Solvent and H/D Isotope Effects on the Proton Transfer Pathways in Heteroconjugated Hydrogen-Bonded Phenol-Carboxylic Acid Anions Observed by Combined UV-Vis and NMR Spectroscopy

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Supporting Information

Syntheses

4-coumaric acid methylthioester A1H. The thioester was obtained from 4-coumaric acid (4-hydroxycinnamic acid) through activation with carbonyldiimidazole and subsequent reaction with sodium thiomethoxide.[1]

1-^{13}C-4-nitrophenol A2H and 1-^{13}C-2-chloro-4-nitrophenol A3H. 1-^{13}C-4-nitrophenol was obtained by cyclization[2] of ^{13}C2-acetone with sodium nitromalonaldehyde.[3] The former was then converted into 1-^{13}C-2-chloro-4-nitrophenol.[4,5]

CDF_3/CDF_2Cl. A liquefied mixture of both gases was obtained by fluorination of $CDCl_3$.[6]

2,5-dichloro-4-nitrophenol, 3,5-dichloro-4-nitrophenol. These nitrophenols were obtained from the corresponding chlorophenols by nitration.[7] Isomeric products were separated by steam distillation. Pure products were obtained by recrystallization from mixture of chloroform and hexane. ^{1}H NMR 2,5-dichloro-4-nitrophenol (500 MHz, acetone-d6): 10.70 (s, 1H, OH), 8.19 (s, 1H, H-3), 7.26 (s, 1H, H-6).

Spectroscopic experiments

UVNMR measurements. The experimental setup for combined UV-vis and NMR experiments has been described previously.[4,8] Generally, 5 mm NMR quartz tubes equipped with a flat bottom and a Teflon needle valve for vacuum operations were employed. ^{1}H NMR spectra were referenced to $CHDCl_2$ (5.32 ppm) or CHF_2Cl (7.18 ppm), depending on the solvent employed. In all figures UV-vis spectra were normalized to equal maxima in absorbance.

^{13}C NMR measurements. For ^{13}C NMR measurements a standard (not inversed) ^{1}H/^{13}C NMR probe was used. Inverse gated ^{1}H broad band decoupling was employed; relaxation delay was between 1 and 2 s. Spectra were calibrated to $^{13}CD_2Cl_2$ (53.5 ppm) or $^{13}CDF_2Cl$ (117.37 ppm), respectively.

UV-vis spectra deconvolution. UV-vis spectra were analyzed by least-squares fitting using log-normal band shapes in the wavenumber dimension as described previously.[4] Following the nomenclature of Siano *et al.*[9] the fitting function I can be written as

$$I\left(\tilde{\nu}, A, \tilde{\nu}_0, H, \rho\right) = \frac{Ab}{\tilde{\nu} - a} \exp\left(-c^2\right) \exp\left(-\frac{1}{2c^2} \left\{ \ln\left(\frac{\tilde{\nu} - a}{b} \right) \right\}^2 \right) \qquad \textbf{(1)}$$

for $\tilde{\nu} > a$, otherwise $I\left(\tilde{\nu}, A, \tilde{\nu}_0, H, \rho\right) = 0$,

where $a = \tilde{\nu}_0 - H\left\{\rho / \left(\rho^2 - 1\right)\right\}$, $b = H\left\{\rho / \left(\rho^2 - 1\right)\right\} \exp\left(c^2\right)$ and $c = (\ln \rho) / \sqrt{2 \ln 2}$. The meaning of the four fitting parameters is as follows: A is the amplitude factor, $\tilde{\nu}_0$ is the wavenumber at band's maximum, H is full width at half-height and ρ is the skewness.

General techniques for the preparation of samples for spectroscopic experiments

To facilitate the sample preparation certain preliminary and general actions were taken, which are described below. The specific details for each of the samples are given in the following subsection.

Stock solutions. 5-100 mM stock solutions (0.5 ml) of the different acids and phenols in dry CD_2Cl_2, CH_2Cl_2, or methanol were prepared. For that purpose, substances were weighed and dissolved in 2 ml glass vials with PTFE lined screw caps (Wheaton). Solvents and solutions were handled with microliter pipettes (Eppendorf). Mixing of the components for the sample preparation was based on these stock solutions.

Preparation of tetraethylammonium salts TEA^+X^- of proton donors HX. A certain amount (in the order of 1-20 µmol) of HX (as stock solution) was mixed in a 10 ml flask with 0.7-1.0 equivalents of tetraethylammonium hydroxide in methanol solution. The solvents were removed

on a rotary evaporator (40 °C water bath, < 10 mbar). After pressure equilibration with inert gas, approximately 1 ml of CH_2Cl_2 (dried over molecular sieve 4 Å) was added and evaporated in vacuum to remove residual methanol and water. The latter procedure was repeated twice leaving the dry salt.

