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# $S_0$ and $S_1$ States of Monochlorophenols: Ab Initio CASSCF MO Study

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Optimized geometries and total energies for the $S_0$ and $S_1$ states of five monochlorophenols and phenol were calculated using a 10-electron, 8-orbital CASSCF/6-31G(d). We investigated the effects of a substituent chlorine atom and the $S_1 \leftarrow S_0$ excitation on the geometries and charge distributions. It is common to all monochlorophenols that the substituent chlorine atom makes the C−O bond shorten and that an empirical rule with respect to the internal ring angle concerned with the substituent chlorine atom holds true. The $S_1 \leftarrow S_0$ excitation enlarges the carbon ring and reduces the C−H, C−O, and C−Cl bond lengths. The O−H bond length and the C−O−H bond angle are almost invariant upon excitation. A structural approach based on van der Waals radii has clarified that *cis*-*o*-chlorophenol has a hydrogen bond in the $S_1$ state and that the interaction between the chlorine and oxygen atoms in a *trans*-*o*-chlorophenol affects its geometries for the $S_0$ and $S_1$ states. As to the origin energies of the $S_1 \leftarrow S_0$ transitions, the present method can compete in terms of accuracy with a 8-electron, 7-orbital CASSCF/6-31G(d,p). The increasing order of the calculated origin transition energies of monochlorophenols and phenol is in qualitative agreement with experimental results. Zero-point corrections are important in identifying the electronic spectra of monochlorophenols. The relative stabilities of rotational isomers, and dipole moments as well, have been also studied in relation to experimental results.

## I. Introduction

Chlorophenols are important chemicals in a number of industrial processes. Today they are also known as the chemical precursors of highly toxic dibenzo-*p*-dioxins in municipal waste incinerators.[1] Knowledge of their structures is essential for the understanding of the physical and chemical processes and properties of these molecules. However, as far as we know, there has been no measurement of the geometries of chlorophenols. The rotational constants of *p*-chlorophenol in the ground state were determined through the analysis of microwave specra.[2,3] Larsen studied the geometry of *p*-chlorophenol on the basis of the phenol substitution structure. Ab initio MO theory can provide a powerful tool to investigate the geometries of molecules. Shin et al.[4] studied the relative stability of *o*-chlorophenols by using a DFT theory. Recently, CASSCF MO studies of the $S_0$ and $S_1$ states of phenol have been made by Schumm et al.[5] and Fang.[6] The purpose of the present CASSCF MO study is to clarify the geometries of five monochlorophenols in the $S_0$ and $S_1$ states and to determine their origin energies in the $S_1 \leftarrow S_0$ transitions. Phenol will be also studied as a reference molecule. The effects of substitution on molecular geometry have been extensively studied in terms of benzene derivatives. We will study the geometry obtained using the CASSCF MO calculation in comparison with empirical rules for bond angles and bond lengths.[7,8]

Electronic excitation energy is in general quite different between the rotational isomers. The electronic spectra of vapor monochlorophenols have been extensively studied in terms of UV absorption,[9−11] supersonic jet spectra,[12,13] and REMPI spectra.[14−16] It is a well-established fact that there exists an intramolecular hydrogen bond in *cis*-*o*-chlorophenol.[17] OH stretching and torsional frequencies[2,3,18−21] and the NMR chemical shift[22] have been investigated so far. Cockett et al.[16] have argued that no firm assignment of the electronic spectra of isomers can be drawn without firm conclusions regarding the relative stability of cis and trans isomers. The experimental values of the enthalpy differences between the *cis*- and *trans*-*o*-chlorophenols are fairly scattered.[18,20,22] Further, no study of the relative stability of *cis*- and *trans*-*m*-chlorophenol has been made until now. We will study the relative stability of the rotational isomers of monochlorophenols by taking into account zero-point corrections. The $S_1 \leftarrow S_0$ transition deforms the geometry of each molecule and the electron distribution in it. It is not evidently understood whether the hydrogen bond in a *cis*-*o*-chlorophenol is affected by the electronic excitation. The van der Waals radii cutoff criteria for hydrogen bonding are valuable as a rule of thumb, though they can sometimes give rise to incorrect conclusions.[23] Jeffrey and Saenger have shown that van der Waals constant radii given by Allinger[24] make it possible to use the cutoff criteria for hydrogen bonding under certain conditions. A structural approach based on the van der Waals radii cutoff criteria and a Mulliken population analysis will be taken in order to study the characteristics of the geometries. We will provide a qualitative insight into the bonding by comparing those Mulliken charges on different molecules which have been obtained using the same basis set.

