7736 *J. Phys. Chem. A* **2004,** *108,* 7736−7743

Theoretical Study of Molecular Structures and Properties of the Complete Series of Chlorophenols

Jun Han, Richard L. Deming, and Fu-Ming Tao*

Department of Chemistry and Biochemistry, California State University, Fullerton, California 92834

Received: May 14, 2004; In Final Form: July 12, 2004

Density functional theory and ab initio molecular orbital calculations have been carried out to investigate the molecular structures and properties of all 19 chlorophenol congeners. The results have been delineanated systematically in terms of the position and the total number of chlorine substitutions. Intramolecular hydrogen bonding in ortho chlorophenols and the induction by the electron-withdrawing chlorine are identified as strongly affecting the stability, structure, and properties of these compounds. Ortho chlorophenols are found to be more stable than other isomers as a result of intramolecular hydrogen bonding. Correlations between the known acidities of chlorophenols and the molecular structures are presented. Ortho chlorophenols are more acidic than other isomers because of the large inductive effect of chlorine on the hydroxyl group in close proximity. For the same reason, the acidity of a chlorophenol increases with the number of chlorine substitutions. Major trends and variations in molecular structure and properties, including O−H and C−O bond lengths, O−H stretching and torsional frequencies, average C−C bond lengths, and C−Cl bond lengths, are discussed in light of the intramolecular hydrogen bonding and the induction of chlorine.

1. Introduction

Chlorophenols are widely distributed in the environment due to their agricultural and industrial uses as insecticides, herbicides, fungicides, and wood preservatives.[1−3] They are also generated from phenols in the chlorination of drinking water.[4] Moreover, chlorophenols have high toxicity, and it is well-known that these compounds exhibit properties that are hazardous to human health and the ecosystem.[5] Because of their toxicity and persistence in the environment, the US Environmental Protection Agency has designated eleven phenolic compounds as major priority pollutants and four chlorophenols (e.g., 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and PCP) are classified into the most toxic and carcinogenic class.[6] The World Health Organization formally qualified some of the chlorophenols, i.e., 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, and PCP, as compounds suspected of having carcinogenic properties.[7,8]

The environmental effects and fates of chlorophenols depend on their physical−chemical properties, and it is therefore important to establish structure−property relationships that allow a complete understanding of their environmental consequences. Extensive experimental and theoretical studies have been reported on molecular and vibrational structures of phenol and some substituted phenols.[9−12] However, very few studies have focused on chlorinated phenols.[13,14] No experimental structures of chlorophenols in the gas phase have been reported. Of the 19 possible chlorophenol congeners, only four of their crystal molecular structures were examined by X-ray diffraction.[15] Moreover, there is apparent lack of systematic studies on the complete series of chlorinated phenols. Previous experimental and theoretical studies[16−19] highlighted ortho-substituted phenols where intramolecular hydrogen bonding seemed to play a major role in determining the molecular structure and properties.

Among the molecular properties, the acid dissociation constant (as pK_a) has received the most attention. It correlates strongly with the solubility and partition coefficients as well as the chemical and biological activities of the compounds. It is known that the toxicity of a chlorophenol depends on the number and position of chlorine substitutions,[5,20] whereas the latter largely determine the acidity and solubility of the compound. Other physical and chemical properties of chlorophenols, particularly the acidity, are also determined by the molecular structure. Hence, it is important to obtain the structures of the complete series of chlorophenols and examine the relationships between molecular structures and properties.

In the present study, the molecular structures of the complete series of chlorophenols (19 possible compounds) have been calculated with the density functional theory and ab initio method using the extended 6-311++G(d,p) basis set. The computational results are delineanated systematically in the order of increasing number of chlorine substitution. Possible correlations of the calculated geometrical parameters and properties with the acidities of the chlorophenols are carefully examined. Intramolecular hydrogen binding in ortho-substituted chlorophenols is reemphasized, along with its profound impact on relevant geometrical parameters and properties. A detailed theoretical analysis of the structures and properties is presented to reveal the fundamental effects of chlorine substitution.

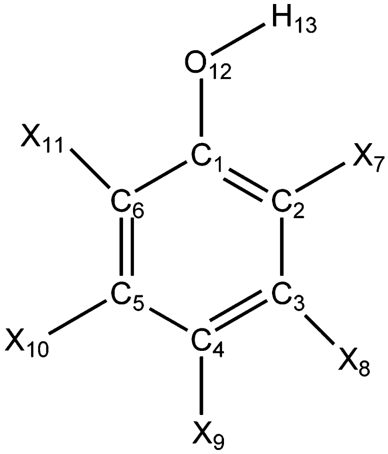
2. Method of Calculation

All 19 possible congeners of chlorophenols (CPs) are considered. They include three monochlorophenols (2-CP, 3-CP, and 4-CP), six dichlorophenols (2,3-DCP, 2,4-DCP, 2,5-DCP, 2,6-DCP, 3,4-DCP, and 3,5-DCP), six trichlorophenols (2,3,4-TCP, 2,3,5-TCP, 2,3,6-TCP, 2,4,5-TCP, 2,4,6-TCP, and 3,4,5-TCP), three tetrachlorophenols (2,3,4,5-TeCP, 2,3,4,6-TeCP, and 2,3,5−6-TeCP), and pentachlorophenol (PCP). It should be noted that there are two geometric conformers resulting from

---

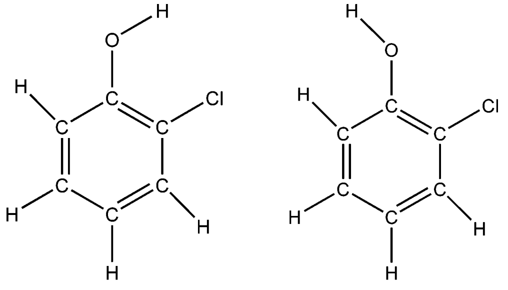
* To whom correspondence should be addressed. E-mail: ftao@fullerton.edu.

10.1021/jp047923r CCC: $27.50



X = H, or Cl

Figure 1. Structure and atom numbering scheme for the title chlorophenol.



2-CP 2-CP(*a*)

Figure 2. syn 2-CP and anti 2-CP (*a*) conformers of 2-chlorophenol.

the two main orientations of the hydroxyl hydrogen for each of the asymmetric chlorine substitutions. The conformer with the hydroxyl hydrogen facing toward the closest neighboring chlorine is labeled as the syn conformer and otherwise the anti (*a*) conformers. Figure 1 shows the schematic structure of the title molecule and its atomic numbering scheme. Figure 2 gives the syn and anti conformers for 2-chlorophenol. Only planar geometries are known to be stable for all halogen substituted phenols[10,13,16] and are thus considered in our study.

