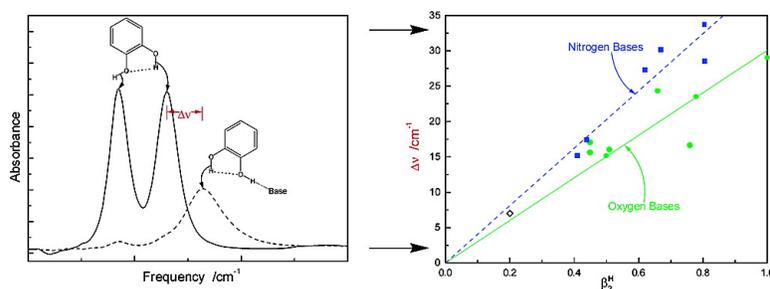## Article

Overlooked Difference between Hydrogen Bonds of Equal Strength Formed between Catechol and an Oxygen or Nitrogen Base. Experiments and DFT Calculations

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Overlooked Difference between Hydrogen Bonds of Equal Strength Formed between Catechol and an Oxygen or Nitrogen Base. Experiments and DFT Calculations

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Abstract: The IR spectrum of catechol in CCl$_4$ shows two fairly sharp O−H stretching bands of roughly equal absorbance at 3615.0 and 3569.6 cm^{-1} due, respectively, to the "free" OH and the intramolecularly H-bonded OH groups. Intermolecular H-bond formation between the "free" OH and a hydrogen bond acceptor (HBA) decreases its stretching frequency by several hundred wavenumbers and simultaneously decreases the frequency of the intramolecularly H-bonded OH by a few tens of wavenumbers. The magnitude of these frequency shifts, Δv_{inter} and Δv_{intra}, respectively, are very well reproduced by DFT calculations. As would be expected, the magnitudes of Δv_{inter} and Δv_{intra} increase as the HB accepting ability of the HBA increases as quantified, on a relative scale, by the HBA's β_2^H values (Abraham et al. *J. Chem. Soc. Perkin Trans. 2* **1990**, 521). However, plots of experimental, or calculated, frequency shifts versus β_2^H reveal that Δv_{inter} and Δv_{intra} are ca. 40% larger for a nitrogen atom HBA than for an oxygen atom HBA having equal HBA activity. We hypothesize that for HBAs of equal strength, i.e., of equal β_2^H, the H-bond in (O−H- - -O)$_{inter}$ is shorter and, hence, intrinsically stronger than the H-bond in the (O−H- - -N)$_{inter}$. However, we further hypothesize that there is more charge separation in the H-bond to N because N is a better proton acceptor than O. Hence, it is the greater Coulombic attraction in (O−H- - -N)$_{inter}$ which strengthens this H-bond and compensates for its greater length. Theoretical calculations lend support to these hypotheses.

We recently described a previously overlooked feature in the IR spectra of intermolecularly hydrogen-bonded 1,2-benzene-diols (catechols) and naphthalene diols.[1] These diols contain either a five-membered cyclic intramolecular H-bond (catechols and 2,3-naphthalene diol) or a six-membered cyclic intramolecular H-bond (1,8-naphthalene diol). In CCl$_4$, the IR spectra of all the diols show two fairly sharp O−H fundamental stretching bands of roughly equal absorbance separated by 42−138 cm^{-1}. Addition of a low concentration of DMSO, a strong hydrogen bond acceptor (HBA), causes the band due to the intramolecularly H-bonded OH group to decrease in absorbance to roughly half the extent that the "free" OH band decreases in absorbance. The "free" OH forms an intermolecular H-bond with the DMSO (to give a very broad band ca. 400 cm^{-1} lower in frequency), whereas the intramolecularly H-bonded OH does not. What had been overlooked was that as the DMSO concentration was increased the band due to the intramolecularly H-bonded OH group first broadened and then evolved into a new, relatively sharp band 23.5−92 cm^{-1} lower in frequency.

The magnitude of the HBA-induced shift in the IR frequency,

Δv_{intra}, of the intramolecularly H-bonded OH group, identified hereafter as (O−H- - -O)$_{intra}$, for 3,5-di-*tert*-butylcatechol was found to give an excellent linear correlation with the relative HB-accepting abilities of seven added bases (as conveniently quantified on a scale ranging from 0.00 to 1.00, by the β_2^H values of Abraham et al.[2]), see Figure 1. The seven bases were mesitylene, ethyl acetate, acetone, THF, DMF, DMSO, and HMPA. With the exception of mesitylene, these bases were, fortuitously, HBAs in which an oxygen atom is the acceptor of an intermolecular H-bond from the "free" OH group in this catechol, represented hereafter as (O−H- - -O)$_{inter}$. Later, three nitrogen atom-acceptor bases were employed, pyridine, triethylamine, and quinuclidine, giving intermolecular H-bonds (O−H- - -N)$_{inter}$. All these nitrogen bases gave larger frequency shifts to the (O−H- - -O)$_{intra}$ moiety than would have been predicted from the data for the oxygen bases (see Figure 1).