## II. Computational Details

The calculations were performed using Gaussian programs.[25,26] The CASSCF method[27−33] in this work is based on

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the active space that is made up with 10 active electrons distributed among eight orbitals. This method will be denoted as CAS(10,8). We adopted a 6-31G(d) basis set.[34,35] The active space for monochlorophenols consists of six ring $\pi$ orbitals, one oxygen lone pair having $\pi$ symmetry with respect to the molecular plane, and one chlorine lone pair having $\pi$ symmetry; that for phenol consists of the six ring $\pi$ orbitals and two oxygen lone pairs. Our active space is not particularly large, having 1176 configuration state functions. The calculation of the harmonic frequencies was important in order to ensure that the optimized geometry really corresponds to a total energy minimum. We calculated the harmonic frequencies in the $S_0$ and $S_1$ states by use of the CAS(10,8). Schumm et al.[5] used a Dunning's cc-pVDZ basis set to obtain the energy of the electronic origin of the $S_1 \leftarrow S_0$ transition of phenol, using the CAS(8,7) and CAS(8,9); they calculated the harmonic frequencies using the CAS(8,7). Fang[6] adopted CAS(8,7)/6-31G(d,p) to obtain the geometry and total electronic energy of phenol; he calculated the harmonic frequencies by using the HF and CIS methods. The present results for phenol will be compared with those of CAS(8,7)/6-31G(d,p) and CAS(8,9)/cc-pVDZ.

The CASSCF geometry optimizations were made under the tight convergence criteria of the Gaussian programs, except for the $S_1$ states of *trans-o*-chlorophenol (hereafter written as *trans-o*-CP) and *p*-CP. In the case of the $S_1$ states of *trans-o*-CP and *p*-CP, we applied the default convergence criteria to the displacements and the tight convergence criteria to the force constants because of very slow convergence. The optimized geometries for the $S_1$ states of *cis-o*-CP and *trans-m*-CP under the tight convergence criteria required the calculation of the force constants at every point in the geometry optimization. No constraint was imposed on the molecules in the geometry optimization. The CAS(10,8) calculation with the cc-pVDZ basis set[36] and that with a 6-31+G(d) basis set[37] were also made in the case of *p*-CP by using the default convergence criteria for optimization, though the harmonic frequencies were not calculated because of limited computer resources. The CIS calculation[38] for the $S_1$ states was made in order to obtain an initial geometry for the CAS optimization, though the total energy minimum on the potential surface was not always searched. The CIS optimization for the $S_1$ states often yielded saddle points on the potential energy surface. Further, the CAS geometry optimization for the $S_1$ states on the basis of the CIS optimized geometry did not necessarily lead to the total energy minimum on the potential energy surface. Several trials based on the vibrational normal modes of imaginary frequencies[39] were necessary in order to determine the total energy minimums for the $S_1$ states of monochlorophenols.

Schumm et al.[5] have given a scaling factor $\lambda$ for each type of the vibrational normal modes in the $S_0$ and $S_1$ states of phenol in the case of the CAS(8,7)/cc-pVDZ. Little information is available regarding the scaling factor for the harmonic frequencies obtained using the CASSCF/6-31G(d). We will use a value,[40] $\lambda = 0.8953$, recommended for the harmonic frequencies obtained with the HF/6-31G(d). To test the validity of the use of this value of $\lambda$ for both $S_0$ and $S_1$ states, we computed the values of $\lambda$ using the harmonic frequencies of phenol obtained using the CAS(10,8)/6-31G(d). A least-squares procedure[40] gave $\lambda = 0.9115$ for the $S_0$ state of phenol and $\lambda = 0.9035$ for its $S_1$ state. We ignored the discrepancies between the calculated and experimental frequencies with respect to the energetic sequence,[5,41] because the precise assignment of the normal modes was outside of this work. It will be shown later that these values of $\lambda$ give almost the same origin energy for the $S_1 \leftarrow S_0$ transition of phenol as the recommended value of $\lambda$.