The geometries of all chlorophenols have been optimized by density functional theory (DFT)[21] calculations using Becke's three-parameter functional[22−24] and the nonlocal correlation of Lee, Yang, and Parr (B3LYP)[25] as well as by second-order Møller−Plesset perturbation approximation (MP2)[26,27] calculations. An extended basis set of Pople and co-workers, 6-311++G(d,p)[28−30] has been used. Harmonic vibrational frequencies and infrared intensities of the optimized geometries have also been obtained at the B3LYP/6-311++G(d,p) level. The density functional theory is known to give reliable harmonic frequencies based on available experimental data.[9,10,12,13] The structure of all chlorophenols considered carries the C_s symmetry. Since both the B3LYP and MP2 methods produce very similar values for all molecules, the discussion will be based on the B3LYP/6-311++G (d,p) results, unless otherwise specified. All calculations have been performed using the GAUSSIAN 98 computer program package.[31]

3. Results and Discussion

3.1. Energies of Chlorophenols. Table 1 shows the calculated energies, thermodynamic functions (enthalpy and free energy), and dipole moments of all chlorophenols including both syn and anti conformers. The stability of a conformer with a given number of chlorine atoms is determined by its relative energy, ΔE, or ΔE_0 (including the zero-point energy correction), with respect to the most stable isomer. It is clear from the table that the syn conformers are more stable than the corresponding anti conformers. For monochlorophenols, the ortho isomer (2-CP) is the most stable, whereas the para isomer (4-CP) is the least stable and is 1.42 kcal mol^{-1} higher. The meta isomer (3-CP) is 0.92 kcal mol^{-1} higher than the ortho isomer. Similarly, 2,5-DCP, 2,3,5-TCP, and 2,3,5,6-TeCP are shown to be the most stable isomers, whereas 3,4-DCP, 3,4,5-TCP, and 2,3,4,5-TeCP are the least stable isomers for the di-, tri-, and tetrachlorophenols, respectively. The relative energies vary in the range from less than 0.5 kcal mol^{-1} to more than 4.0 kcal mol^{-1}. The relative stability of chlorophenols appears to be assisted and dominated by the effect of intramolecular hydrogen bonding, as discussed below. In contrast, chlorine substituent at adjacent positions seems to destabilize the isomers, and the resulting steric effect may also strongly affect the relative stability of chlorophenol isomers.

The hydroxyl group and the ortho-substituted chlorine may interact and result in intramolecular hydrogen bonding in the syn conformers. Clearly, such hydrogen bonding is absent in the anti conformers except those with chlorine substitutions at both ortho positions. The hydrogen bond energy can thus be determined by the difference in energy between the syn and anti conformers. The hydrogen bond energies are typically 3.0 kcal mol^{-1} and tend to increase slightly with the chlorine substitution. For example, the hydrogen bond energies of 2-CP, 2,3-DCP, 2,3,4-TCP, 2,3,4,5-TeCP are 3.09, 3.18, 3.22, and 3.12 kcal mol^{-1}. A similar trend was observed for nitrophenols.[12] The hydrogen bonding appears to stabilize the isomers with ortho substitutions. However, isomers with ortho substitutions are not consistently more stable than those without ortho substitutions. For example, 3,5-DCP is 1.23 kcal mol^{-1} more stable than 2,3-DCP. This may indicate that chlorine substitutions at adjacent positions would destabilize the isomers. For example, 2,3,4-TCP has multiple chlorine substitutions and is thus the least stable among all ortho isomers of TCP. Lack of intramolecular hydrogen bonding combined with multiple chlorine substitutions at neighboring positions make 3,4,5-TCP the least stable among all isomers of TCP. Similarly, 2,3,4,5-TeCP is the least stable among all isomers of TeCP. This may suggest that the steric effect resulting from chlorine substituents at close neighboring positions is responsible for the destabilization of chlorophenol isomers.

Other thermodynamic energies such as enthalpy and free energy as well as their relative values are shown in Table 1. The relative values, ΔH and ΔG, follow the same trend and remain nearly constant as ΔE. These thermodynamic data are valuable for characterizing the molecular properties of chlorophenols in the gas phase. In the table are also listed the calculated dipole moments for all the chlorophenols. The dipole moment of a chlorophenol has contribution mainly from the O−H bond dipole and C−Cl bond dipoles and is approximately the vector sum of the contributing bond dipoles. The dipole moments are expected be related to the bulk properties of the chlorophenols and should be valuable for predicting and understanding the solvent chemistry.

3.2. Structural Parameters. Table 2 summarizes the ranges of calculated bond lengths and bond angles of the 19 chlorophenols from the B3LYP and MP2 calculations with the 6-311++G(d,p) basis set (the complete geometric data are available in the Supporting Information). Table 3 gives selected

TABLE 1: Calcultaed Energies E (Hartree), Zero-Point Energies (ZPE; kcal mol^{-1}), Enthalpies H (Hartree), Free Energies G (Hartree), Dipole Moments μ (Debye) of All Chlorophenols and Phenol from B3LYP/6-311++G(d,p) Level[a]

compound	E	ZPE	ΔE	ΔE_0	E(MP2)	ΔE(MP2)	H	ΔH	G	ΔG	μ
phenol	−307.55873	65.23			−306.66628		−307.44823		−307.48384		1.384
2-CP	−767.18281	59.51	0	0	−765.72801	0	−767.08039	0	−767.11910	0	1.044
2-CP(*a*)	−767.17788	59.37	3.09	2.90	−765.72384	2.62	−767.07558	3.02	−767.11453	2.87	3.096
3-CP	−767.18134	59.33	0.92	0.74	−765.72646	0.97	−767.07908	0.82	−767.11811	0.62	0.873
3-CP(*a*)	−767.18130	59.27	0.95	0.71	−765.72641	1.00	−767.07914	0.78	−767.11817	0.58	3.095
4-CP	−767.18055	59.29	1.42	1.20	−765.72529	1.71	−767.07834	1.29	−767.11740	1.07	2.285
2,3-DCP	−1226.80032	53.45	2.37	2.39	−1224.78488	1.40	−1226.70633	2.38	−1226.74834	2.48	1.151
2,3-DCP(*a*)	−1226.79525	53.34	5.55	5.46	−1224.78058	4.10	−1226.70136	5.46	−1226.74357	5.47	3.932
2,4-DCP	−1226.80335	53.45	0.47	0.49	−1224.78638	0.46	−1226.70935	0.44	−1226.75153	0.48	0.846
2,4-DCP(*a*)	−1226.79865	53.35	3.42	3.34	−1224.78229	3.02	−1226.7046	3.45	−1226.74701	3.31	3.019
2,5-DCP	−1226.80410	53.43	0	0	−1224.78711	0	−1226.71014	0	−1226.75229	0	1.500
2,5-DCP(*a*)	−1226.79926	53.37	3.04	2.98	−1224.78304	2.55	−1226.70528	3.01	−1226.74765	2.91	1.301
2,6-DCP	−1226.80084	53.58	2.05	2.00	−1224.78501	1.32	−1226.70668	2.13	−1226.74870	2.25	2.155
3,4-DCP	−1226.79803	53.31	3.81	3.69	−1224.78204	3.18	−1226.70415	3.70	−1226.74650	3.64	2.301
3,4-DCP(*a*)	−1226.79791	53.25	3.88	3.70	−1224.78187	3.29	−1226.70413	3.77	−1226.74649	3.64	3.545
3,5-DCP	−1226.80229	53.27	1.14	0.98	−1224.78545	1.04	−1226.70848	1.00	−1226.75091	0.87	2.184
2,3,4-TCP	−1686.41596	47.33	2.84	2.78	−1683.84010	2.07	−1686.33046	2.76	−1686.37581	2.84	1.553
2,3,4-TCP(*a*)	−1686.41083	47.29	6.06	6.05	−1683.83570	4.83	−1686.32532	6.02	−1686.37085	5.95	3.930
2,3,5-TCP	−1686.42048	47.39	0	0	−1683.84340	0	−1686.33491	0	−1686.38033	0	0.872
2,3,5-TCP(*a*)	−1686.41551	47.34	3.12	3.07	−1683.83919	2.64	−1686.32992	3.14	−1686.37554	3.01	2.544
2,3,6-TCP	−1686.41749	47.52	1.88	2.01	−1683.84119	1.39	−1686.33174	2.01	−1686.37704	2.06	0.971
2,3,6-TCP(*a*)	−1686.41732	47.50	1.98	2.09	−1683.84105	1.47	−1686.3316	2.07	−1686.37689	2.16	2.549
2,4,5-TCP	−1686.41970	47.34	0.49	0.44	−1683.84216	0.78	−1686.33417	0.44	−1686.37965	0.43	1.861
2,4,5-TCP(*a*)	−1686.41506	47.31	3.40	3.32	−1683.83830	3.20	−1686.32948	3.39	−1686.37517	3.24	2.164
2,4,6-TCP	−1686.42007	47.47	0.26	0.18	−1683.84256	0.53	−1686.33437	0.31	−1686.37984	0.31	1.411
3,4,5-TCP	−1686.41398	47.23	4.08	3.92	−1683.83777	3.53	−1686.32855	3.95	−1686.37414	3.88	3.033
2,3,4,5-TeCP	−2146.03114	41.31	1.19	1.07	−2142.89529	0.96	−2145.954	1.07	−2146.00255	1.09	1.799
2,3,4,5-TeCP(*a*)	−2146.02616	41.22	4.32	4.11	−2142.89111	3.58	−2145.94907	4.14	−2145.99784	4.04	3.020
2,3,4,6-TeCP	−2146.03219	41.40	0.53	0.50	−2142.89606	0.48	−2145.9549	0.50	−2146.00352	0.48	0.890
2,3,4,6-TeCP(*a*)	−2146.03187	41.40	0.73	0.70	−2142.89574	0.68	−2145.95458	0.69	−2146.00318	0.69	2.310
2,3,5,6-TeCP	−2146.03304	41.43	0	0	−2142.89682	0	−2145.95572	0	−2146.00428	0	1.395
PCP	−2605.64257	35.32			−2601.94800		−2605.57373		−2605.62540		1.754