Deuteration of NMR samples in mobile proton sites. Whenever the deuteration of the sample was needed, the NMR tube equipped with a J. Young valve and containing the already prepared sample (see below) was attached to a high vacuum line and the solvent was evaporated. About 0.2 ml of methanol-OD (99.5%) was added to the sample and subsequently evaporated. In samples with volatile components a trade-off between the desirable complete evaporation of methanol and the danger of too high losses of sample substance needs to be considered. Finally, the aprotic solvent was reintroduced.

Specific techniques for the preparation of samples for spectroscopic experiments

In this work, several types of experiments have been performed which may be grouped as follows. Combined low-temperature UV-vis and ^{1}H NMR spectra were obtained at concentrations of the chromophore moiety A^- of approx. 1 mM. Corresponding samples were prepared in NMR/UV-vis cuvettes (see ref. 4 and below) in cases the solvent was CD_2Cl_2 (99.9% or 99.7%, Eurisotope, dried over molecular sieve 4 Å) and medium wall sized NMR tubes (5 mm outer diameter, 0.8 mm walls, 3.4 mm inner diameter) equipped with J. Young valves (Wilmad, Buena) in cases of CDF_3/CDF_2Cl as solvent. The latter type of sample container was also used when only NMR experiments were performed. CDF_3/CDF_2Cl samples were usually derived from samples in CD_2Cl_2 solution by evaporation of the latter solvent in vacuum followed by addition of CDF_3/CDF_2Cl by vacuum transfer. Procedural details will follow immediately.

Samples of chromophores in neutral forms A1H, A2H, and A3H. In cases of A2H and A3H 1 mM and 3 mM solutions in CD_2Cl_2 were used for combined UV-vis and ^{1}H NMR, and ^{13}C NMR spectra, respectively. In the latter case, 1-^{13}C enriched compounds were used. In case of A1H a saturated solution (< 1mM) was used to obtain optical spectra. Corresponding samples in CDF_3/CDF_2Cl were obtained by solvent exchange.

Samples of chromophore anions A1, A2, and A3. Samples combined UV-vis and ^{1}H NMR: 20 µmol of TEA pivalate (prepared from the acid as described above) acting as proton scavenger were dissolved in 300 µl of CD_2Cl_2 and transferred to a NMR/UV-vis cuvette. 0.3 µmol of the chromophore as 10 mM solution were subsequently added, except for A1H of which, for reasons of low solubility, an approximate amount of solid substance was added. Samples for ^{13}C NMR (A2 and A3 only): 1 µmol of TEA salts were prepared from 1-^{13}C enriched phenols and TEA

hydroxide as described in the previous subsection, dissolved in 350 µl of CD_2Cl_2 and transferred to a sample tube. CDF_3/CDF_2Cl samples were derived from these samples by solvent exchange.

Samples for A1HX, A2HX, A3HX. The appropriate tetraethylammonium (TEA) salt TEAX (freshly prepared as described above) was dissolved in 350 µl of dry CD_2Cl_2 and transferred to a sample tube. To this were added in the order of 0.4 µmol of AH for samples for combined ^{1}H NMR and optical spectroscopy and in the order of 1.2 µmol of 1-^{13}C-HA for ^{13}C NMR samples. In cases of A2H and A3H these additions were made as CD_2Cl_2 solutions; A1H was added as the solid. Then a solution of the acid HA was added stepwise under ^{1}H NMR monitoring in order to shift equilibria in the direction of the desired hetero-conjugated complexes AHX. In samples for optical spectroscopy, the composition was carefully adjusted such that AHX became in good approximation the exclusive species containing the chromophore moiety at measurement conditions. This procedure is described in detail in Ref. 8. Samples for ^{13}C NMR were deuterated in the mobile proton sites, as described above, as soon as a satisfactory fraction of AHX was found; thus, in these samples the AHX complexes not necessarily were the exclusive form of the chromophore moiety. To ensure the consistency of the NMR results obtained from these samples with those obtained from the corresponding samples, matching ^{1}H NMR chemical shifts of the studied complexes were confirmed. CDF_3/CDF_2Cl samples were principally derived from CD_2Cl_2 samples by solvent exchange. However, as described in the Results and Discussion section, relative proton donating abilities of phenols and carboxylic acids vary with solvent properties and these variations also affect complex equilibria. Thus, for optical spectra in CDF_3/CDF_2Cl a solvent specific adjustment of sample composition was necessary to ensure AHX as the exclusive form of the chromophore moiety present.