**TABLE 1: Bond Lengths (in Angstroms) and Bond Angles (in Degrees) for the $S_0$ States of Monochlorophenols and Phenol Obtained Using the CAS(10,8)/6-31G(d)**

| | *cis-o*-CP | *trans-o*-CP | *cis-m*-CP | *trans-m*-CP | *p*-CP | phenol | |
|---|---|---|---|---|---|---|---|
| | | | | | | calc | exp[a] |
| Bond Lengths | | | | | | | |
| $C_1-C_2$ | 1.394 | 1.396 | 1.392 | 1.393 | 1.392 | 1.393 | 1.3912 (46) |
| $C_2-C_3$ | 1.396 | 1.394 | 1.395 | 1.397 | 1.397 | 1.398 | 1.3944 (50) |
| $C_3-C_4$ | 1.391 | 1.393 | 1.389 | 1.392 | 1.389 | 1.393 | 1.3954 (36) |
| $C_4-C_5$ | 1.399 | 1.395 | 1.399 | 1.395 | 1.395 | 1.398 | 1.3954 (36) |
| $C_5-C_6$ | 1.390 | 1.393 | 1.391 | 1.389 | 1.391 | 1.392 | 1.3922 (50) |
| $C_1-C_6$ | 1.399 | 1.398 | 1.397 | 1.397 | 1.397 | 1.397 | 1.3912 (46) |
| Av. C−C | 1.395 | 1.395 | 1.394 | 1.394 | 1.394 | 1.395 | 1.3933 |
| $C_2-X_2$ | 1.750 | 1.077 | 1.075 | 1.077 | 1.077 | 1.077 | 1.0856 (42) |
| $C_3-X_3$ | 1.073 | 1.075 | 1.745 | 1.075 | 1.073 | 1.075 | 1.0835 (36) |
| $C_4-X_4$ | 1.074 | 1.074 | 1.073 | 1.073 | 1.746 | 1.075 | 1.0802 (28) |
| $C_5-X_5$ | 1.075 | 1.073 | 1.075 | 1.745 | 1.073 | 1.075 | 1.0836 (36) |
| $C_6-X_6$ | 1.074 | 1.738 | 1.074 | 1.072 | 1.074 | 1.074 | 1.0813 (44) |
| Av. C−H | 1.074 | 1.075 | 1.074 | 1.074 | 1.074 | 1.075 | 1.0828 |
| $C_1-O$ | 1.347 | 1.349 | 1.354 | 1.354 | 1.355 | 1.358 | 1.3745 (45) |
| $O-H_1$ | 0.948 | 0.947 | 0.947 | 0.947 | 0.947 | 0.947 | 0.9574 (57) |
| Distances | | | | | | | |
| $C_1\cdots C_4$ | 2.806 | 2.804 | 2.799 | 2.798 | 2.779 | 2.794 | |
| $O\cdots X_6$ | 2.540 | 2.930 | 2.554 | 2.555 | 2.554 | 2.553 | |
| $H_1\cdots X_2$ | 2.486 | 2.285 | 2.319 | 2.317 | 2.319 | 2.307 | |
| Bond Angles | | | | | | | |
| $C_1-C_2-C_3$ | 121.3 | 120.6 | 118.9 | 119.6 | 120.1 | 119.8 | 119.43 (31) |
| $C_2-C_3-C_4$ | 119.6 | 120.1 | 121.7 | 120.8 | 119.4 | 120.4 | 120.48 (26) |
| $C_3-C_4-C_5$ | 119.6 | 119.6 | 118.4 | 118.5 | 120.8 | 119.4 | 119.24 (22) |
| $C_2-C_1-C_6$ | 118.7 | 118.9 | 120.4 | 120.5 | 120.0 | 120.2 | 120.85 (36) |
| $C_4-C_5-C_6$ | 120.4 | 120.1 | 121.0 | 121.8 | 119.6 | 120.5 | 120.79 (26) |
| $C_1-C_6-C_5$ | 120.4 | 120.6 | 119.5 | 118.8 | 120.0 | 119.7 | 119.22 (31) |
| $C_2-C_1-O$ | 123.8 | 122.4 | 122.2 | 122.7 | 122.7 | 122.5 | 122.14 (31) |
| $C_6-C_1-O$ | 117.6 | 118.6 | 117.4 | 116.8 | 117.3 | 117.3 | 117.01 (30) |
| $C_1-C_2-X_2$ | 119.4 | 119.2 | 121.0 | 120.2 | 120.3 | 120.1 | 120.01 (41) |
| $C_1-C_6-X_6$ | 118.1 | 119.9 | 119.0 | 119.7 | 119.1 | 118.9 | |
| $C_3-C_2-X_2$ | 119.4 | 120.1 | 120.0 | 120.2 | 119.6 | 120.1 | 120.57 (36) |
| $C_2-C_3-X_3$ | 119.3 | 119.5 | 118.7 | 119.6 | 120.3 | 119.4 | 119.48 (29) |
| $C_3-C_4-X_4$ | 119.8 | 120.6 | 120.4 | 121.2 | 119.7 | 120.3 | 120.25 (23) |
| $C_4-C_5-X_5$ | 120.1 | 120.8 | 119.4 | 119.2 | 120.0 | 120.0 | 119.78 (28) |
| $C_5-C_6-X_6$ | 121.5 | 119.5 | 121.5 | 121.4 | 120.9 | 121.4 | 121.55 (36) |
| $C_1-O-H_1$ | 111.2 | 110.5 | 111.0 | 110.8 | 110.9 | 110.6 | 108.77 (35) |