A systematic underestimation of β_2^H for nitrogen bases or overestimation of β_2^H for oxygen bases could account for the data in Figure 1, but this seemed very improbable in view of the rigor with which Abraham established his β_2^H scale.[2] Nevertheless, we immediately checked that each of the three nitrogen bases (plus 3,5-dichloropyridine) and two oxygen bases

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(1) Foti, M. C.; Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **2002**, *124*, 12 881−12 888.

(2) Abraham, M. H.; Grellier, P. L.; Prior, D. V.; Morris, J. J.; Taylor, P. J. *J. Chem. Soc., Perkin Trans 2* **1990**, 521−529.
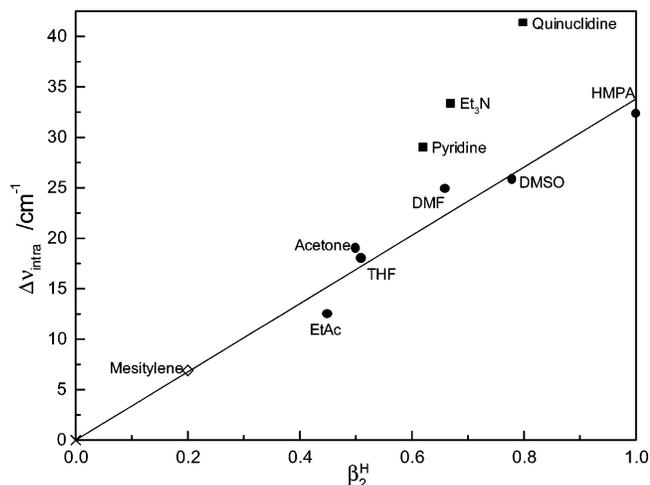
Figure 1. Plot of Δv_{Intra} versus β_2^H for 3,5-di-*tert*-butylcatechol complexed with various oxygen (●) and nitrogen (■) bases. The straight line is the best fit to all of the data except those marked with ■, and is taken from ref 1. The fit is forced through (0,0).

Table 1. Measured α_2^H Values for 3,5-Dichlorophenol Using Four Reference Bases and β_2^H Values for Various Bases Using Both 3,5-dichlorophenol and Phenol as the Reference Acids, with Literature Values of β_2^H (ref 2) for Comparison

	phenol			
	$3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{OH}$		$\text{C}_6\text{H}_5\text{OH}$	literature
base	$\alpha_2^{H\ a}$	β_2^H	β_2^H	β_2^H
ethyl acetate	0.79	0.48	0.40	0.45
pyridine	0.79	0.65	0.61	0.62
3,5-dichloropyridine		0.41	0.41	
triethylamine	0.79	0.67	0.67	0.67
dimethyl sulfoxide	0.74	0.76	0.78	0.78
quinuclidine		0.81	0.79	0.80

a Literature,[4] 0.77.

(ethyl acetate and DMSO) had β_2^H values that not only agreed with the literature[2] but also were essentially identical whether calculated from the measured equilibrium constants for 1:1 H-bond complex formation in CCl_4 with phenol or 3,5-dichlorophenol in the usual way.[1-3] These two phenols were chosen because their HB-donating abilities (as conveniently quantified on a relative scale ranging from 0.00 to nearly 1.0 by the α_2^H values of Abraham et al.[4]) bracket the HB-donating abilities of 3,5-di-*tert*-butylcatechol ($\alpha_2^H = 0.685$)[1] and catechol ($\alpha_2^H = 0.726$),[1] viz.,[4] phenol ($\alpha_2^H = 0.590$) and 3,5-dichlorophenol ($\alpha_2^H = 0.774$). The results are given in Table 1. We also made certain[5] that the α_2^H value for the very strong HBD, 3,5-dichlorophenol, was in agreement with the literature[4] and essentially the same whether measured with oxygen bases (ethyl acetate and DMSO) or with nitrogen bases (pyridine and triethylamine). These data are also included in Table 1. The method for calculating β_2^H and α_2^H values has been so thoroughly described[1-4] that it will not be repeated here.

Because there are no systematic errors in the relevant β_2^H values, the results shown in Figure 1 require that intermolecular

H-bonds *of equal strength* formed with oxygen and nitrogen bases differ in some fundamental manner. Because of the way in which β_2^H values are obtained,[2] "equal intermolecular H-bond strengths" means equal equilibrium constants, K^i, for 1:1 complex formation between dilute solutions of an oxygen or nitrogen base (HBA) and a dilute solution of a given acid (ArOH) in CCl_4 at room temperature, viz., $K^i = ([\text{ArOH-}--\text{HBA}]_{H-\text{bonded}}/([\text{ArOH}]_{\text{free}}[\text{HBA}]_{\text{free}})$. This is the case because the entropy change that occurs upon H-bond formation will be approximately the same for all HBAs.