Samples for A2HX5, A2HX6. These samples were prepared in analogy to those for the ^{13}C NMR spectra of A1HX, however, only ^{1}H NMR spectra were recorded and substances were neither ^{13}C enriched nor deuterated in mobile proton sites.

Samples for A3HX10, and X8HX10. 10 µmol of the commercially available salt TEACl was dried by repeated addition and evaporation of dry CH_2Cl_2 in a rotary evaporator, taken up in 350 µl of dry CD_2Cl_2 and transferred to a sample tube. To this were added in the order of 1.2 µmol of the proton donor, A3H or X8H, respectively, readily yielding the desired complexes at low temperatures.

Acquisition and processing of combined ^{1}H, ^{13}C NMR and UV-vis spectra.

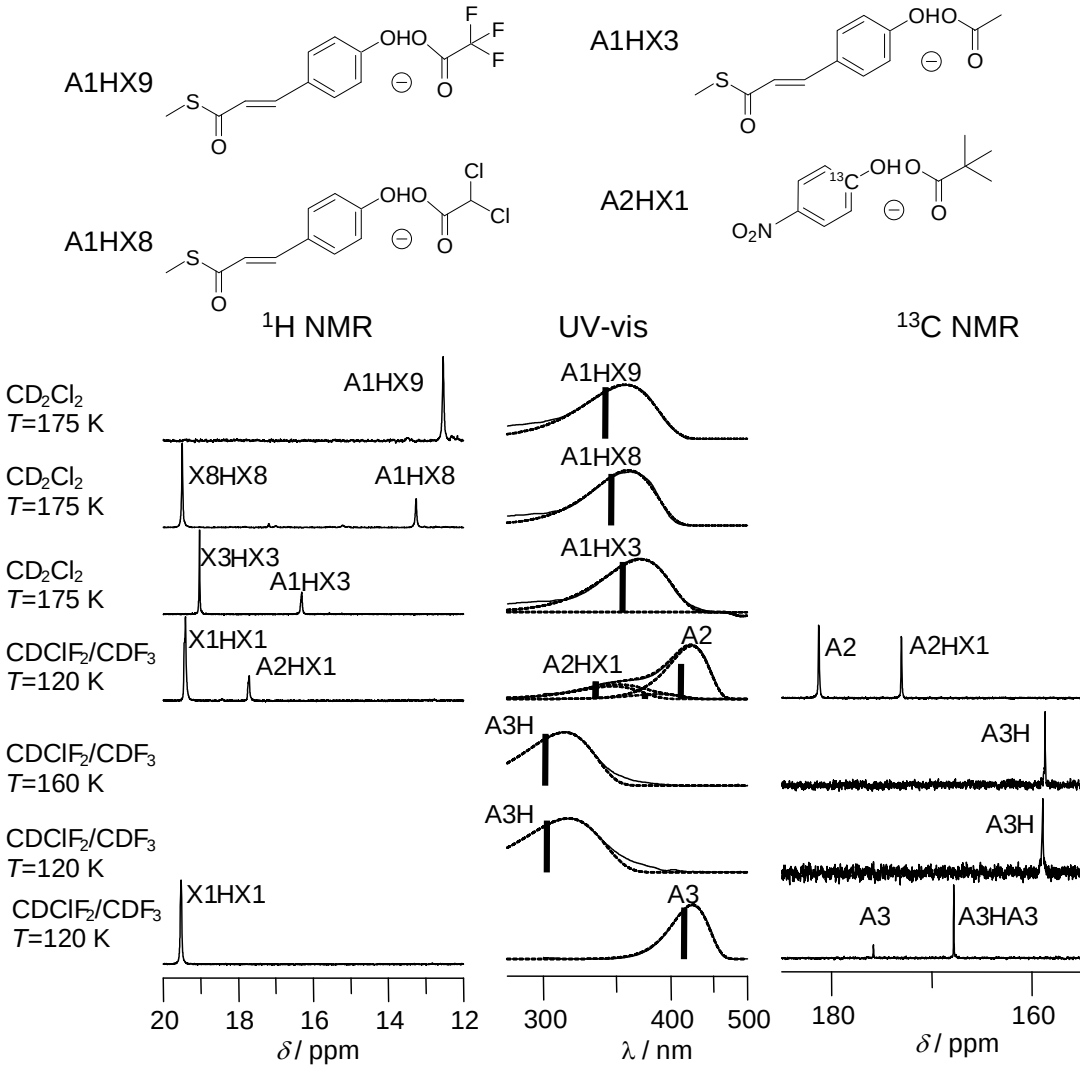
Combined UV-vis and ^{1}H NMR measurements. The experimental setup was the same as those described in Refs. 4 and 8 (experiments with NMR/UV-vis cuvettes and standard NMR tubes,

respectively). ^{1}H NMR spectra were calibrated to $CHDCl_2$ (5.32 ppm) or $CHClF_2$ (7.18 ppm), depending on the solvent employed. In all figures UV-vis spectra were normalized to equal maxima in absorbance.

