Supporting Information

Direct measurements of electric fields in weak OH··π hydrogen bonds

Miguel Saggu,[1*] Nicholas M. Levinson,[1*] and Steven G. Boxer[1*]

[1] Department of Chemistry, Stanford University, Stanford, CA 94305-5080, USA

[*] To whom correspondence should be addressed. E-mail: miguel.saggu@gmail.com (M.S.),

nickerrific@gmail.com (N.M.L.), sboxer@stanford.edu (S.G.B.)

Materials and methods

Chemicals. Phenol, 2,6-di-t-butylphenol, carbon tetrachloride and the substituted liquid benzene derivatives were purchased from Sigma-Aldrich (St. Louis, MO) except para-xylene (Thermo Fisher Scientific, Waltham, MA). Methanol-d4 ($\geq$99.6%) was ordered from Acros Organics (Geel, Belgium). Dry phenol was dissolved under nitrogen atmosphere in different substituted anhydrous liquid benzene derivatives to form phenol/aromatic complexes with a final phenol concentration of 200 mM. Electron rich benzene derivatives with methyl groups as electron-donating groups were toluene, para-xylene and mesitylene. To form weaker phenol/aromatic complexes, substituted benzene derivatives with electron-withdrawing chlorine groups were used, namely chlorobenzene, o-dichlorobenzene and m-dichlorobenzene. Deuteration of the hydroxyl group of phenol was carried out by dissolving phenol in methanol-d_4 under nitrogen atmosphere. The methanol was removed under vacuum and the dry phenol was dissolved in the different benzene derivatives which produced yields of deuterated phenol >90%. To prepare samples containing a mixture of free and complexed phenol, the aromatic solvents were diluted in CCl_4. The ratios of aromatic solvent/CCl_4 were adjusted to obtain approximately equal peak intensities of free/complexed phenol. The diluted samples contained 200 mM phenol in mesitylene/CCl_4 (1:5 wt), p-xylene/CCl_4 (1:7 wt), toluene/CCl_4 (1:6 wt), benzene/CCl_4 (1:5 wt) chlorobenzene/CCl_4 (1:4 wt), o-dichlorobenzene/CCl_4 (1:3 wt) and m-dichlorobenzene/CCl_4 (1:3 wt).

Vibrational spectroscopy. FTIR spectra were recorded on a Bruker Vertex 70 spectrometer equipped with a liquid nitrogen-cooled indium antimonide detector with a spectral resolution of 1 cm^{-1}. Samples measured at room temperature were placed in a gas-tight IR cell (volume ~20 μL) with sapphire windows. Two teflon spacers with different thickness (75 μm and 100 μm) on either side of the cell were used to minimize reflections between the windows. Spectra were baseline corrected using a spline function implemented in the OPUS 5.5 software (Bruker Photonics, Billerica, MA). Vibrational Stark spectroscopy was performed at liquid nitrogen temperature in a home-built cryostat.[S1] The samples were loaded in a home-built liquid cell containing sapphire windows (thickness 1 mm, diameter 13 mm, Meller Optics, Providence, RI) that were coated with a 45 Å thick layer of nickel at the inside to provide a homogeneous electric field across the sample. The windows were separated by two teflon spacers of 26 μm thickness. Unfortunately phenol prefers hydrogen-bonding to itself at low temperatures instead of complex forming with toluene. The same effect was observed in other glass-forming solvents like methylcyclohexane or dichloromethane/dichloroethane. To circumvent this problem we used 2,6-di-t-butylphenol in the vibrational Stark experiments. The bulky tert-butyl groups prevent this phenol from hydrogen-bonding to itself and enable the measurement of free phenol-OH/OD at low temperatures. Samples containing 200 mM 2,6-di-t-butylphenol in toluene were frozen rapidly into a glass in liquid nitrogen. A high voltage power supply was connected to the setup (Trek Instruments Inc., Medina, NY) and the output voltage was synchronized with the FTIR scanning time. Spectra were recorded with an applied electric field of 1 MV/cm. In addition spectra were recorded under the same conditions but without an applied electric field and subtracted from the field-on spectra. To obtain the Stark tuning rate the spectra were fitted using the program *spectfit*.[S2] The Stark tuning rate was determined from three independent measurements for both the OH and OD stretch. To guarantee the same applied electric fields in the experiments, samples with a 1:1 mixture of protonated to deuterated 2,6-di-t-butylphenol were prepared and both Stark tuning rates for OH and OD were determined in the same sample.