Recognizing the existence of an O-base/N-base difference led us to hypothesize that *for equal strength H-bonds the H-bond in $(O-H---O)_{inter}$ is shorter than the H-bond in $(O-H---N)_{inter}$.* Because oxygen is more electronegative than nitrogen the electron density maxima of the orbitals containing the lone pairs of electrons on oxygen are closer to the oxygen nucleus than the electron density maximum of the lone pair orbital on nitrogen is to the nitrogen nucleus. Because H-bonding involves these lone pairs, the H-bond in $(O-H---O)_{inter}$ will tend to be shorter than that in $(O-H---N)_{inter}$, and the shorter bond will be intrinsically the stronger. However, there is expected to be a compensating factor that will strengthen the longer $(O-H---N)_{inter}$ H-bond (and to some extent, shorten it). That is, there is likely to be more charge separation in $(O-H---N)_{inter}$ than in $(O-H---O)_{inter}$ because nitrogen is a stronger proton acceptor than oxygen. Coulombic forces will therefore tend to make the intrinsically weaker and longer $(O-H---N)_{inter}$ H-bond equal in strength, though not in length, vide infra, to the $(O-H---O)_{inter}$ H-bond:

$$\overset{\delta\delta-}{O}-H---\overset{\delta\delta+}{O} \qquad\qquad \overset{\delta-}{O}-H---\overset{\delta+}{N}$$

With no obvious way to check these hypotheses, a combination of density functional theory (DFT) calculations validated, when possible, by experimental measurements was (again)[6] employed. To simplify the calculation we moved from 3,5-di-*tert*-butylcatechol to catechol itself where the calculations were validated by the excellent agreement between the observed HBA-induced shift in the intramolecular H-bond band frequencies and the calculated shifts.

Catechol   Catechol/HBA complex
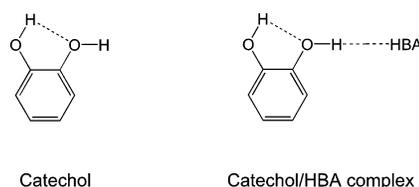
Calculations and experiments were also carried out on 1,8-naphthalene diol with results concordant with the catechol data. Nevertheless, these results have been relegated to the Supporting Information because the same validation test largely failed. This was not because of failed calculations but because the HBA-induced shifts in the intramolecular H-bonded OH group could not be experimentally determined in many cases (see Figure S1 in Supporting Information).

(3) (a) Astolfi, P.; Greci, L.; Paul, T.; Ingold, K. U. *J. Chem. Soc., Perkin Trans 2* **2001**, 1631−1633. (b) Snelgrove, D. W.; Lusztyk, J.; Banks, J. T.; Mulder, P.; Ingold, K. U. *J. Am. Chem. Soc.* **2001**, *123*, 469−477.

(4) Abraham, M. H.; Grellier, P. L.; Prior, D. V.; Duce, P. P.; Morris, J. J.; Taylor, P. J. *J. Chem. Soc., Perkin Trans 2* **1989**, 699−711.

(5) This was in the nature of "overkill" because 3,5-dichlorophenol is one of Abraham's reference acids.[2] Equilibrium constants in CCl_4 for 1:1 complex formation between this phenol and 27 bases make its α_2^H value well defined and, by implication, independent of the base.

(6) (a) Pratt, D. A.; Wright, J. S.; Ingold, K. U. *J. Am. Chem. Soc.* **1999**, *121*, 4877−4882. (b) Pratt, D. A.; de Heer, M. I.; Mulder, P.; Ingold, K. U. *J. Am. Chem. Soc.* **2001**, *123*, 5518−5526. (c) Pratt, D. A.; DiLabio, G. A.; Valgimigli, L.; Pedulli, G. F.; Ingold, K. U. *J. Am. Chem. Soc.* **2002**, *124*, 11 085−11 092. (d) DiLabio, G. A.; Litwinienko, G.; Lin, S.; Pratt, D. A.; Ingold, K. U. *J. Phys. Chem. A* **2002**, *106*, 11 719−11 725.

Results

HBA-Induced Shifts in the O−H Stretching Frequencies of Catechol. Fourier Transform infrared (FTIR) spectra were obtained in CCl_4 at room temperature using low catechol concentrations (ca. 3 mM) where self-association does not occur.[1] There are two O−H stretching bands, the one at 3615.0 cm^{-1} is due to the "free" OH group, and the one at 3569.6 cm^{-1} is due to the intramolecularly H-bonded OH group. Addition of a HBA (3−50 mM) reduces the absorbance of both bands and, at sufficiently high HBA concentrations, both bands are replaced by new bands at lower frequencies (for quinuclidine see Figure 2 and for DMSO see Figure 4 in ref 1).[7] The "free" OH band shifts to dramatically lower frequencies (by hundreds of wavenumbers). The (O−H- - -HBA)$_{inter}$ band becomes extremely broad (e.g., width at half-height, $\Delta v_{(1/2)} \approx 190$ cm^{-1} for acetone as the HBA) which makes the assignment of many band maximum frequencies difficult or even impossible. The (O−H- - -O)$_{intra}$ band shifts to lower frequencies by only a few tens of wavenumbers and broadens (see Figure 2). This broadening reflects the thermal distribution of intermolecular HB complexes (as is indicated by the large $\Delta v_{(1/2)}$ values for (O−H- - -HBA)$_{inter}$ complexes). The integrated band intensities of the shifted (O−H- - -O)$_{intra}$ bands, at least in those cases where reliable measures of band areas could be obtained, remain essentially unchanged.