[a] The relative energies (ΔE, ΔE_0, ΔH, ΔG) are with respect to the most stable isomer with a given number of chlorine atoms.

TABLE 2: Ranges of Bond Lengths (Å) and Bond Angles (°) of Chlorophenols and Phenol Optimized with B3LYP and MP2 Methods Using the 6-311++G(d,p) Basis Set

	chlorophenol		phenol		
parameters	B3LYP	MP2	B3LYP	MP2	exp.[a]
r(O$_{12}$−H$_{13}$)	0.963−0.968	0.962−0.967	0.963	0.963	0.956
r(C$_1$−O$_{12}$)	1.347−1.369	1.350−1.370	1.370	1.371	1.364
r(C$_2$-X$_7$) X=H	1.083−1.086	1.087−1.088	1.086	1.087	
X=Cl	1.749−1.765	1.729−1.740			
r(C$_3$-X$_8$) X=H	1.081−1.083	1.085−1.086	1.084	1.085	1.076
X=Cl	1.735−1.759	1.719−1.737			
r(C$_4$-X$_9$) X=H	1.080−1.083	1.084−1.086	1.083	1.087	1.082
X=Cl	1.737−1.761	1.719−1.737			
r(C$_5$-X$_{10}$) X=H	1.081−1.084	1.085−1.086	1.084	1.086	
X=Cl	1.735−1.756	1.720−1.735			
r(C$_6$-X$_{11}$) X=H	1.081−1.083	1.084−1.096	1.083	1.086	
X=Cl	1.735−1.748	1.716−1.727			
r(C$_1$−C$_2$)	1.393−1.405	1.397−1.408	1.396	1.400	
r(C$_2$−C$_3$)	1.387−1.402	1.394−1.409	1.394	1.399	
r(C$_3$−C$_4$)	1.388−1.401	1.394−1.407	1.393	1.401	
r(C$_4$−C$_5$)	1.390−1.404	1.395−1.407	1.396	1.401	
r(C$_5$−C$_6$)	1.385−1.398	1.392−1.404	1.391	1.400	
r(C$_6$−C$_1$)	1.391−1.404	1.393−1.407	1.396	1.400	
$\angle C_1C_2C_3$	118.6−122.5	118.8−122.2	119.7	119.8	
$\angle C_2C_3C_4$	118.4−122.2	118.5−122.0	120.5	120.4	
$\angle C_3C_4C_5$	117.4−121.1	117.6−121.0	119.3	119.4	
$\angle C_4C_5C_6$	119.2−122.4	119.2−122.2	120.8	120.6	
$\angle C_5C_6C_1$	118.5−121.8	118.7−121.4	119.6	119.6	
$\angle C_6C_1C_2$	117.2−120.5	117.6−120.8	120.2	120.2	
$\angle C_1O_{12}H_{13}$	109.1−110.3	107.6−108.9	109.7	108.4	109.0
$\angle C_2C_1O_{12}$	122.2−123.5	122.4−123.5	122.5	122.7	122.5
$\angle C_1C_2X_7$ X=H	120.3−121.1	120.2−121.1	120.0	120.0	
X=Cl	117.1−118.8	117.0−118.6			

[a] Reference 9.

bond lengths and bond angles from the B3LYP/6-311++G(d,p) calculations. Equilibrium geometries of phenol are also obtained at both levels for comparison. It should be noted that no experimental gas phase geometries have been reported for the chlorophenols. As shown in Table 2, the calculated and the experimental geometries for phenol are in good agreement.[9,20] The calculated geometries for chlorophenols are thus expected to be reasonable.

As shown in Table 3, the O−H bond lengths, r(O−H), are nearly constant at 0.963 Å for all structures without intramolecular hydrogen bonding, such as 2-CP(*a*), 3-CP, 3,5-DCP, and 3,4,5-TCP. In contrast, the O−H bond lengths are considerably longer and increase slightly farther with multiple chlorine substituents for structures with intramolecular hydrogen bonding. For example, the O−H bond lengths of 2-CP, 2,3-DCP, 2,3,4-TCP, and 2,3,5,6-TeCP are 0.9668, 0.9671, 0.9672, and 0.9679 Å, respectively. The lengthening of the O−H bond length may primarily result from the intramolecular hydrogen bonding between the hydroxyl hydrogen and the neighboring chlorine atom. However, the O−H bond length may also be influenced by a secondary effect from substituted chlorine, as evidenced by the further increase in the O−H bond length resulting from multiple chlorine substitutions. Such an effect might be attributed to the inductive nature of chlorine, as will be discussed in section 3.4.