Theory. DFT calculations of the different phenol/aromatic complexes were performed

with Gaussian 09.[S3] For all calculations the functional was B3LYP[S4,S5] with 6-31+G(d,p) as a basis set. First, the complexes were geometry optimized and then electrostatic potentials were calculated at the position of the OH/OD spectral probe by replacing them with ghost atoms. From this the projection of the electric field on the probe was calculated. All calculations were performed on the isolated complexes in the gas-phase and do not include any solvation effects.

Calculations of the vibrational frequencies of the OH stretch for phenol with and without the presence of an electric field were carried out as described elsewhere.[S6] In brief, the B3LYP functional and 6-31+G(d,p) or 6-311++G(2d,2p) basis sets were used. First the geometry was optimized with the presence of a uniform electric field parallel to the OH bond. Then the frequency was calculated with the presence of the same electric field. The electric field values ranged from -0.01 au to +0.02 au (1 au = 5.14225 GV/cm). All frequencies are reported without any further scaling.

Effect of isotope exchange on the Stark tuning rate. Our experiments demonstrate that the Stark tuning rate for OH is larger than for OD and the ratio is $\left|\Delta\vec{\mu}_{OD}\right|/\left|\Delta\vec{\mu}_{OH}\right| = 0.7$. Qualitatively this difference is expected from the reduced mass dependence of the zero point energy. The Stark tuning rate arises partly from the anharmonicity of the potential for the molecular vibration.[S2] Since the zero point energy of OD is lower than that of OH, the $0{\rightarrow}1$ vibrational transition of OD occurs in a more harmonic range of the potential curve, and lower anharmonicity leads to a smaller Stark tuning rate. The greater anharmonicity of OH is also seen in 2D IR experiments where the anharmonicity can be directly extracted from the spectra since two vibrational transitions ($0{\rightarrow}1$ and $1{\rightarrow}2$) are observed.[S7] A similar relationship between the electric field and the OH (or OD) stretch of water has been shown earlier by computational studies with computed values, 2.4 cm^{-1}/(MV/cm) for OH and 1.7 cm^{-1}/(MV/cm) for OD,[S8] that are quite close to what we obtained experimentally for the OH and OD stretch of phenol.