The experimental frequency shifts for the two catechol OH stretching bands which have been produced by 15 HBAs are summarized in Table 2. Hydrogen bonding of the HBAs to the intramolecularly bonded O−H group does not occur to any significant extent under the current experimental conditions. (In this connection, we have previously reported that it takes ca. 200 mM DMSO to reduce the intensity of the O−H stretch in 2-methoxyphenol by 40%. This band is not broadened and a second broad band "grows in" ca. 325 cm^{-1} lower in frequency, see Figure 5 of ref 1).

Density Functional Theory (DFT) calculations on the H-bonded complexes were performed using the B3LYP[8] functional with 6-31G(d) basis sets for geometry optimization and frequency calculations. This level of theory is known to yield vibration frequencies that are generally too large by ca. 4%.[9] It is therefore not surprising that catechol's two O−H stretching frequencies were calculated to be 3774.0 and 3716.2 cm^{-1}, values which are somewhat higher than the measured (in CCl_4) frequencies[1] of 3615.0 and 3569.6 cm^{-1}. The method of calculation is therefore expected to produce reliable values for HBA-induced *shifts* in O−H stretching frequencies, Δv. Similar conclusions were reached by Korth et al. in their study of intramolecular hydrogen bonding in 2-substituted phenols.[10] The calculated values of Δv for (O−H- - -O)$_{intra}$, Δv_{intra}, and (O−H- - -HBA)$_{inter}$, Δv_{inter}, are given beside the experimental values in Table 2.

The enthalpies of H-bond formation were computed at the MP2 = FC/6-31+G(d,p)//B3LYP/6-31G(d) level and basis set incompleteness effects were approximated using the counter-

Table 2. Experimental and Calculated Δv_{Intra} and Δv_{Inter} (in cm^{-1}) in Catechol/HBA Complexes

HBA	$\beta_2^{H\ a}$	Δv_{Intra}		Δv_{Inter}	
		expt[b]	calcd[c]	expt[b]	calcd
1 mesitylene	0.20	7.0	6.7	112	113
2 3,5-dichloropyridine	0.41	15.1	18.1	289	339
3 acetonitrile	0.44	17.4	18.3	197	157
4 ethyl acetate	0.45	15.6	16.5	*d*	283
5 diethyl ether	0.45	17.0	16.4	327	298
6 acetone	0.50	15.1	15.7	297	292
7 tetrahydrofuran	0.51	16.0	18.4	345	343
8 pyridine	0.62	27.3	27.8	*d*	462
9 dimethylformamide	0.66	24.3	22.4	*d*	375
10 triethylamine	0.67	30.1	30.3	(740)[e]	726
11 trimethoxyphosphine oxide	0.76	16.6	16.5	375	307
12 dimethyl sulfoxide	0.78	23.5[f]	18.9	432	500
13 quinuclidine	0.80	33.7	31.7	*d*	684
14 1,4-diazabicyclo[2.2.2]octane	0.81	28.5	29.8	*d*	663
15 hexamethylphosphoramide	1.00	29.0	29.4	*d*	413

[a] Ref 2. *[b]* In CCl_4 at room temperature. *[c]* The calculated O−H stretching frequency in the catechol anion is 3151 cm^{-1}, corresponding to $\Delta v_{Intra} = 565$ cm^{-1}. *[d]* Indeterminate. *[e]* Broad band, maximum subject to considerable error because of incomplete cancellation of contributions from C−H stretching bands. *[f]* Incorrectly given as 19 cm^{-1} in ref 1.
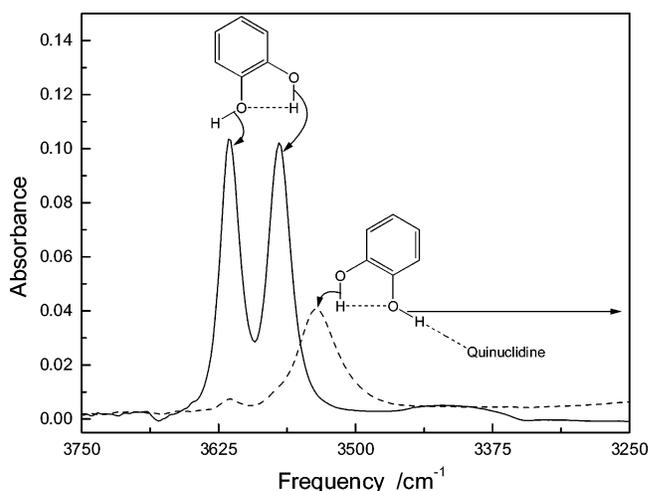