[a] The experimental data were taken from ref 42.

All calculations were done using the Gaussian 94 program on a HITACHI SR2201 at the Information Technology Center, the University of Tokyo, and using the Gaussian 98 program on a FUJITSU VPP700/56 at the Computing and Communications Center, Kyushu University.

## III. Results and Discussion

**A. $S_0$ State.** The bond lengths and bond angles of monochlorophenols and phenol in the $S_0$ states obtained with the CAS(10,8)/6-31G(d) are listed in Table 1. The labeling of the atoms in a molecule is denoted in Figure 1. The present CASSCF calculations have shown that every molecule under consideration is almost completely planar in the $S_0$ state.

We first study phenol in order to examine the accuracy of the calculated results. The CAS(10,8)/6-31G(d) gives exactly the same geometry for phenol as the CAS(8,7)/6-31G(d,p).[6] It is common to both CAS(10,8)/6-31G(d) and CAS(8,9)/cc-pVDZ that the largest deviations from experimental results occur for the bond angle $C_1-O-H_1$ and the bond length $C_1-O$. In comparison with the geometry determined through microwave measurement,[42] the error of the average C−C bond length is 0.12%. The error of the $C_1-O$ bond length is relatively large, 1.2%. The deviation of the bond angle $C_1-O-H_1$ of phenol from experimental results is 1.8° and that of the $C_2-C_1-C_6$ is 0.7°. The average deviation of the calculated bond angles is about 0.4°. As seen from Table 2, the error of the calculated

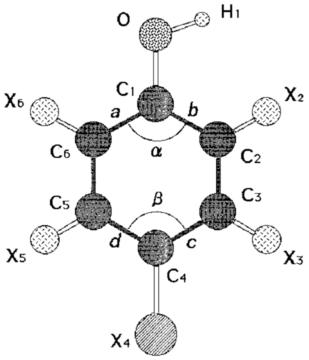

**Figure 1.** Labeling of the atoms in a monochlorophenol, where X signifies either Cl or H. This figure illustrates *p*-chlorophenol.