Supporting figures

Figure S1. FTIR spectra of different phenol/aromatic mixtures diluted in CCl_4 to observe both free and complexed phenol in the same samples. The peak for the free phenol around 3611 cm^{-1} remains nearly constant throughout the entire series. Only the peak for the complexed species shifts significantly. This indicates that the influence of the solvent reaction field is very small and observed peak shifts are mainly due to complex formation (see Fig. 1). The reason for the small peak shifts of free phenol in the chlorobenzenes/CCl_4 mixtures most probably arises because the peaks for free and complexed phenol have the most overlap and for that reason their free peak is shifted.
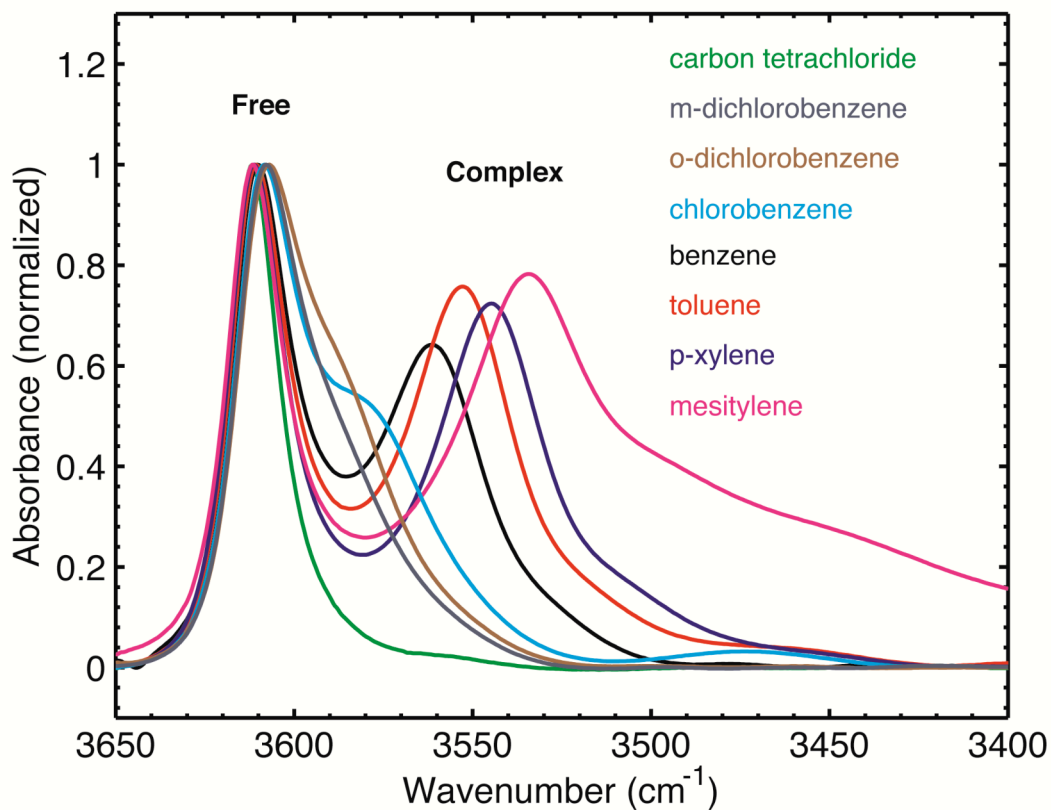
Figure S2. Observed OH stretch frequency plotted vs. the calculated solvent reaction field according to the Onsager model.