Figure 2. FT-IR spectra of catechol in CCl_4 (solid line) and catechol complexed with quinuclidine (dashed line). The origins of the bands are indicated.

poise correction scheme.[11] Comparisons between calculated and experimental[12] H-bond enthalpies, $(-\Delta H_{HB})_{inter}$, for 1:1 complexes of p-fluorophenol with acetone (6.1 vs 4.8 kcal/mol[13]), ethyl acetate (6.0 vs 4.7 kcal/mol), and tetrahydrofuran (7.2 vs 5.7 kcal/mol) indicate that the present theoretical method overestimates $(-\Delta H_{HB})_{inter}$ by 1.3−1.5 kcal/mol. The $(-\Delta H_{HB})_{inter}$ data for the catechol-HBA 1:1 complexes, which are also expected to be overestimated by ca. 1.4 kcal/mol, are presented in Table 3 together with some relevant geometric data for these complexes. Table 3 also includes the charge (q/e^-) transferred from the HBA to catechol, as determined using Natural Bond Orbital (NBO) analysis[14] at the MP2 = FC/ 6-31+G(d,p)//B3LYP/6-31G(d) level. In some cases, the NBO

(7) A detailed description of the changes in the IR spectrum of 3,5-di-*tert*-butylcatechol as a function of DMSO concentration has been given previously.[1]
(8) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys Rev. B.* **1988**, *37*, 785−789.
(9) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16 502−16 513.
(10) Korth, H.-G.; de Heer, M. I.; Mulder, P. *J. Phys. Chem. A* **2002**, *106*, 8779−8789.

(11) See, for example: Schwenke, D. W.; Truhlar, D. G. *J. Chem. Phys.* **1985**, *82*, 2418−2426, and references therein.
(12) Gurka, D.; Taft, R. W. *J. Am. Chem. Soc.* **1969**, *91*, 4794−4801.
(13) This experimental value is for 2-butanone.[12]
(14) Version 3.1 is implemented in the Gaussian-98 program package[15] and used in the present work. A more recent version of the program is NBO 4.M Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F., Theoretical Chemistry Institute, University of Wisconsin, Madison 1999.
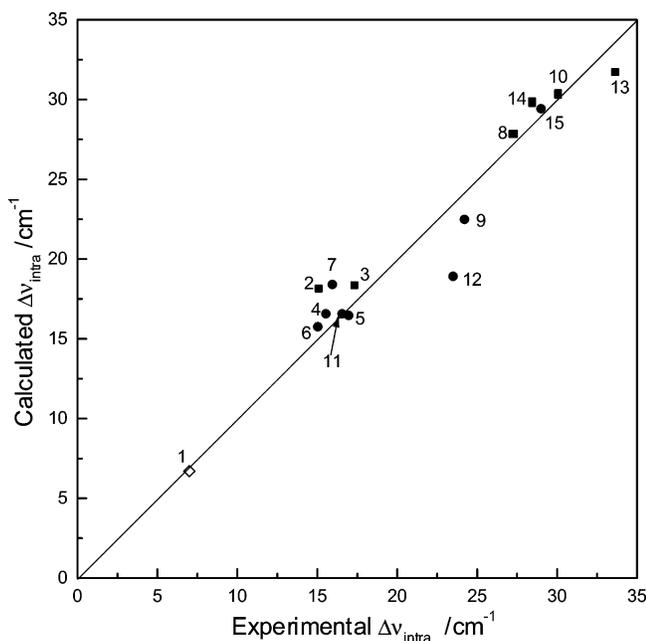
Figure 3. Plot of calculated versus experimental Δv_{intra} values for catechol/HBA complexes. Oxygen atom acceptor bases, ●; nitrogen atom acceptor bases, ■; mesitylene, ◊. The HBAs are numbered as in Table 2. The straight line drawn in this Figure has a slope of 1.0.
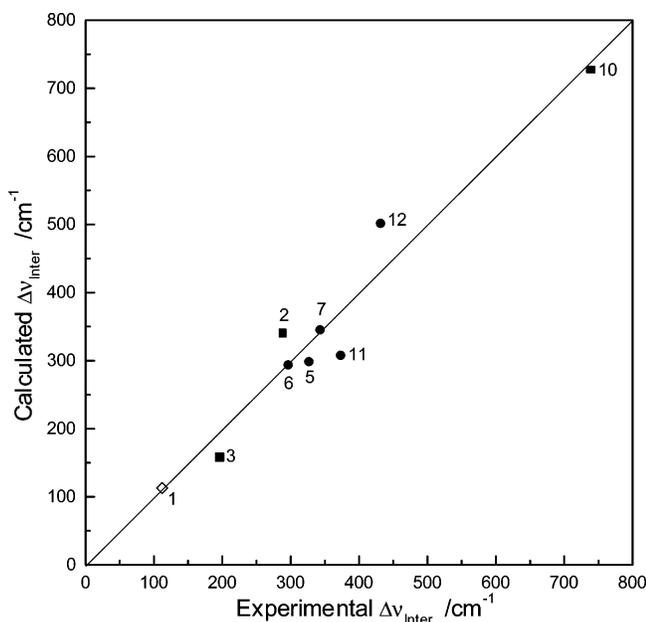

Figure 4. Plot of calculated versus experimental Δv_{inter} values for catechol/HBA complexes. Oxygen atom acceptor bases, ●; nitrogen atom acceptor bases, ■ and mesitylene, ◊. The HBAs are numbered as in Table 2. The straight line has a slope of 1.0.

calculations did not complete properly due to problems with basis set linear dependencies.