^{13}C NMR measurements. For ^{13}C NMR measurements a standard (not inversed) ^{1}H/^{13}C NMR probe was used. Inverse gated ^{1}H broad band decoupling was employed; relaxation delay was between 1 and 2 s. Spectra were calibrated to $^{13}CD_2Cl_2$ (53.5 ppm) or $^{13}CDF_2Cl$ (117.37 ppm), respectively.

Additional Data of Heteroconjugated Phenol-Carboxylic Acid Complexes A2HX^- in Polar Solvents

Figure 1. Additional ^{1}H, ^{13}C NMR, and normalized UV-vis absorption spectra of heteroconjugated anions of phenols with carboxylic acids.



^{1}H NMR and optical spectra have been recorded of the same samples; ^{13}C NMR may have been recorded separately. Vertical bars in optical spectra indicate centers of gravity of log-normal fit functions (dashed lines). ^{13}C NMR signals are referenced to TMS *via* calibration to solvent signals.

Table S1. ^{1}H NMR and UV-vis data of hydrogen-bonded PYP model anions AHX^{-} in polar solvents.

species	solvent	T/K	δ(A<u>H</u>X)	λ_{max}	$\tilde{\nu}_{COG}$	$\Delta\tilde{\nu}$	$\tilde{\nu}_{blue}$	$\Delta\tilde{\nu}_{bue}$	$\tilde{\nu}_{red}$	$\Delta\tilde{\nu}_{red}$	ρ	q_1	q_2	x_{blue}
A1H	CD_2Cl_2	175		317	33000	7400					1.5			1
$A1HX1^{-}$	CD_2Cl_2	175	16.57	372	27900	4700					1.5	-0.21	2.50	1
$A1HX1^{-}$	Freon	120	15.99	359	29000	5100					1.5	-0.23	2.52	1
$A1HX3^{-}$	CD_2Cl_2	175	16.31	371	28100	5200					1.5	-0.22	2.51	1
$A1HX4^{-}$	CD_2Cl_2	175	15.62	368	28300	5100					1.5	-0.24	2.53	1
$A1HX4^{-}$	Freon	120	15.26	355	29400	5400					1.5	-0.25	2.54	1
$A1HX8^{-}$	CD_2Cl_2	175	13.27	360	28900	5000					1.5	-0.30	2.60	1
$A1HX9^{-}$	CD_2Cl_2	175	12.57	357	29300	5600					1.5	-0.33	2.64	1
$A1^{-}$	CD_2Cl_2	175		463	22400	2400					1.8			0
A2H	CD_2Cl_2	175		314	33150	6190					1.5			1
$A2HX1^{-}$	CD_2Cl_2	175	18.13	362	30000	5000	29600	4900	26200	3700	1.5	-0.18 0.12	2.48 2.44	0.60
$A2HX1^{-}$	Freon	120	17.66	350	29700	5000	30000	5100	26700	3900	1.5	-0.21 0.07	2.50 2.42	0.77
$A2HX2^{-}$	CD_2Cl_2	175	18.02	357	30100	5600	29800	5000	26500	3900	1.5	-0.19 0.09	2.49 2.43	0.68
$A2HX2^{-}$	freon	120	17.32	347	29600	4900	30100	5600	26800	4000	1.5	-0.23 0.06	2.52 2.42	0.88

A2HX5$^-$	CD_2Cl_2	175	16.46											1
A2HX5$^-$	freon	120	15.83											1
A2HX6$^-$	CD_2Cl_2	175	16.00											1
A2HX6$^-$	freon	120	15.94											1
A2HX7$^-$	CD_2Cl_2	175	15.45											1
A2HX7$^-$	freon	140	15.02											1
A2$^-$	CD_2Cl_2	175		431	23800	2800					1.5			0
A2$^-$	freon	120		425	24400	3200					1.5			0
A3H	CD_2Cl_2	175	6.70*	310	33220	6000					1.5			1
A3H	freon	160		314	33200	5500					1.5			1
A3H	freon	120		316	33100	6200					1.5			1
A3HX2$^-$	CD_2Cl_2	175	17.98	402	25900	4100	28700	4700	25400	3500	1.5	-0.11 0.22	2.44 2.51	0.16
A3HX2$^-$	freon	120	18.81	391	26900	5800	29100	5000	25800	4000	1.5	-0.14 0.17	2.45 2.47	0.28
A3HX4$^-$	CD_2Cl_2	175	18.69	391	26900	5800	29000	4800	25700	3600	1.5	-0.13 0.18	2.45 2.48	0.38
A3HX4$^-$	freon	120	18.91	353	28700	6700	29900	5100	26200	3900	1.5	-0.21 0.12	2.50 2.44	0.67
A3HX10$^-$	CD_2Cl_2	200	12.39											1
A3HX10$^-$	CD_2Cl_2	185	12.35											1