[S9] The dielectric constants and the refractive indices for the methylated benzenes are very similar, consequently the calculated solvent fields are very similar as well (see Table S1). Since there is no clear correlation and the points are scattered, the solvent reaction field alone is not responsible for the observed peak shifts in the FTIR spectra of phenol/aromatic complexes. This is in contrast to a previous solvatochromic study done on the nitrile stretch frequency of ethyl thiocyanate in simple non-aromatic solvents, where the interaction is of the reaction field type, primarily due to the large and localized ground state dipole moment of ethyl thiocyanate, and shows a correlation between peak frequency and solvent reaction field.[S10]
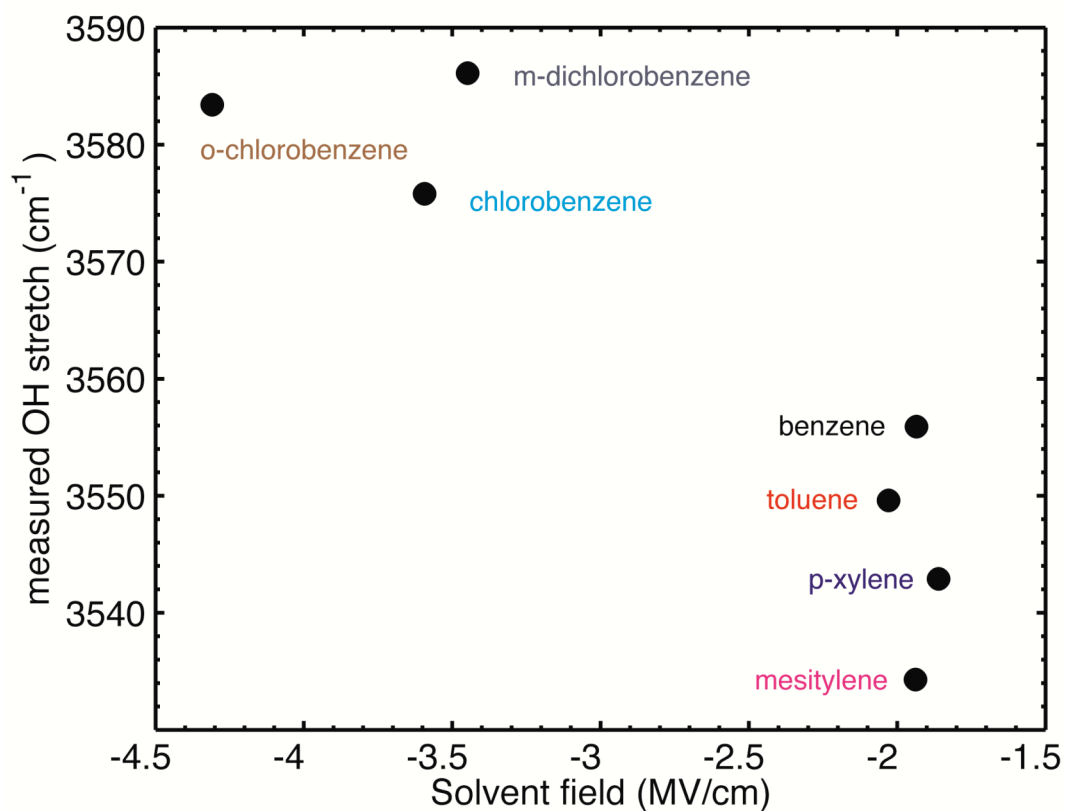
Figure S3. Structures of the different geometry optimized phenol/aromatic complexes (for coordinates see below). The complexes have been optimized using B3LYP and 6-31+G(d,p).
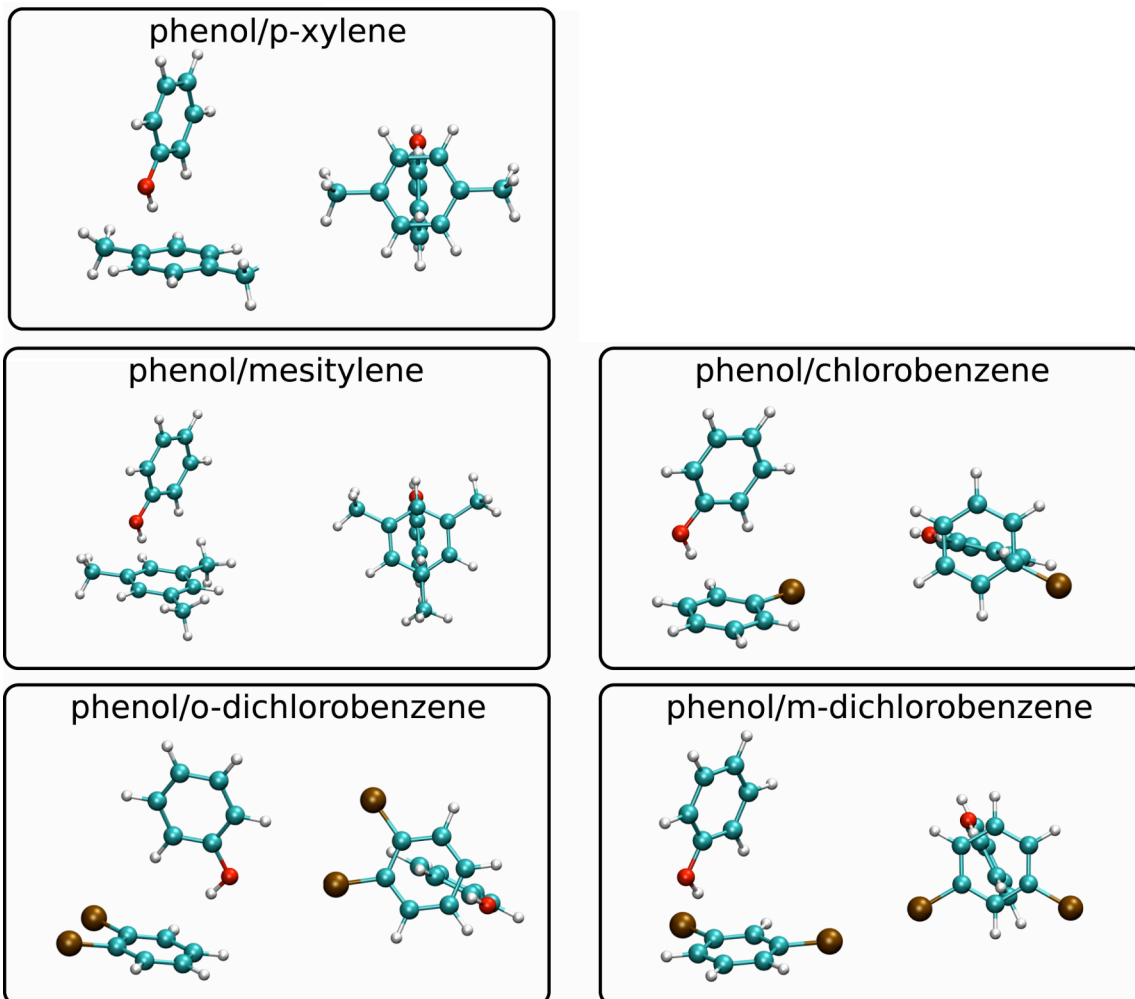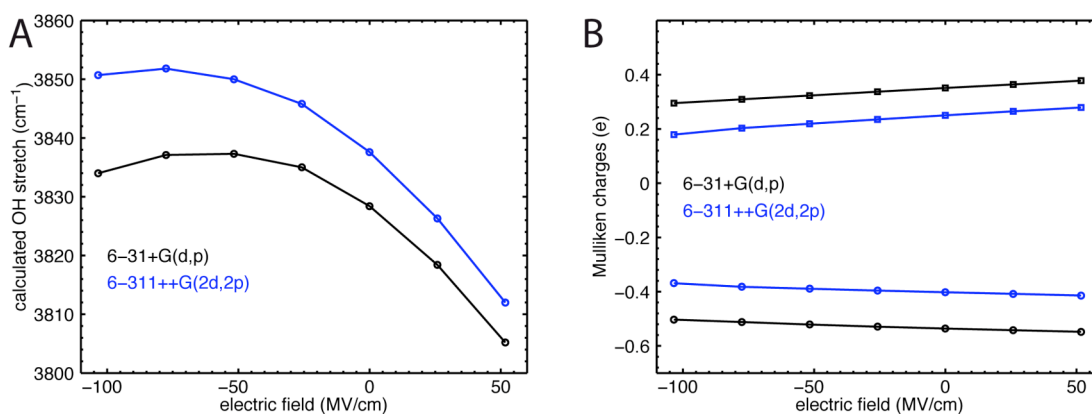