Additional calculations were performed on catechol-Et₂O and catechol-DABCO complexes with the HBA H-bonded to the intramolecularly H-bonded O−H group of catechol. These binding energies are more than 3 kcal/mol lower than those in which the bases are bound to the "free" O−H group. In addition, the calculated Δv_{intra} values for these two structures are 187 (Et₂O) and 548 (DABCO) cm⁻¹, supporting our conclusion that the complexes examined by IR spectroscopy in the present work have the HBA H-bonded to the "free" O−H group.

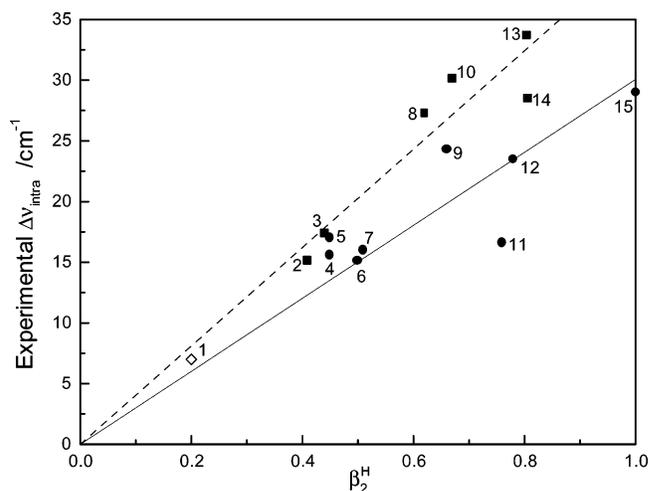**Figure 5.** Plot of experimental Δv_{intra} values for catechol/HBA complexes versus β_2^H. Oxygen atom acceptor bases, ●, solid line; nitrogen atom acceptor bases, ■, dashed line and mesitylene, ◊ (not included in either fitting). The HBAs are numbered as in Table 2. The lines have been forced through (0,0).

Table 3. Calculated Hydrogen-Bond Enthalpies $((-\Delta H_{HB})_{Inter}$ /kcal/mol), Hydrogen-Bond Lengths $(r(O-H\cdots HBA)_{Inter}$ /Å), and Charge Transferred (q/e^-) in Catechol/HBA Complexes

HBA[a]	$(-\Delta H_{HB})_{inter}$	$r(O-H\cdots HBA)_{inter}$	q^b
1	4.1	2.322[c]	d
2	7.0	1.879	−0.045
3	5.7	1.954	−0.031
4	7.4	1.806	−0.036
5	7.5	1.791	−0.045
6	6.4	1.811	−0.039
7	7.7	1.747	d
8	8.8	1.827	−0.056
9	8.1	1.754	−0.049
10	12.5	1.781	−0.072
11	8.5	1.763	d
12	10.5	1.715	−0.059
13	10.8	1.762	−0.068
14	10.3	1.768	−0.065
15	11.2	1.699	d

[a] The HBAs are numbered as in Table 2. [b] Electron density is transferred from the HBA to the catechol. [c] Distance to nearest ring carbon. [d] Calculation fails due to linear dependency problems.

Discussion

The agreement between theory and experiment for the HBA-induced shifts in frequency of the intramolecularly bonded O−H group stretching bands of catechol is excellent (see Table 2 and Figure 3). The corresponding plot for Δv_{inter} is also excellent (see Figure 4) but has fewer data points because the band maximum could not always be determined. The good agreement between theory and experiment shown in Figures 3 and 4 is extremely gratifying in view of the small size of the basis set used for the geometry optimization/frequency calculations.[16]

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Rega, N.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11.3, Gaussian, Inc., Pittsburgh, PA, 2002. This package was used for all the calculations in the present work.

Table 4. Calculated Δv_{inter} (cm^{-1}) and $\Delta \delta$ (ppm) for *p*-Fluorophenol/HBA Complexes Plus Experimental $\Delta \delta$ (ppm) from Ref 12

HBA[a]	Δv_{inter}[b]	$\Delta\delta$(calc)[c]	$\Delta\delta$(exptl)
1	86	1.89	
2	269	2.38	1.62
3	119	4.34	1.88
4	231	3.00	1.85
5	246	2.73	1.88
6	243	2.98	2.02[d]
7	292	3.23	2.00
8	373	4.23	2.49
9	307	4.10	2.72
10	588	3.39	2.66
11	254	3.32	
12	438	2.92	2.74
13	568	4.71	
14	540	3.11	
15	327	4.87	3.71

[a] The HBAs are numbered as in Table 2. [b] The calculated reference O−H stretching frequency of p-fluorophenol is 3754 cm^{-1}. [c] The calculated shielding tensor for the fluorine atom is 300.63 ppm. The calculated shielding tensor for the fluorine atom in *p*-fluorophenoxide is 343.47 ppm. [d] Experimental $\Delta\delta$ is for 2-butanone.