$A3^-$	CD_2Cl_2	175		432	23500	2700					1.5			0
$A3^-$	freon	120		423	24100	2900					1.5			0
$X8HX10^-$	CD_2Cl_2	175	14.22											
$X8HX10^-$	freon	150	14.04											
$X8HX10^-$	freon	120	13.95											

Freon: CDF_3/CDF_2Cl. Chemical shifts δ in ppm. Wavelengths λ_{max} in nanometers, wavenumbers $\tilde{\nu}$ in cm^{-1}, geometric parameter q_1 in Å, temperature T in K. $\tilde{\nu}_{COG}$: Center of gravity of single or dual bands. $\tilde{\nu}_{blue}$, $\tilde{\nu}_{red}$: Centers of gravity of components of the dual bands; $\Delta\tilde{\nu}$ experimental band widths; $\Delta\tilde{\nu}_{bue}$, $\Delta\tilde{\nu}_{red}$: Corresponding band widths of the log normal fit functions of eq 1 with skewness parameter ρ. q_1 = ½(r_{AH}-r_{HX}) and q_2 = r_{AH}+r_{HX} estimated according to eq 6 in cases of species $A2HX^-$and $A3HX^-$. In cases of species A1HX values have been estimated from □(A<u>H</u>X) using eq 5. x_{blue}: mole fraction of the "blue" tautomer estimated from the integral band intensities assuming equal extinction coefficients of the blue and the red bands.

Table S2. ^{13}C NMR chemical shifts of phenolic 1-^{13}C of hydrogen-bonded PYP model anions AHX^- in polar solvents

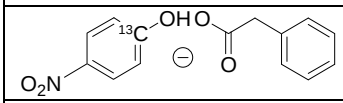
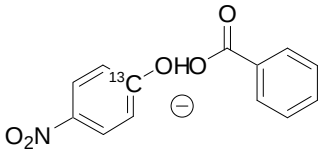
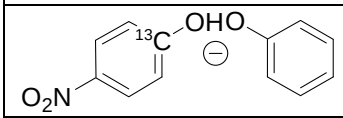
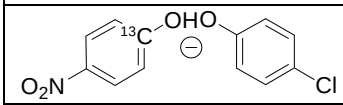
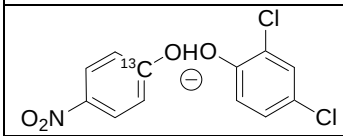
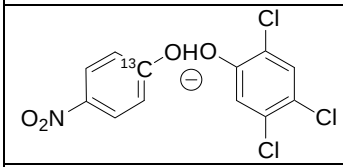
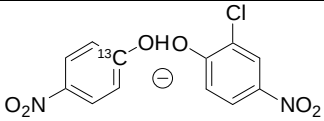
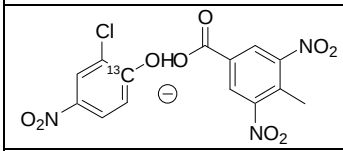
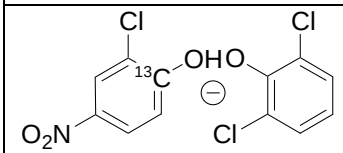
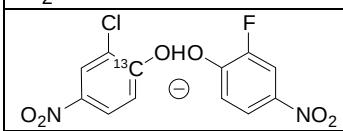
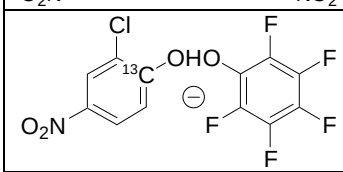
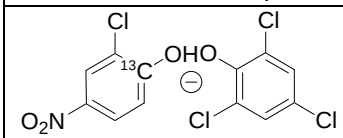
species	solvent	T/K	δ(AHX) ppm	δ^*(AHX) ppm	Δ(ADX) ppm
A2H	CD_2Cl_2	175	160.52*	-10.38*	
A2H	freon	175	163.13*	-9.91*	
A2H	freon	140	163.98*	-9.06*	
$A2HA2^-$	CD_2Cl_2	175	170.90	0	-0.08
$A2HA2^-$	freon	120	173.04	0	-0.04
$A2HX1^-$	CD_2Cl_2	175	169.57	-1.31	-1.01
$A2HX1^-$	freon	120	169.52	-3.49	-1.27
$A2HX2^-$	CD_2Cl_2	175	168.70	-2.21	-1.16
$A2HX2^-$	freon	125	169.00	-4.04	-1.08
$A2HX5^-$	CD_2Cl_2	170	166.25		-
$A2HX5^-$	freon	140	167.78		-0.55
$A2HX6^-$	CD_2Cl_2	175	165.95		
$A2HX6^-$	freon	140	167.86		-0.59
$A2HX7^-$	CD_2Cl_2	170	165.58		
$A2HX7^-$	freon	140	167.25		-0.48
$A2^-$	CD_2Cl_2	175	179.85*	8.95*	
$A2^-$	freon	130	181.30*	8.25*	
A3H	CD_2Cl_2	175	155.90*	-9.58*	
A3H	freon	140	158.70*	-9.13*	
$A3HA3^-$	CD_2Cl_2	175	165.50	0	-0.10
$A3HA3^-$	freon	120	167.83	0	
$A3HX2^-$	CD_2Cl_2	175	168.43	2.94	0.99
$A3HX2^-$	freon	130	169.95	2.16	1.09
$A3HX4^-$	CD_2Cl_2	175	166.68	1.18	0.52
$A3HX4^-$	freon	120	166.68	-1.01	-0.90
$A3^-$	CD_2Cl_2	175	172.86*	7.38*	
$A3^-$	freon	140	175.84*	8.01*	