phenol/p-xylene

phenol/mesitylene

phenol/chlorobenzene

phenol/o-dichlorobenzene

phenol/m-dichlorobenzene

Figure S4. (A) Electric field dependence of the vibrational frequency for the OH stretch of phenol calculated by DFT. (B) Mulliken charges q_O (o) and q_H (□) of the OH group as a function of the electric field parallel to the OH bond.

The linear relationship between vibrational frequency and electric field described by the linear Stark effect is known to break down in very large electric fields, where non-linear effects become significant. The results show that the effect of electric field on the frequency is linear within the studied range of the phenol/aromatic complexes.

More importantly, our experimental data indicate no deviation from the linear response of the OH probe within the range of fields studied (Fig. 3). A reasonable estimate of the absolute field can be obtained by combining the Onsager reaction field with the field due to complex formation (Fig. S2). For the aromatic solvents used in this study the obtained reaction fields are smaller than 5 MV/cm, and the total field less than ~35 MV/cm, supporting the assumption that our experiments are within the linear regime. As a result the Stark tuning rate of OH/OD is the same in each phenol/aromatic complex and the character of the OH/OD bond is not significantly changed.

Figure S5. FTIR spectra of 250 mM methanol in different organic solvents.
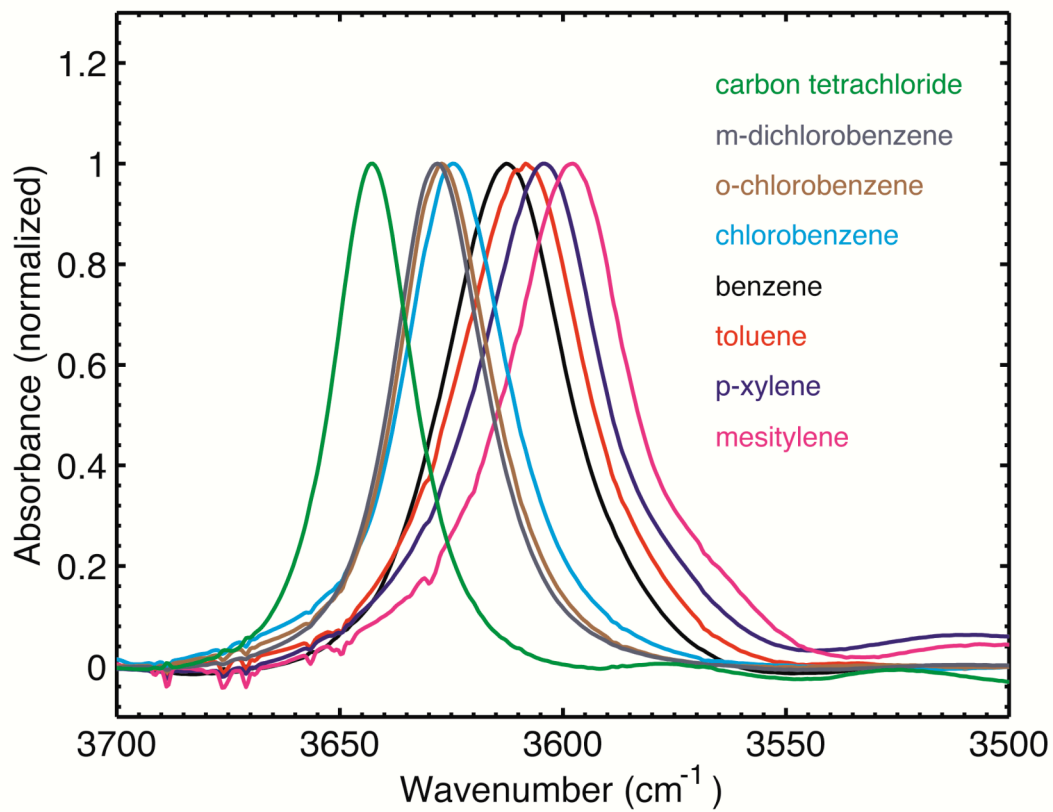
Supporting tables