We confirmed (probably unnecessarily) that β_2^H parameters are true, i.e., acid-independent, measures of the relative HB-accepting abilities of bases and, hence, of the relative strengths of the HBs they form with acids. The plot of experimental Δv_{intra} vs β_2^H for 3,5-di-*tert*-butylcatechol (Figure 1) and the similar plot for catechol (Figure 5) show that these frequency shifts correlate poorly with the strengths of the (O−H- - -HBA)$_{\text{inter}}$ H-bonds as indicated by β_2^H, with R = 0.75 and SD = 4.6 cm^{-1} (line not shown in Figure 5). Korth et al.[10] have also reported a poor correlation between the OH band frequencies of ortho-substituted phenols and $(-\Delta H_{\text{HB}})_{\text{intra}}$. However, improved relationships are obtained by analyzing the data in terms of whether the acceptor atom in the HBA is oxygen, viz., $R = 0.83$, SD = 3.3 cm^{-1} or nitrogen, viz., $R = 0.94$, SD = 2.6 cm^{-1}. (The Δv_{intra} value for mesitylene, shown by a diamond in Figure 5 was not included in these correlations). The least-squares fitting (forced through (0,0)) of the data for the oxygen and nitrogen bases give lines with slopes of 30.1 ± 1.8 and 40.5 ± 1.7 cm^{-1} (errors represent one standard deviation of the slope), respectively. A statistical analysis of the data (student's t-test) indicates that the two data sets (fit to $y = mx + b$) are distinct sets with a level of confidence >95%.

Turning to the intermolecular HBs, a plot of calculated Δv_{inter} for catechol/HBAs vs β_2^H (see Figure S2) can also be divided into two data sets, one for oxygen atom-acceptor HBAs, slope = 528 ± 41 cm^{-1}, $R = 0.68$, SD = 78 cm^{-1} and one for the nitrogen atom-acceptors, slope = 828 ± 77 cm^{-1}, $R = 0.89$, SD = 123 cm^{-1}. Similarly, a plot of calculated Δv_{inter} for HBA complexes for *p*-fluorophenol[18] (from Table 4) vs. β_2^H (Figure

(16) It is particularly gratifying in view of a report[17] that B3LYP/6-31G(d, p) fails to predict experimental Δv_{inter}, $(-\Delta H_{\text{HB}})_{\text{inter}}$ and intermolecular distances for a number of H-bonded complexes, including the water dimer. We note that Korth et al. found B3LYP/6-31G(d, p) works quite well for intramolecular H-bonds in 2-substituted phenols.[10]
(17) Del Bene, J. E.; Person, W. R.; Szczepaniak, K. *J. Phys. Chem.* **1995**, *99*, 10 705−10 707.
(18) This phenol was chosen for these calculations because there are also extensive experimental data on HBA-induced shifts in the ^{19}F NMR signal,[12] $\Delta\delta$. We had hoped that ^{19}F $\Delta\delta$ values would provide another, independent, method for distinguishing between oxygen and nitrogen bases of equal HBA activity. However, neither the experimental[12] nor the calculated[19] $\Delta\delta$ values (Table 4) could make this distinction.
(19) Chemical shifts were computed within the GIAO framework[20] at the B3LYP/6-311G(d)//B3LYP/6-31G(d) level.
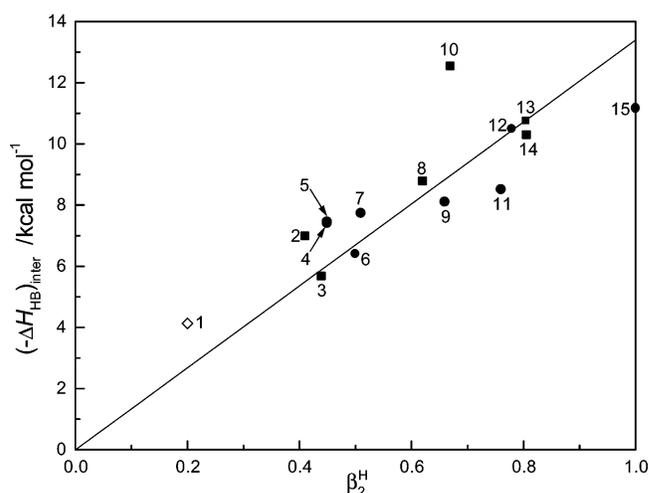
Figure 6. Plot of calculated hydrogen bond enthalpies for catechol/HBA complexes versus β_2^H. Oxygen atom acceptor bases, ●; nitrogen atom acceptor bases, ■ and mesitylene, ◇. The HBA's are numbered as in Table 2. The straight line has been forced through (0,0).
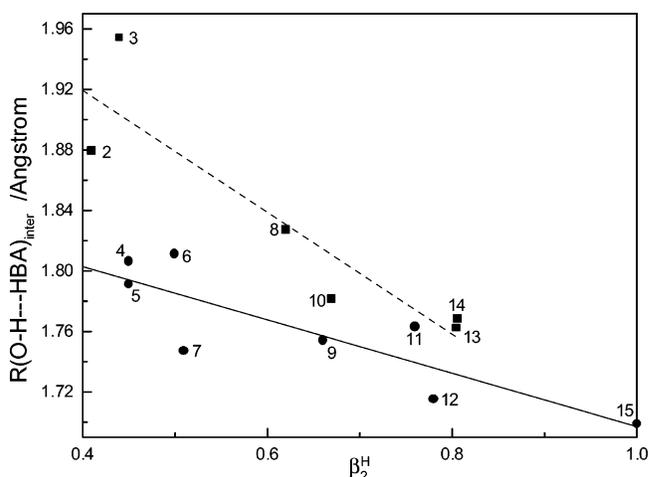