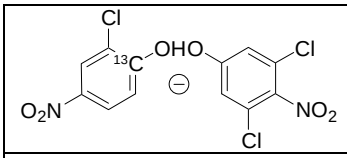
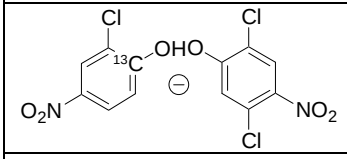
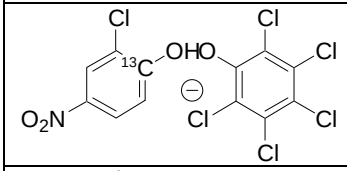
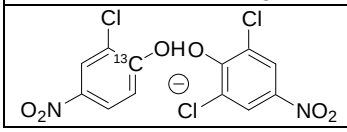
δ^*(AHX)=δ(AHX)−δ(AHA), Δ(ADX)=δ(ADX)−δ(AHX). *Chemical shift of selfassociates of AH of unkown composition. *The chemical shift refers to a self-associate of AH of unkown size or to a solvated anion.

Table S3. Parameters of eq 5 of the main text for hydrogen-bonded PYP model anions AHX^- in polar solvents.

$\tilde{\nu}_{AH}$ /cm^{-1}	$\tilde{\nu}_{A}$ /cm^{-1}	a/Å	b/Å	systems	reference
33300	22400	0.20	0.26	$A1HX^-$ in CD_2Cl_2	this work
34000	23500	0.11	0.22	$A3HX^-$ in CD_2Cl_2	4
34000	23500	0.11	0.22	$A2HX^-$ and $A3HX^-$ in CD_2Cl_2 or Freons	this work

Table S4. ^{1}H Chemical shifts δ(A<u>H</u>X) and ^{13}C chemical shifts of the phenolic 1-^{13}C-position δ^*(<u>A</u>HX) and δ^*(<u>A</u>DX) of various homo- and heteroconjugated anions of phenols with acids

structure	conditions	δ(A<u>H</u>X) /ppm	δ(<u>A</u>HX) /ppm	δ^*(<u>A</u>HX) /ppm	δ^*(<u>A</u>DX) /ppm
	CD_2Cl_2 175 K	17.17	166.93	-3.97	-1.05
	Freon 120 K	16.24	167.99	-5.06	-0.71
	CD_2Cl_2, 175 K	17.18	166.98	-3.93	
	CD_2Cl_2 175 K	14.35	176.83	5.93	
	CD_2Cl_2 175 K	14.96	176.45	5.54	0.42
	CD_2Cl_2 175 K	17.27	174.44	3.54	1.04
	CD_2Cl_2 175 K	18.28	171.67	0.76	
	CD_2Cl_2 175 K	16.49	166.04	-4.86	-0.97
	CD_2Cl_2 175 K	17.40	161.85	-3.63	-0.82
	CD_2Cl_2 175 K	16.91	167.17	1.69	0.72
	CD_2Cl_2 175 K	18.41	165.96	0.48	0.17
	CD_2Cl_2, 175 K	18.13	164.55	-0.93	-0.88
	CD_2Cl_2 175 K	17.39	164.66	-0.83	-0.71