Table S1. Dielectric constants (ε) and refractive indices (n) for the used aromatic solvents.[S11] The solvent reaction field (F) was calculated using Onsager's equation below. The radius (a) used for the spherical solute volume was 3.5 Å with a dipole moment (μ) of 1.7 D for the OH group.

solvent	ε	n
mesitylene	2.279	1.498
p-xylene	2.2	1.496
toluene	2.379	1.497
benzene	2.274	1.5011
chlorobenzene	5.689	1.524
o-dichlorobenzene	10.12	1.551
m-dichlorobenzene	5.02	1.546

$$F = \frac{2(\varepsilon - 1)(n^2 + 2)}{3(2\varepsilon + n^2)} \cdot \frac{\mu_0}{a^3}$$

Cartesian coordinates of the geometry optimized phenol/aromatic complexes

phenol/benzene

C	-0.35118	-1.73493	-1.04343
C	0.97033	-1.72093	-1.49026
C	1.60696	-0.50691	-1.74954
C	0.92308	0.69378	-1.55820
C	-0.39684	0.67994	-1.10651
C	-1.03466	-0.53423	-0.85085
H	-0.85004	-2.68243	-0.85464
H	1.50298	-2.65639	-1.64304
H	2.63566	-0.49683	-2.10099
H	1.41862	1.64008	-1.76011
H	-0.92981	1.61603	-0.95888
H	-2.06729	-0.54327	-0.51049
C	1.83580	-0.10991	2.26492
C	2.97028	0.58549	2.68254
C	3.32712	0.59119	4.03077
C	2.54892	-0.09894	4.96197
C	1.41344	-0.79447	4.54433
C	1.06517	-0.79476	3.19927
H	1.56885	-0.10782	1.21504
H	3.57437	1.12178	1.95566
H	4.21133	1.13299	4.35598
H	2.82660	-0.09507	6.01230
H	0.80439	-1.33292	5.26437
O	-0.05008	-1.48317	2.82125
H	-0.15003	-1.38195	1.85880

phenol/toluene

C	2.24877400	-1.69728400	0.76194500
C	2.39014800	-0.59125600	1.60488100
C	2.62536700	0.67716700	1.06543400
C	2.72363500	0.86904000	-0.32092700
C	2.57466200	-0.24929200	-1.15642700
C	2.34211100	-1.52063600	-0.62416800
C	3.00287800	2.23525600	-0.90419000
H	4.02997200	2.29790300	-1.28405000
H	2.33322000	2.45668100	-1.74201600
H	2.87901400	3.02245800	-0.15507600
H	2.07103300	-2.68483500	1.17752900
H	2.31621700	-0.71465700	2.68155800

H	2.73403100	1.53050300	1.73040200
H	2.64126900	-0.12402600	-2.23450500
H	2.23709300	-2.37290600	-1.28996000
C	-1.52134700	0.52704400	0.27482300
C	-2.45916000	1.53765900	0.50455700
C	-3.81932300	1.31284100	0.27825900
C	-4.23670700	0.05906500	-0.18287600
C	-3.31169300	-0.95833900	-0.41648500
C	-1.95035700	-0.72339800	-0.18738000
H	-0.46379700	0.70557100	0.45379700
H	-2.11916500	2.50527600	0.86337800
H	-4.54364700	2.10109100	0.45835600
H	-5.29137700	-0.12998200	-0.36275600
H	-3.62326200	-1.93452400	-0.77406600
O	-1.08524600	-1.75523700	-0.43230300
H	-0.17256700	-1.48386100	-0.24885000