It is interesting to note that the O−H bond lengths correlate with the known pK_a values of chlorophenols[32−35] in aqueous solution, as shown in Figure 3. The pK_a values are listed in Table 3 and are selected from recent experimental results. For a given number of chlorine substitutions, all ortho isomers have relative longer O−H bond lengths and lower pK_a values, whereas meta or para isomers have shorter O−H bond lengths and higher pK_a values. The weakening of O−H bond enhances

TABLE 3: Selected Bond Lengths (Å) and Bond Angles (°) of Chlorophenols Calculated at B3LYP/6-311++G(d,p) Level of Theory and Related pK_a Values in Aqueous Solution

compound	pK_a[a]	r(O−H) (Å)	r(C−O) (Å)	r_{av}(C−Cl) (Å)	∠$C_1C_2X_7$ (°)	∠$C_1O_{12}H_{13}$(°)	∠$C_2C_1O_{12}$ (°)
phenol	9.92	0.9627	1.3702		120.05	109.73	122.53
2-CP	8.52	0.9668	1.3579	1.7648	118.41	109.33	123.23
2-CP(*a*)		0.9629	1.3611	1.7514	119.62	109.56	118.50
3-CP	8.79	0.9630	1.3669	1.7595	120.97	110.14	122.18
3-CP(*a*)		0.9629	1.3665	1.7594	119.88	109.94	116.77
4-CP	9.37	0.9628	1.3685	1.7605	120.26	109.99	122.79
2,3-DCP	7.71	0.9671	1.3557	1.7504	118.01	109.53	122.51
2,3-DCP(*a*)		0.9631	1.3595	1.7437	118.89	109.61	117.63
2,4-DCP	7.9	0.9667	1.3567	1.7590	118.54	109.47	123.38
2,4-DCP(*a*)		0.9630	1.3598	1.7526	119.71	109.79	118.46
2,5-DCP	7.51[b]	0.9670	1.3550	1.7584	118.55	109.42	123.30
2,5-DCP(*a*)		0.9631	1.3582	1.7524	119.75	109.92	118.48
2,6-DCP	6.78	0.9672	1.3504	1.7552	117.78	109.10	123.34
3,4-DCP	8.62	0.9628	1.3650	1.7482	120.87	110.33	122.55
3,4-DCP(*a*)		0.9629	1.3657	1.7479	119.69	110.06	116.96
3,5-DCP	8.25	0.9631	1.3639	1.7555	121.09	110.23	122.36
2,3,4-TCP	6.97	0.9672	1.3546	1.7454	117.67	109.60	122.85
2,3,4-TCP(*a*)		0.9631	1.3587	1.7411	118.46	109.74	117.83
2,3,5-TCP	6[c]	0.9675	1.3530	1.7491	118.12	109.59	122.57
2,3,5-TCP(*a*)		0.9632	1.3568	1.7450	119.03	109.96	117.61
2,3,6-TCP	5.8	0.9676	1.3485	1.7473	117.41	109.28	122.65
2,3,6-TCP(*a*)		0.9675	1.3484	1.7473	118.26	109.07	118.48
2,4,5-TCP	6.72	0.9669	1.3544	1.7495	118.76	109.54	123.50
2,4,5-TCP(*a*)		0.9632	1.3574	1.7456	119.92	110.09	118.52
2,4,6-TCP	5.99	0.9672	1.3492	1.7531	117.88	109.21	123.52
3,4,5-TCP	7.8[d]	0.9631	1.3633	1.7435	121.08	110.33	122.72
2,3,4,5-TeCP	5.64	0.9673	1.3525	1.7419	117.76	109.61	122.97
2,3,4,5-TeCP(*a*)		0.9633	1.3565	1.7388	118.57	109.99	117.92
2,3,4,6-TeCP	5.22	0.9676	1.3479	1.7434	117.08	109.34	122.99
2,3,4,6-TeCP(*a*)		0.9674	1.3482	1.7434	117.83	109.16	118.68
2,3,5,6-TeCP	5.03	0.9679	1.3473	1.7245	117.70	109.26	122.40
PCP	4.74	0.9678	1.3471	1.7380	117.30	109.27	122.70

[a] Reference 32. [b] Reference 33. [c] Reference 34. [d] Reference 35.

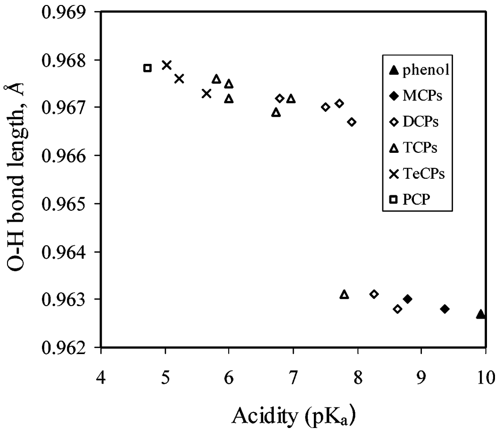


Figure 3. Dependence of the O−H bond lengths (Å) on pK_a values of chlorophenols. In the upper left region are data points for ortho-chlorophenols that have relative longer bond lengths and lower pK_a values, whereas points for other chlorophenols are located in the lower right area. For the data point of a specific compound, refer to the pK_a value listed in Table 3. Structural data in Figures 3−6 are for the syn conformers.

the deprotonation of the hydroxyl hydrogen, and consequently increases the acidity of chlorophenols.

Similarly, the C−O bond lengths of chlorophenols are influenced by chlorine substitutions. As shown in Table 4, all C−O bond lengths of chlorophenols are consistently shorter than 1.3702 Å, the bond length of phenol, and generally decrease with increasing chlorine substitution. The ortho-substitution has the largest effect and the C−O bond lengths of ortho-substituted chlorophenols are typically 0.021 Å shorter than the C−O bond length of phenol. All meta or para isomers have relative longer C−O bond distances compared to the corresponding ortho isomers. For example, 2-CP, 3-CP, and 4-CP have C−O bond lengths of 1.3579, 1.3665, and 1.3685 Å, respectively. The similar observation can be found in dichlorophenols as well as in trichlorophenols. This effect may be attributed to the fact that the electron withdrawing chlorine atom reduces the electron population in the antibonding orbitals between the electron rich oxygen and its neighboring carbon. The immediate consequence of such an effect is the reduction in the C−O bond length, and therefore, an increase in the bond strength. It is anticipated that the electron withdrawing effect on the C−O bond length decreases with the distance of the substituted chlorine atom from the OH group. Additionally, the C−O bond lengths of anti conformers are systematically 0.003 Å longer that those of syn conformers in ortho-substituted chlorophenols, which may be due to the lack of intramolecular hydrogen bonding in these anti conformers.

The C−O bond lengths also correlate with the pK_a values of chlorophenols. As in Figure 4, a shorter C−O bond length corresponds to a lower pK_a value, both resulting from the electron withdrawing effect of substituted chlorine. It should be noted that the chlorine substituent tends to stabilize the phenolate anion as a result of enhanced induction and resonance effects[36] and therefore increases the acidity of a chlorophenol.