	CD_2Cl_2 175 K	17.31	168.40	2.92	0.92
	CD_2Cl_2 175 K	14.78	160.45	-5.03	-0.40
	CD_2Cl_2 175 K	16.12	161.21	-4.28	-0.76
	CD_2Cl_2 175 K	14.78	160.45	-5.03	-0.40

$\delta^*(\mathbf{\underline{A}HX}) = \delta(\mathbf{\underline{A}HX}) - \delta(\mathbf{\underline{A}HA})$

$\delta^*(\mathbf{\underline{A}DX}) = \delta(\mathbf{\underline{A}DX}) - \delta(\mathbf{\underline{A}DA})$

Table S5. pK_a values of the proton donors used in this study

Name	pK_a	reference
4-methylphenol	10.19	10
phenol	9.92	11
4-chlorophenol	9.38	10
2,4-dichlorophenol	7.80	12
4-nitrophenol	7.14	10
2,4,5-trichlorophenol	7.00	12
2,6-dichlorophenol	6.79	11
3,5-dibromo-2,4-dichlorophenol	6.13	13
2-fluoro-4-nitrophenol	5.95	13
pentafluorophenol	5.53	11
2,4,6-trichlorophenol	5.50	14
3,5-dichloro-4-nitrophenol	5.50	13
2-chloro-4-nitrophenol	5.45	15
pivalic acid	5.01	16
2,5-dichloro-4-nitrophenol	4.81	13
4-phenylbutyric acid	4.76	10
acetic acid	4.76	16
3-phenylpropionic acid	4.66	10
pentachlorophenol	4.50	11

4-tert-butylbenzoic acid	4.40	10
phenylacetic acid	4.31	16
benzoic acid	4.20	10
4-chlorophenylacetic acid	4.18	11
4-chlorobenzoic acid	3.99	10
formic acid	3.77	16
2,6-dichloro-4-nitrophenol	3.55	13
3,5-dichlorobenzoic acid	3.54	11
3,5-dinitro-4-toluic acid	2.86	13
chloroacetic acid	2.86	16
2,3,5-trichlorobenzoic acid	2.18	13
dichloroacetic acid	1.29	16
trifluoroacetic acid	0.23	16
hydrochloric acid	-3.7	9
hydroiodic acid	-4.9	9
tetrafluoroboric acid	-4.9	9
hydrobromic acid	-5.2	17

Hydrogen bond correlation analysis

The hydrogen bond correlation analysis used in this work has been described recently for OHO[18] and for OHN hydrogen bonds[19] in detail. For a hydrogen bonded system A-H···X we define the coordinates

$$q_1 = ½ (r_1 - r_2),\ q_2 = r_1 + r_2. \qquad (2)$$

where $r_1 = r_{AH}$ and $r_2 = r_{HX}$. In the case of a linear hydrogen bond, q_1 corresponds directly to the distance of the proton with respect to the hydrogen bond center, and q_2 is equal to the heavy atom distance r_{AX}.

According to the valence bond order concepts proposed by Pauling [20] and Brown,[21] one can associate to both hydrogen bond distances valence bond orders given by

$$p_1 = \exp\{-(r_1-r_1^{o})/b_1\} \text{ and } p_2 = \exp\{-(r_2-r_2^{o})/b_2\}. \qquad (3)$$

where r_1^o and r_2^o represent the equilibrium distances in the fictive free diatomic units AH and HB, and b_1 and b_2 describe bond order decays with increasing bond distances. Assuming that the total valency of hydrogen is unity it follows that

$$p_1 + p_2 = \exp\{-(r_1-r_1°)/b_1\} + \exp\{-(r_2-r_2°)/b_2\} = 1. \quad (4)$$

Thus, both distances r_1 and r_2 depend on each other. Using eq (4), it is possible to express r_1 as a function of r_2, or q_1 as a function of q_2. Eq (4) can describe equilibrium geometries resulting from *ab initio* calculations, *i.e.* cases of almost harmonic potentials for the proton motions. However, eq (4) fails for strong hydrogen bonds involving anharmonic proton potentials. Thus, eq (4) is valid only in the absence of quantum zero point vibrational effects (QZPVE) present in strong hydrogen bonds.