phenol/p-xylene

C	2.27979100	-0.69966600	-1.10971900
C	2.31638100	-1.42637500	0.09229500
C	2.34716200	-0.69814900	1.28795100
C	2.34721300	0.70103700	1.28657000
C	2.31648500	1.42689900	0.08947300
C	2.27983600	0.69782000	-1.11109300
H	2.36840400	-1.22943500	2.23653400
H	2.25286500	1.22997800	-2.05944000
H	2.36847300	1.23419500	2.23410400
H	2.25284100	-1.23369200	-2.05702000
C	2.34551100	-2.93718700	0.08664300
H	1.64229800	-3.34868500	-0.64494300
H	3.34330800	-3.31107400	-0.17492700
H	2.08777800	-3.34469400	1.06847700
C	2.34584900	2.93768900	0.08085100
H	3.34432200	3.31089400	-0.17913400
H	1.64440700	3.34779800	-0.65319600
H	2.08591500	3.34722500	1.06126400
C	-1.70154200	0.00053400	0.62298200
C	-2.73589100	0.00266600	1.56306300
C	-4.07156200	0.00256500	1.15365600
C	-4.36614300	0.00029900	-0.21460900
C	-3.34398100	-0.00186700	-1.16366700
C	-2.00810400	-0.00175900	-0.74361800
H	-0.66335500	0.00066000	0.94614900

H	-2.49031800	0.00441700	2.62152400
H	-4.87121100	0.00422800	1.88781700
H	-5.40039300	0.00020700	-0.54748200
H	-3.56021900	-0.00364800	-2.22722600
O	-1.04399500	-0.00397400	-1.71503500
H	-0.15919100	-0.00361800	-1.31688900

phenol/mesitylene

C	2.070000	-1.336000	0.001000
C	2.115000	-0.650000	1.221000
C	2.192000	0.752000	1.198000
C	2.235000	1.462000	-0.007000
C	2.189000	0.742000	-1.213000
C	2.110000	-0.654000	-1.229000
H	2.015000	-2.424000	0.004000
C	2.109000	-1.397000	2.536000
H	1.718000	-2.412000	2.418000
H	3.124000	-1.478000	2.943000
H	1.497000	-0.884000	3.284000
H	2.212000	1.284000	-2.156000
C	2.351000	2.969000	-0.018000
H	1.711000	3.415000	-0.787000
H	2.072000	3.399000	0.948000
H	3.381000	3.281000	-0.234000
C	2.082000	-1.421000	-2.531000
H	3.008000	-1.992000	-2.670000
H	1.253000	-2.138000	-2.555000
H	1.972000	-0.750000	-3.387000
H	2.218000	1.298000	2.138000
C	-1.854000	0.644000	0.020000
C	-2.877000	1.596000	0.013000
C	-4.218000	1.202000	-0.003000
C	-4.528000	-0.162000	-0.012000
C	-3.517000	-1.123000	-0.005000
C	-2.176000	-0.719000	0.011000
H	-0.812000	0.954000	0.032000
H	-2.620000	2.652000	0.020000
H	-5.009000	1.946000	-0.009000
H	-5.566000	-0.483000	-0.025000
H	-3.746000	-2.184000	-0.012000
O	-1.223000	-1.701000	0.017000
H	-0.333000	-1.313000	0.034000

phenol/chlorobenzene

C	1.99179700	-1.68144400	-1.03744200
C	1.83692000	-2.24038100	0.23602500
C	2.06368700	-1.45391400	1.37078000
C	2.44512500	-0.11604200	1.24030400
C	2.59551800	0.42422500	-0.03873100
C	2.37195900	-0.34362900	-1.18284200
H	1.81863200	-2.28521900	-1.92329500
H	1.54803900	-3.28154300	0.34306200
H	1.94466100	-1.87996900	2.36239600
H	2.49377200	0.09672400	-2.16631200
H	2.62372600	0.49999300	2.11475800
Cl	3.07792000	2.10597400	-0.21082500
C	-1.73157300	0.56651200	0.10099900
C	-2.55254200	1.69098600	0.22423200
C	-3.94210200	1.56862900	0.15058800
C	-4.50742800	0.30402000	-0.04898200
C	-3.69964700	-0.82630500	-0.17332700
C	-2.30820000	-0.69362900	-0.09737200
H	-0.65034000	0.66733000	0.15762800
H	-2.09757400	2.66546800	0.37770800
H	-4.57590300	2.44461200	0.24674200
H	-5.58672200	0.19488300	-0.10837900
H	-4.12638700	-1.81202400	-0.32838700
O	-1.56015200	-1.83465500	-0.22566100
H	-0.61639700	-1.62875700	-0.15199200