The C−Cl bond lengths of chlorophenols also vary with the positions and the total number of chlorine substitutions. Generally, the bond lengths decrease with the increasing number of chlorine substitutions, as shown in Table 3. For example, the average bond lengths for 2-CP, 2,3-DCP, 2,3,4-TCP, 2,3,4,5-TeCP, and PCP are 1.7648, 1.7504, 1.7454, 1.7419, and 1.7380 Å, respectively. It should be noted that the C−Cl bond at the ortho position is longer in the syn conformer than the corre-

TABLE 4: Average Values of C−C Bond Length r_{av} (Å) and Standard Deviations σ

	B3LYP/6-311++G(p,d)		MP2/6-311++G(p,d)	
compound	r_{av}	$\sigma \times 10^3$	r_{av}	$\sigma \times 10^3$
phenol	1.3943	2.1	1.3994	1.4
2-CP	1.3939	4.2	1.3991	3.1
2-CP(*a*)	1.3942	3.7	1.3994	2.7
3-CP	1.3931	3.2	1.3982	2.1
3-CP(*a*)	1.3930	2.7	1.3982	1.8
4-CP	1.3928	2.6	1.3982	1.8
2,3-DCP	1.3947	5.5	1.3998	4.6
2,3-DCP(*a*)	1.3952	5.5	1.4002	4.9
2,4-DCP	1.3927	4.2	1.3982	3.3
2,4-DCP(*a*)	1.3932	4.3	1.3985	3.3
2,5-DCP	1.3928	4.8	1.3981	3.8
2,5-DCP(*a*)	1.3932	4.7	1.3985	3.6
2,6-DCP	1.3942	6.2	1.3995	4.5
3,4-DCP	1.3936	3.6	1.3988	3.3
3,4-DCP(*a*)	1.3936	3.3	1.3987	3.2
3,5-DCP	1.3922	3.6	1.3974	2.5
2,3,4-TCP	1.3956	6.2	1.4008	5.8
2,3,4-TCP(*a*)	1.3962	6.6	1.4011	6.1
2,3,5-TCP	1.3941	5.8	1.3991	5.0
2,3,5-TCP(*a*)	1.3945	6.4	1.3995	5.6
2,3,6-TCP	1.3952	6.7	1.4002	5.4
2,3,6-TCP(*a*)	1.3953	7.1	1.4003	5.7
2,4,5-TCP	1.3936	5.2	1.3988	4.7
2,4,5-TCP(*a*)	1.3940	4.4	1.3991	3.9
2,4,6-TCP	1.3935	6.4	1.3987	4.8
3,4,5-TCP	1.3948	5.9	1.3998	5.5
2,3,4,5-TeCP	1.3970	6.6	1.4022	6.8
2,3,4,5-TeCP(*a*)	1.3975	6.4	1.4029	5.6
2,3,4,6-TeCP	1.3963	6.4	1.4016	5.6
2,3,4,6-TeCP(*a*)	1.3965	7.6	1.4012	6.3
2,3,5,6-TeCP	1.3963	6.3	1.4012	5.0
PCP	1.3999	2.5	1.4037	2.9

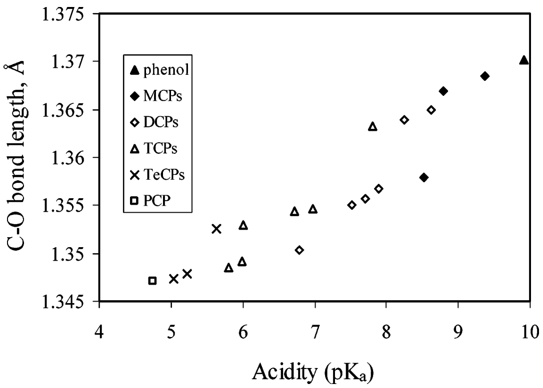


Figure 4. Dependence of the C−O bond lengths (Å) on pK_a of chlorophenols. For chlorophenols with a given number of chlorine atoms, the ortho-isomer has a shorter C−O bond length and a lower pK_a value than that for the meta- or para-isomer.

sponding anti conformer or C−Cl bonds at other positions. This is primarily due to the intramolecular hydrogen bonding present in the syn conformer of an ortho-substituted chlorophenol. The C−Cl bond of the syn conformer is typically 0.013 Å longer than that of the corresponding anti conformer. The inductive effect of chlorine seems to explain why the C−Cl bond lengths are so influenced by multiple chlorine substitutions. Because the electron density shifting to the chlorine atoms occupies molecular orbitals with strong antibonding characteristics, the C−Cl bond is longer for fewer chlorine substitutions. The electron density available from the phenol ring for each chlorine atom to withdraw decreases with the increasing number of chlorine substitutions. As a result, the C−Cl bond length decreases with the increase in chlorine substitutions.

It is interesting to note that the average C−C bond length in the phenol ring, r_{av}, depends on the degree of chlorine substitution. As shown in Table 4, the r_{av} initially decreases with the first or second chlorine substitution and then increases with a higher number of substitutions. Relative to phenol, slight reductions in r_{av}, 0.001 and 0.002 Å, are observed for the mono- and dichlorophenols, respectively. However, the r_{av} increases progressively by 0.001 to 0.006 Å from trichlorophenols to pentachlorophenol. A similar pattern was observed by Koll et al. for a series of chloro-substituted *N*,*N*-dimethylaminomethylphenols.[18] Apparently, the chlorine substitution has a rather complicated and yet systematic effect on the electronic structure at the phenol ring. Section 3.4 below provides a detailed theoretical analysis and explanation for such an interesting observation.

The C−C bond lengths for each chlorophenol vary over a considerable range. The degree of the variations for a given phenol ring can be described by the standard deviation, σ, which measures the extent of the ring distortion. Overall, as given in Table 4, the ring distortion systematically increases with the number of substituted chlorine atoms at the phenol ring. A notable exception is for PCP where there is virtually no ring distortion, attributed to the restoration of symmetry with the full substitution on the aromatic system.

Intramolecular hydrogen bonding also affects certain bonding angles such as $\angle C_1O_{12}H_{13}$ and $\angle C_1C_2Cl_7$. As shown in Table 4, the angles $\angle C_1O_{12}H_{13}$ for ortho-substituted chlorophenols are relatively small (109.2−109.5°) compared to those without ortho substitutions such as 3,4- and 3,5-dichloro and 3,4,5-trichloro phenols (110.1−110.3°). It is worth noting that the calculated $\angle C_1O_{12}H_{13}$ angle for phenol is in good agreement with the experimental value (109.0°) from the microwave study of phenol vapor.[9] Slightly larger $\angle C_1O_{12}H_{13}$ angles are observed for the anti conformers where intramolecular hydrogen bonding is absent. For the same reason, the $\angle C_1C_2Cl_7$ angles for all ortho chlorophenols are smaller (about 118.0°) than those for all nonortho forms (by at least 2°). The $\angle C_1C_2Cl_7$ angles are larger for the anti conformers without intramolecular hydrogen bonding. Clearly, intramolecular hydrogen bonding plays a key role in the variations of these bond angles.

Other bond angles also vary with the different chlorine substitutions, in the range of 118−122°. The largest variation is in the bond angle of $\angle C_2C_1O_{12}$. As shown in Table 3, smaller $\angle C_2C_1O_{12}$ angles are obtained for all anti conformers than for the corresponding syn conformers. For example, the $\angle C_2C_1O_{12}$ angles for 2-CP, 2-CP(*a*), 2,3,4,5-TeCP, and 2,3,4,5-TeCP(*a*) are 123.23°, 118.50°, 122.97°, and 117.92°, respectively. The relatively large variation in the $\angle C_2C_1O_{12}$ angle results from the steric interactions of the OH group with the neighboring hydrogen and chlorine atoms.