Some of us have, therefore, proposed to calculate the corrected bond orders p_{AL} and p_{LX} of ALX hydrogen bonds as a function of the equilibrium bond orders accessible by *ab initio* calculations in the following way[22]

$$\begin{aligned}
p_{AL} &= \exp\{-(r_{AL}-r_1^o)/b_1\} = p_{1L}* - 2d^L p_1 (p_{1L}* p_{2L}*)^g, \\
p_{LX} &= \exp\{-(r_{LX}-r_2^o)/b_2\} = p_{2L}* - 2d^L p_2 (p_{1L}* p_{2L}*)^g, \\
p_{1L}* &= p_1 - c^L (p_1 p_2)^f (p_1-p_2), \\
p_{2L}* &= p_2 + c^L (p_1 p_2)^f (p_1-p_2).
\end{aligned} \quad (5)$$

The parameters c^L and d^L determine the size of the isotope sensitive correction term for QZPVE. c^L describes isotope shifts along the correlation line, keeping the total bond valencies of H and of D equal to unity (eq (4)). By contrast, d^L describes the deviation of the total valency of the hydrons from unity; this term leads to a flattening of the correlation curve q_1 *vs.* q_2 in the minimum. f and g are empirical numbers and may depend on the system studied. The parameter values used in the present work are listed in Table S6.

Table S6. Parameters of the geometric hydrogen bond correlations of OHO hydrogen bonds heteroconjugated anions AHX^- of phenols with carboxylates in polar solvents

	b_{OH}/Å	$r_{OH}°$/Å	f	g	c^H	d^H	c^D	d^D
OHO	0.371	0.942	5	2	440	0.2	5	0.4

Eq (6) defines the *primary geometric hydrogen bond isotope effect* (primary GIE),[23]

$$\Delta q_1 = q_{1D} - q_{1H}, \tag{6}$$

and Eq (7) of the *secondary geometric hydrogen bond isotope effect* (secondary GIE),

$$\Delta q_2 = q_{2D} - q_{2H}. \tag{7}$$

The secondary effect has also been called the "Ubbelohde effect", as it was observed by this author for a number of hydrogen bonded systems.[24] It describes a different position of the heavy atoms after isotopic substitution. By contrast, the *primary geometric isotope effect* describes a different location of hydrogen isotopes in the hydrogen bond.

The NMR parameters of hydrogen bonds can be related to their geometries. For example, Benedict *et al.* have proposed to express the chemical shifts of the nuclei of the hydrogen bridge as a function of the valence bond orders[25e]

$$\begin{aligned} \delta(\mathrm{A\underline{H}X}) &= \delta(\mathrm{A\underline{H}})^{o}\, p_1 + \delta(\mathrm{\underline{H}X})^{o}\, p_2 + \Delta(\mathrm{A\underline{H}X})(4 p_1 p_2)^{m}, \\ \delta(\mathrm{\underline{A}HX}) &= \delta(\mathrm{\underline{A}H})^{o}\, p_1 + \delta(\mathrm{\underline{A}})^{o}\, p_2 + \Delta(\mathrm{\underline{A}HX})(4 p_1 p_2)^{m}. \end{aligned} \tag{8}$$

Here, ^{1}H chemical shifts are symbolized by underlining the letter H and ^{13}C chemical shifts by underlining the letter A. $\delta(\mathrm{A\underline{H}})^{o}$, $\delta(\mathrm{\underline{H}X})^{o}$, $\delta(\mathrm{\underline{A}H})^{o}$ and $\delta(\mathrm{\underline{A}})^{o}$ are the limiting chemical shifts of the separate fictive groups. The terms $\Delta(\mathrm{A\underline{H}X})$ and $\Delta(\mathrm{\underline{A}HX})$ represent excess hydrogen bond shifts which describe the chemical shift deviation of a symmetric or quasisymmetric complex with $p_1 = p_2 = 0.5$ from the average limiting values. m is an empirical fitting parameter with a value normally set to unity. We note that the value of $\Delta(\mathrm{AH\underline{X}})$ might be different for equilibrium structures and structures where QZPVE is taken into account.

The solid correlation lines in Figure 7b and 7c of the main paper were calculated using the values $\delta(\mathrm{A\underline{H}})^{o}$ = 3 ppm, $\delta(\mathrm{\underline{H}X})^{o}$ = 3 ppm, $\Delta(\mathrm{A\underline{H}X})$=17.5 ppm, $\delta(\mathrm{\underline{A}H})^{o}$ =-9 ppm, $\delta(\mathrm{\underline{A}})^{o}$ =9 ppm and $\Delta(\mathrm{\underline{A}HX})$ =0.

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