phenol/o-dichlorobenzene

C	-1.34189400	2.37479900	0.42908200
C	-1.89055700	1.37074700	1.22828100
C	-2.32834300	0.17356800	0.65344800
C	-2.21340000	-0.01737200	-0.73232700
C	-1.66187700	0.99055000	-1.52932600
C	-1.22755100	2.18453700	-0.95194900
H	-1.01082500	3.30215800	0.88597600
H	-1.98592500	1.50484200	2.30022900
H	-0.80570900	2.96167400	-1.58147000
H	-1.57898000	0.82891300	-2.59843700
Cl	-2.74847100	-1.49426400	-1.49546800
Cl	-3.01324900	-1.05511300	1.68807400
C	2.20571600	-0.61524700	0.07161600
C	2.98011400	-1.77842900	0.10022100

S13

C	4.37489000	-1.70376800	0.10079300
C	4.99269700	-0.44831100	0.07239800
C	4.23153000	0.72021800	0.04374500
C	2.83460200	0.63492400	0.04362200
H	1.12009800	-0.67947400	0.07131000
H	2.48478500	-2.74494400	0.12236900
H	4.97265200	-2.60951800	0.12328100
H	6.07668700	-0.37630900	0.07250600
H	4.69905300	1.69933400	0.02144700
O	2.13262900	1.81254400	0.01503400
H	1.18081500	1.63509400	0.01058200

phenol/m-dichlorobenzene

C	1.608000	-0.358000	1.968000
C	1.885000	0.947000	1.553000
C	2.294000	1.160000	0.236000
C	2.431000	0.105000	-0.669000
C	2.147000	-1.188000	-0.226000
C	1.735000	-1.436000	1.086000
H	1.293000	-0.539000	2.991000
H	1.786000	1.783000	2.236000
H	1.527000	-2.450000	1.410000
H	2.751000	0.285000	-1.688000
Cl	2.652000	2.790000	-0.305000
Cl	2.320000	-2.526000	-1.346000
C	-2.232000	0.385000	-0.524000
C	-3.174000	1.007000	-1.348000
C	-4.541000	0.851000	-1.109000
C	-4.961000	0.061000	-0.033000
C	-4.032000	-0.566000	0.797000
C	-2.664000	-0.403000	0.549000
H	-1.169000	0.509000	-0.715000
H	-2.831000	1.616000	-2.180000
H	-5.269000	1.336000	-1.752000
H	-6.022000	-0.069000	0.164000
H	-4.346000	-1.181000	1.634000
O	-1.792000	-1.039000	1.394000
H	-0.878000	-0.860000	1.130000

Supporting References

(S1)   Andrews, S. S.; Boxer, S. G. *Rev. Sci. Instrum.* **2000,** *71*, 3567-3569.

(S2)   Andrews, S. S.; Boxer, S. G. *J. Phys. Chem. A* **2002,** *106*, 469-477.

(S3)   Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision A.02.*, Gaussian, Inc.: Wallingford CT, 2009.

(S4)   Becke, A. D. *J. Chem. Phys.* **1993,** *98*, 5648-5652.

(S5)   Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988,** *37*, 785-789.

(S6)   Dalosto, S. D.; Vanderkooi, J. M.; Sharp, K. A. *J. Phys. Chem. B* **2004,** *108*, 6450-6457.

(S7)   Zheng, J. R.; Kwak, K.; Asbury, J.; Chen, X.; Piletic, I. R.; Fayer, M. D. *Science* **2005,** *309*, 1338-1343.

(S8)   Corcelli, S. A.; Lawrence, C. P.; Skinner, J. L. *J. Chem. Phys.* **2004,** *120*, 8107-8117.

(S9)   Onsager, L. *J. Am. Chem. Soc.* **1936,** *58*, 1486-1493.

(S10) Fafarman, A. T.; Sigala, P. A.; Herschlag, D.; Boxer, S. G. *J. Am. Chem. Soc.* **2010,** *132*, 12811-12813.

(S11) Lide, D. R. *CRC handbook of chemistry and physics;* CRC Press: Boca Raton, FL, 2005.

Complete Citation of Reference 22
See supporting reference (S3).