3.3. Infrared Vibrational Frequencies. Harmonic frequencies and IR intensities are calculated for all 33 conformers of the 19 chlorophenol congeners. For each conformer, there are 33 normal modes of vibration. The calculated harmonic frequencies and IR intensities at the B3LYP/6-311++G(d,p) level are available in the Supporting Information Table 3. Selected harmonic frequencies and IR intensities for the O−H and C−O stretching, O−H torsional and bending modes are given in Table 5. These frequencies and intensities vary systematically depending on the number and the position of chlorine substitutions at the phenolic ring. The calculated harmonic vibrational frequencies and IR intensities for phenol and 4-chlorophenol are in good agreement with available experimental values.[9,13] No experimental frequencies have been

TABLE 5: Selected Vibrational Frequencies ν (cm^{-1}) and IR Intensities A (km mol^{-1}) of chlorophenols and phenol calculated with B3LYP/6-311++G(d,p) Level of Theory[a]

	ν(O−H)		τ(O−H)		δ(O−H)		ν(C−O)	
compound	ν	A	ν	A	ν	A	ν	A
phenol	3837.3	61.7	311.5	110.8	1191.7	124.5	827.3	22.8
exp.[b]	3656.7	50	309.2	47	1176.5	80	823.2	20
2-CP	3767.1	92.1	409.3	108.3	1210.8	115.8	842.5	13.2
2-CP(*a*)	3835.7	73.1	315.8	95.3	1189.6	84.3	841.7	21.1
3-CP	3833.9	66.7	308.1	11.4	1191.0	88.1	893.7	83.6
3-CP(*a*)	3835.2	73.0	306.4	111.1	1192.4	110.3	894.9	108.8
4-CP	3837.4	72.9	302.2	102.5	1186.4	169.4	835.6	1.6
exp.[c]	3609	55	303		1176	35.6	823	11.3
2,3-DCP	3760.7	93.4	413.6	105.6	1195.6	74.0	910.1	75.7
2,3-DCP(*a*)	3834.5	81.3	316.7	86.6	1164.0	72.7	908.0	113.8
2,4-DCP	3768.6	99.5	399.5	108.2	1208.4	151.3	859.5	13.1
2,4-DCP(*a*)	3836.8	91.2	297.3	98.9	1187.1	79.3	861.6	21.5
2,5-DCP	3764.7	103.7	407.3	106.9	1208.2	115.7	910.9	74.4
2,5-DCP(*a*)	3834.9	80.6	326.9	54.1	1186.5	86.7	909.4	63.2
2,6-DCP	3760.5	99.5	415.9	92.6	1188.9	56.8	843.7	13.4
3,4-DCP	3837.7	79.4	302.5	105.3	1188.3	165.8	907.2	41.6
3,4-DCP(*a*)	3837.4	76.4	300.8	109.6	1191.8	134.4	908.8	61.5
3,5-DCP	3834.6	80.0	310.9	109.9	1186.5	110.4	941.6	98.4
2,3,4-TCP	3759.5	100.9	407.0	105.3	1219.4	115.9	925.0	34.2
2,3,4-TCP(*a*)	3834.6	91.8	297.1	84.7	1212.6	129.6	924.7	62.4
2,3,5-TCP	3755.2	102.0	417.0	103.9	1243.1	55.5	955.0	98.9
2,3,5-TCP(*a*)	3833.7	88.5	325.9	25.1	1239.9	101.0	951.4	109.3
2,3,6-TCP	3753.3	105.3	418.4	96.1	1238.7	58.9	919.6	62.7
2,3,6-TCP(*a*)	3756.4	115.5	416.4	90.9	1250.0	88.7	919.8	78.8
2,4,5-TCP	3767.4	109.6	396.0	107.5	1208.4	135.9	935.9	13.2
2,4,5-TCP(*a*)	3835.2	89.9	304.2	99.9	1180.9	122.9	935.3	10.0
2,4,6-TCP	3761.5	112.6	404.4	96.1	1177.7	119.6	869.5	14.6
3,4,5-TCP	3835.4	90.8	303.3	106.9	1190.4	104.6	956.3	39.1
2,3,4,5-TeCP	3759.2	107.9	405.3	104.0	1221.4	141.9	976.0	18.4
2,3,4,5-TeCP(*a*)	3833.1	96.6	306.9	88.7	1203.3	236.3	973.6	23.8
2,3,4,6-TeCP	3754.1	111.5	407.6	96.5	1218.2	85.2	943.0	6.5
2,3,4,6-TeCP(*a*)	3759	120.0	398.8	93.4	1229.0	145.2	942.5	15.0
2,3,5,6-TeCP	3748.9	113.3	425.0	91.4	1239.3	80.1	960.6	111.3
PCP	3749.2	113.9	420.7	94.6	1218.1	160.2	983.1	18.6

[a] Abbreviations: ν, stretching; τ, torsional vibration; δ, in-plane bending. [b] Reference 9. [c] Reference 13.

reported for other chlorophenols. It should be noted that most of the vibrational modes are highly delocalized and coupled with multiple functional groups. Among the 33 normal modes, the vibrational modes involving the hydroxyl group are relatively pure and localized, yet reflect the environmental changes at the phenolic ring and consequently will be discussed below.

3.3.1. O-H Stretching Vibration. The harmonic frequencies for the O−H stretch in chlorophenols, ν(O−H), are in the range from 3749 to 3838 cm^{-1}, all with high IR intensities. The values of ν(O−H) are strongly affected by intramolecular hydrogen bonding, which typically reduces ν(O−H) by 70 to 88 cm^{-1} (red shifted). The values of ν(O−H) for all non-hydrogen-bonded conformers are nearly constant regardless of the number of chlorine substituents and close to 3837 cm^{-1} for phenol. In the conformers with intramolecular hydrogen bonding, the red shift increases slightly with multiple chlorine substituents. It should be noted that the calculated harmonic frequencies are usually overestimated, since molecular vibrations are known to be anharmonic. For phenol, the calculated value of ν(O−H) multiplied by a scaled factor of 0.953[10] would give excellent agreement with the experimental value.[9] The similarly scaled frequency for 4-CP, 3657 cm^{-1}, is also in good agreement with the experimental value of 3609 cm^{-1}.[13]

A strong linear correlation ($r^2 = 0.9989$) exists between the harmonic frequency ν(O−H) and the bond length r(O−H) for all stable conformers, as shown in Figure 5. A lower value of ν(O−H) corresponds to a longer bond length r(O−H), both indicating a weakening OH bond. Such a strong correlation may even suggest a reasonable estimate of the O−H stretching frequency based on the O−H bond length.

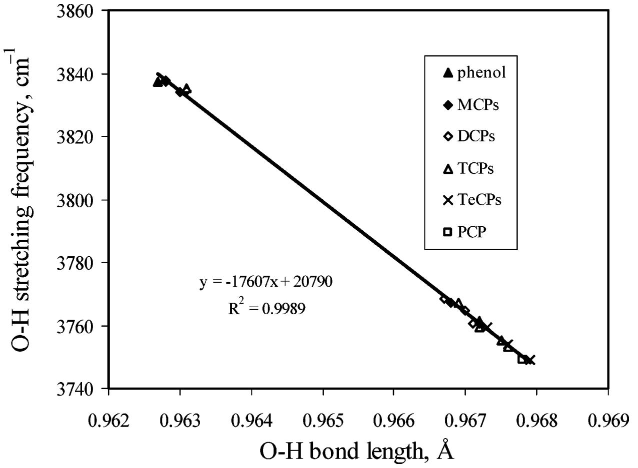


Figure 5. Correlation between O−H stretching frequency (cm^{-1}) and the O−H bond length (Å) of chlorophenols. In the lower right corner are points for *o*-chlorophenols that have relative longer bond lengths and lower frequencies, while points for other chlorophenols are located in the upper left corner.