Figure 7. Plot of intermolecular HB length, R(O−H- - -HBA)$_{\text{inter}}$, for catechol/HBA complexes versus β_2^H. Oxygen atom acceptor bases, ●, solid line and nitrogen atom acceptor bases, ■, dashed line. The HBA's are numbered as in Table 2.

S3) gives for the oxygen-atom acceptors, slope = 438 ± 39, $R = 0.60$, SD = 73 cm^{-1} and for the nitrogen-atom acceptors, slope = 674 ± 65, $R = 0.89$, SD = 103 cm^{-1}. Calculated HB enthalpies, $(-\Delta H_{\text{HB}})_{\text{inter}}$, for catechol-HBA complexes (from Table 3) have been plotted against β_2^H in Figure 6. The points for two HBAs (Et$_3$N (**10**) and HMPA (**15**)) deviate significantly from the least-squares line, but there is obviously no discrimination between the oxygen and nitrogen atom HBAs in this plot. This lack of discrimination is further evidence that HB strengths (i.e., calculated HB enthalpies) are solely related to the β_2^H value of the base.

Because our calculated values of Δv_{intra} and Δv_{inter} are in such good agreement with our experimental measurements we can use other calculated quantities with considerable confidence. In particular, and returning to the hypothesis advanced in the Introduction, a plot of the calculated intermolecular HB lengths, R(O−H- - -HBA)$_{\text{inter}}$, from Table 3 against β_2^H yields two distinguishable data sets, one for oxygen atom-acceptor HBAs

(20) (a) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789−807. (b) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251−8260.

and one for nitrogen atom-acceptors, see Figure 7. Similarly, the calculated electron density that is transferred from the HBA to the catechol, q, increases as β_2^H increases (see Table 3). Moreover, for those stronger HBAs ($\beta_2^H \geq 0.50$) for which q could be calculated, the values of q/β_2^H are larger for the four nitrogen acceptor bases (mean 0.091 e$^-$) than for the three oxygen atom acceptors (mean 0.076 e$^-$). Such a large difference in the extent of charge transfer for HBs of equal strength indicates that there will be a significantly greater Coulombic contribution to the strength of HBs to nitrogen bases than to oxygen bases (and, consequently, a greater Coulombic-induced shortening of (O—H- - -N)$_{inter}$ HBs than of (O—H- - -O)$_{inter}$ HBs). Thus, DFT calculations support our hypotheses regarding the origin of the differences between equal strength (O—H- - -O)$_{inter}$ and (O—H- - -N)$_{inter}$ HBs.

It will be obvious that the transfer of negative charge from the HBA to catechol will increase the HB-accepting ability of the oxygen atom of the intermolecularly H-bonded OH group. As a consequence, the O—H bond in (O—H- - -O)$_{intra}$ will become longer, weaker, and have a lower stretching frequen-cy. That is, Δv_{intra} will increase as charge transfer and the HB-accepting ability of the base increase[21] but at different rates for oxygen and nitrogen atom-acceptor bases.

Supporting Information Available: Calculated and experimental Δv_{intra} values for intramolecularly hydrogen-bonded O—H groups in 1,8-naphthalene diol with HBA solvents, the energies used to compute $(-\Delta H_{HB})_{inter}$ values given in Table 3, IR spectra of 1,8-naphthalene diol in CCl$_4$ and in CCl$_4$ containing acetonitrile, plot of calculated Δv_{inter} values for catechol vs β_2^H, plot of calculated Δv_{inter} for p-fluorophenol/ HBA complexes *vs* β_2^H and B3LYP/6-31G(d) optimized structures for H-bonded complexes and their components. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) In the limit, the catechol anion is calculated to have a $\Delta v_{intra} = 565$ cm^{-1} which is more than 1 order of magnitude greater than Δv_{intra} for any of the catechol- - -HBA complexes, see Table 2, footnote c.