$), 5.18–5.25 (m, 2H; $ArCH_2CH{=}C\mathbf{H}_2$), 5.74 (s, 1H; Ar**OH**), 5.99 (ddt, J = 16.9 Hz, 10.4 Hz, 3.9 Hz, 1H, $ArCH_2C\mathbf{H}{=}CH_2$), 6.86 (d, J = 7.2 Hz, 1H, Ar**H**), 7.24 (s, 1H, Ar**H**), 8.05 (d, J = 7.2 Hz, 1H, Ar**H**); ^{13}C-NMR (126 MHz, $CDCl_3$): δ 34.71 (–CH_2–), 115.86 (=CH_2), 118.08 (C-6), 124.03.(C-3), 124.87 (C-5), 126.39 (C-2), 134.57 (allyl–CH), 141.72 (C-4), 159.65 (C-1); IR ($CDCl_3$): ν_{max}/cm^{-1} 3433 (OH_{ass}), 1609 (C=C), 1522 (NO_2), 1342 (NO_2), 1165 (C–O).

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