3.3.2. O−H Torsional Vibration. The O−H torsional frequencies, τ(O−H), are in the range of 297−425 cm^{-1}, all with large infrared intensities. The calculated value of τ(O−H) for the parent phenol, 311.5 cm^{-1}, matches well the experimental value of 309.2 cm^{-1} measured for phenol vapor.[9] Similarly, calculated value of τ(O−H) for 4-CP, 302.2 cm^{-1}, perfectly matches the experimental value of 302 cm^{-1}.[13] The τ(O−H) values for all non-hydrogen-bonded conformers stay around 300 cm^{-1}, close to 311.5 cm^{-1} for phenol. It is interesting to note that the intramolecular hydrogen bonding produces a blue shift in τ(O−H), in contrast to the red shift in the O−H stretching mode. The τ(O−H) values for the hydrogen-bonded conformers are in the range of 396−425 cm^{-1} and increase with multiple chlorine substitution. The blue shift in τ(O−H) can be explained by intramolecular hydrogen bonding. The force constant for O−H torsional motion increases as a result of the intramolecular hydrogen bonding involving the O−H group, causing an increase in the barrier for the hydrogen rotation out of molecular plane and therefore the blue shift in τ(O−H). Furthermore, the blue shift increases with the polarity of O−H and ultimately with multiple chlorine substitution.

Figure 6 shows a strong linear correlation between τ(O−H) and the O−H bond lengths ($r^2 = 0.9872$). The τ(O−H) ranges from 302.2 to 425.0 cm^{-1}, corresponding to the variation of r(O−H) from 0.9628 to 0.9679 Å. Such a strong correlation is consistent with the strong correlation of υ(O−H) with r(O−H). They share the same physical origin and follow a similar trend.

3.3.3. O−H In-Plane Bending Vibration. As shown in Table 5, the O−H in-plane bending frequencies, δ(O−H), are centered around 1200 cm^{-1} for all chlorophenols, all with large infrared intensities. With a few exceptions, the δ(O−H) values are below 1200 cm^{-1} for monochlorophenols and dichlorophenols and above 1200 cm^{-1} for chlorophenols with higher chlorine substitutions. There are no apparent reasons to explain why multiple chlorine substitutions cause the increase in δ(O−H).

It should be mentioned that the O−H in-plane bending mode strongly couples with the skeletal ring vibration involving C−C stretching and C−H bending, which is in agreement with the experimental observation.[9] There are other vibrational modes involving significant degrees of the O−H in-plane bending

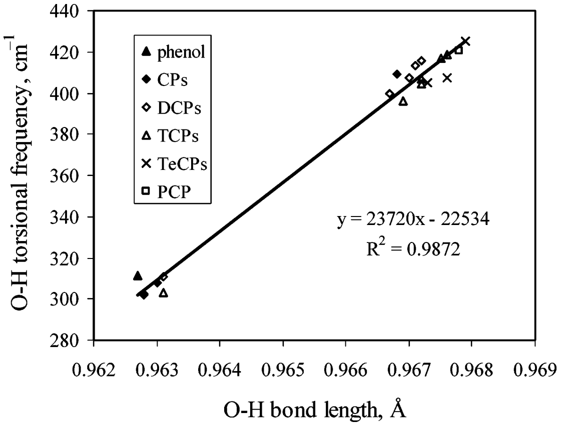


Figure 6. Correlation between O−H torsional frequency (cm^{-1}) and the O−H bond length (Å) of chlorophenols. In the upper left region are points for ortho-chlorophenols that have relative higher frequencies and longer bond lengths, while points for other chlorophenols are located in the lower right area.

motion, the reported δ(O−H) values in Table 5 are chosen because they follow a similar pattern of vibration and are within an expected range.

3.3.4. C−O Stretching Vibration. The C−O stretching frequencies of chlorophenols, ν(C−O), are in the range of 835−983 cm^{-1}, all with different IR intensities, as shown in Table 5. Generally, the values of ν(C−O) increase substantially with the increasing number of substituted chlorines at the phenolic ring. The C−O stretch is strongly coupled with skeletal ring vibrations and can be found in several vibrational modes. The reported ν(C−O) values are for the vibrational mode with the highest C−O stretching amplitude and they follow a similar vibrational pattern at the ring. The blue shifts in C−O stretching frequencies are apparently due to the strengthening of the C−O bond resulting from multiple chlorine substitutions. The same reason is responsible for the decrease in the C−O bond lengths of chlorophenols.

3.4. Physical Origin of Molecular Properties and Acidities of Chlorophenols. A series of molecular properties of chlorophenols have been described and systematic relationships of such properties have been demonstrated with the number of chlorine substitutions as well as with the positions at the phenolic ring. The following discussions are intended to provide a fundamental understanding of these relationships and their origin.

Chlorine on an aromatic ring has been traditionally recognized as an electron-withdrawing group. The induction of the electron-withdrawing chlorine and its interaction with other functional groups, such as the hydroxyl group in chlorophenols, may ultimately be responsible for the systematic trends in the molecular properties and relative acidities of these compounds. The dominant effect on the molecular properties appears from intramolecular hydrogen bonding between the hydroxyl group and ortho-substituted chlorine, primarily an interaction between the partially charged hydroxyl hydrogen (positive) and the partially charged chlorine (negative). All conformers with hydrogen bonding consistently are more stable than other structural conformers for a given number of chlorine substitutions. Characteristic changes in molecular geometries upon intramolecular hydrogen bonding are manifested in the elongation of the O−H bond (by 0.005 Å), in the compression of C−O bond (0.02 Å), in the decrease of the $\angle C_1O_{12}H_{13}$ and $\angle C_1C_2Cl_7$ bond angle (1° and 3°, respectively). Shifts in harmonic frequencies for vibrations involving the O−H group, typically 70 cm^{-1} in stretching and 100 cm^{-1} in torsional vibrations, are also attributed to the formation of intramolecular hydrogen bonding.

The hydroxyl group and chlorine may also interact through the phenolic ring in addition to intramolecular hydrogen bonding. This result from the induction of electron-withdrawing chlorine, and its magnitude may be sensitive to the relative positions of attached chlorine. In a monochlorophenol, chlorine is situated at one of the three different positions relative to the hydroxyl group at the ring. As a result, the inductive effect of chlorine decreases in the order of ortho, meta, and para positions. The induction of chlorine moves the electron density from the hydroxyl group (OH bonding orbital and CO antibonding orbital) to the chlorine through the ring, weakening the O−H bond and strengthening the C−O bond. This is supported by the increase in O−H bond lengths, the decrease in C−O bond lengths, the red shift in O−H stretch, the blue shift in O−H torsional frequencies in the same order, as discussed earlier. The acidity of a chlorophenol directly correlates with the O−H bond strength and is influenced by the inductive effect. This analysis is in agreement with the known aqueous pK_a values for monochlorophenols.

With multiple chlorine substitutions in chlorophenols, the inductive effect on the hydroxyl group is intensified but competition for electron density arises among chlorine substituents. This explains the systematic increase in the O−H bond length and the decrease in the C−O bond length with the increasing number of chlorine substitutions. Similar explanations can be given for the dependence of the vibrational frequencies involving the O−H group. In addition, the C−Cl bond lengths decrease systematically with the increasing number of chlorine substitutions while the average C−C bond length of the phenol ring increases after an initial decrease. The following analysis may account for these observations. Chlorine withdraws electron density from the electron rich hydroxyl group as well as the π system of the phenolic ring. As multiple chlorine substituents are introduced to the ring, each chlorine shares less electron density because of the competition for the total electron density available from the ring and the hydroxyl group. The electron density drawn to the C−Cl bonds is anticipated to fill in orbitals of antibonding character. This explains the decease of C−Cl bond lengths with the increasing chlorination of phenol. On the other hand, the electron density withdrawn by chlorine comes initially from π antibonding orbitals and eventually from π bonding orbitals. This is consistent with the initial decrease and the eventual increase in average C−C bond length.

The molecular properties discussed above and their intimate relationships with the induction of chlorine are ultimately correlated with the acidity of chlorophenols. Fundamentally, the acidity of a chlorophenol is determined by the stability of the phenoxide anion, a deprotonated product of the chlorophenol, which depends on the delocalization of the negative charge. As a result, the induction of substituted chlorine is responsible for stabilizing the phenolate anion and therefore enhances the acidity of the chlorophenol. Clearly, the induction of chlorine at an ortho position is the most effective and consequently the acidities of all ortho chlorophenols are overall stronger than other chlorophenols. For the same reason, the acidities of chlorophenols increase with the number of chlorine substitutions. Of course, the acidity of a specific chlorophenol may also be influenced by other effects such as the resonance of the phenolate anion and the steric effect of chlorine. However, it is the inductive effect that accounts for the major variations in the acidities of all chlorophenols.

4. Conclusions

In this work, theoretical calculations have been applied to investigate the molecular structure and properties of the complete series of 19 chlorophenols. Ortho chlorophenols are found to be more stable than the corresponding para or meta isomers. Intramolecular hydrogen bonding plays a major role in the high stability of ortho isomers. It is also largely responsible for series of geometrical variations such as in the O−H and C−O bond lengths, the $\angle C_1O_{12}H_{13}$ and $\angle C_1C_2Cl_7$ bond angles, and the O−H stretching and torsional frequencies. The induction of chlorine also has considerable influence on these geometrical parameters as well as on others such as the average C−C bond length of the phenolic ring and the C−Cl bond lengths. The acidity of a chlorophenol is largely determined by the induction of substituted chlorine, and as a result, it increases in the order of the para, meta, and ortho position and with the increasing number of substituted chlorines. Strong correlations of the O−H and C−O bond lengths and OH stretching frequencies with the aqueous pK_a values are found due to the common origin of effects on molecular structure and acidity in chlorophenols.

Acknowledgment. This work was supported in part The Camille and Henry Dreyfus Foundation (Award No. TH-00-028) and California State University, Fullerton.

Supporting Information Available: Tables S1−S3 contain the geometrical parameters of all 19 chlorophenols from B3YLP/6-311++G(d,p) and MP2/6-311++G(d,p) calculations as well as the harmonic frequencies and IR intensities from B3LYP-6-311++G(d,p) calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Wegman, R. C. C.; van der Broek, H. H. *Water Res*. **1983**, *17*, 227.

(2) Buisson, R. S. K.; Kirk, P. W. W.; Lester, J. N. *J. Chromatogr. Sci*. **1984**, *22*, 339.

(3) Galceran, M. T.; Jauregui, O. *Anal. Chim, Acta*. **1995**, *304*, 75.

(4) Rodriguez, I.; Llompart, M. P.; Cela, R. *J. Chromatogr. A* **2000**, *885*, 291.

(5) Czaplicka, M. *Sci. Total Environ.* **2004**, *322*, 21.

(6) EPA 822-Z-99-001; U.S. Environmental Protection Agency, Office of Water: Washington, DC, 1999.

(7) WHO (World Health Organization). Environmental health criteria 93. Chlorophenols other than pentachlorophenol. WHO: Geneva, 1989.

(8) WHO (World Health Organization). Environmental health criteria for pentachlorophenol. Supplement Draft; WHO: Geneva, 1986.

(9) Michalska, D.; Bienko, D. C.; Abkowicz-Bienko, A. J.; Latajka, Z. *J. Phys. Chem*. **1996**, *100*, 17786.

(10) Zierkiewicz, W.; Michalska, D.; Czarnik-Matusewicz, B.; Rospenk, M. *J. Phys. Chem. A* **2003**, *107*, 4547.

(11) Chen, P. C.; Tzeng, S. C. *J. Mol. Struct. (THEOCHEM)* **1999**, *467*, 243.

(12) Chis, V. *Chem. Phys*. **2004**, *300*, 1.

(13) Zierkiewicz, W.; Michalska, D.; Zeegers-Huyskens, T. *J. Phys. Chem*. **2000**, *104*, 11685.

(14) Janoschek, R.; Fabian, W. M. F. *J. Mol. Struct*. **2003**, *661*, 635.

(15) Batchelder, L. S.; Clymer, J.; Ragle, J. L. *J. Chem. Phys*. **1981**, *74*, 4791.

(16) Simperler, A.; Lampert, H.; Mikenda, W. *J. Mol. Struct.* **1998**, *448*, 191.

(17) Kovacs, A.; Macsari, I. *J. Phys. Chem. A*. **1999**, *103*, 3110.

(18) Borisenko, Konstantin B.; Hargittai, I. *J. Mol. Struct. (THEOCHEM)* **1996**, *388*, 107.

(19) Koll, A.; Parasuk, V.; Parasuk, W.; Karpfen, A.; Wolschann, P. *J. Mol. Struct*. **2004**, *690*, 165.

(20) Kishino, T.; Kobayashi, K. *Water Res.* **1994**, *28* (7), 1547.

(21) Parr, R. G.; Yang, W. *Density-functional theory of atoms and molecules*; Oxford University Press: New York, 1989.

(22) Becke, A. D. *J. Chem. Phys*. **1992**, *96*, 2155.

(23) Becke, A. D. *J. Chem. Phys*. **1992**, *97*, 9193.

(24) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648.

(25) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(26) Møller C.; Plesset, M. S. *Phys. Rev*. **1934**, *46*, 618.

(27) Krishnan, R.; Frsch, M. J.; Pople, J. A. *J. Chem. Phys*. **1980**, *72*, 4244.

(28) Krishnan, R.; Brinkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys*. **1980**, *72*, 650.

(29) Frisch, M. J.; Pople, J. A.; Brinkly, J. S. *J. Chem. Phys*. **1984**, *80*, 3265.

(30) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem*. **1983**, *4*, 294.

(31) 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.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; 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.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 1998.

(32) Ma, Kuo-Ching; Shiu, Wan-Ying; Mackay, D. *J. Chem. Eng. Data* **1993**, *38*, 364.

(33) Schuurmann, G. *J. Chem. Phys*. **1998**, *109*, 9523.

(34) Fiamegos, Yiannis C.; Nanos, Christos G.; Pilidis, George A.; Stalikas, Constantione D. *J. Chromotagr. A* **2003**, *983*, 215.

(35) Wightman, Peter G.; Fein, Heremy B. *Appl. Geochem.* **1999**, *14*, 319.

(36) Ege, S. N. *Organic Chemistry: Structure and Reactivity*, 4th ed.; Houghton Mifflin Company: New York, 1999; p 618.