**TABLE 2: Rotational Constants *A*, *B*, and *C* (in GHz) for the $S_0$ and $S_1$ States Obtained Using the CAS(10,8)/6-31G(d)**

| | *cis-o*-CP | *trans-o*-CP | *cis-m*-CP | *trans-m*-CP | *p*-CP | | phenol | |
|---|---|---|---|---|---|---|---|---|
| | | | | | calc | exp[a] | calc | exp[b] |
| | | | | | $S_0$ | | | |
| *A* | 2.964 | 2.965 | 3.458 | 3.454 | 5.659 | 5.632 78 (7) | 5.672 | 5.650 515 (6) |
| *B* | 1.545 | 1.548 | 1.194 | 1.197 | 0.974 | 0.975 573 (4) | 2.630 | 2.619 236 (3) |
| *C* | 1.016 | 1.017 | 0.887 | 0.889 | 0.831 | 0.831 655 (4) | 1.797 | 1.789 855 (3) |
| | | | | | $S_1$ | | | |
| *A* | 2.879 | 2.880 | 3.342 | 3.342 | 5.330 | | 5.351 | 5.3136 (2) |
| *B* | 1.505 | 1.509 | 1.169 | 1.170 | 0.966 | | 2.575 | 2.6205 (1) |
| *C* | 0.988 | 0.990 | 0.866 | 0.866 | 0.818 | | 1.739 | 1.756 10 (4) |

[a] The experimental data were taken from ref 2. [b] Reference 47.

**TABLE 3: Mulliken Atomic Charges (in Electronic Units) in the $S_0$ States Obtained Using the CAS(10,8)/6-31G(d)**

| | *cis- o*-CP | trans- *o*-CP | cis- *m*-CP | trans- *m*-CP | *p*-CP | phenol |
|---|---|---|---|---|---|---|
| $C_1$ | 0.414 | 0.425 | 0.399 | 0.394 | 0.391 | 0.390 |
| $C_2$ | −0.196 | −0.256 | −0.243 | −0.259 | −0.257 | −0.263 |
| $C_3$ | −0.170 | −0.191 | −0.125 | −0.190 | −0.171 | −0.192 |
| $C_4$ | −0.202 | −0.201 | −0.186 | −0.185 | −0.139 | −0.206 |
| $C_5$ | −0.191 | −0.174 | −0.192 | −0.126 | −0.172 | −0.193 |
| $C_6$ | −0.220 | −0.180 | −0.221 | −0.202 | −0.219 | −0.225 |
| O | −0.759 | −0.742 | −0.758 | −0.757 | −0.759 | −0.763 |
| $X_2$ | −0.020 | 0.198 | 0.219 | 0.198 | 0.201 | 0.189 |
| $X_3$ | 0.227 | 0.208 | −0.011 | 0.211 | 0.229 | 0.199 |
| $X_4$ | 0.208 | 0.207 | 0.226 | 0.226 | −0.015 | 0.196 |
| $X_5$ | 0.208 | 0.227 | 0.211 | −0.010 | 0.229 | 0.199 |
| $X_6$ | 0.225 | 0.017 | 0.223 | 0.243 | 0.226 | 0.214 |
| $H_1$ | 0.478 | 0.460 | 0.458 | 0.458 | 0.457 | 0.453 |

rotational constants for phenol is about 0.4%. We next consider *p*-CP. The calculated C−Cl bond length agrees with a value, 1.7204 Å, determined by Larsen[3] within the error of 1.5%. The errors of the calculated rotational constants for *p*-CP are less than 0.5%. The above results for phenol and *p*-CP show that the CAS(10,8)/6-31G(d) gives the bond lengths of monochlorophenols within an error of about 1% and the bond angles within an error of about 2°.

The average C−C bond length of every monochlorophenol is almost equal among each other. As seen from Table 3, if we omit the carbon atom bonded to a chlorine atom, the carbon atoms located at the ortho and para positions have negative charges larger than the carbon atoms located at the meta positions, except for *cis*- and *trans-m*-CP. The chlorine atom in every molecule, except for *trans-o*-CP, acts as a very weak electron acceptor and acts as a very weak electron donor in the case of *trans-o*-CP. It is seen from Table 1 that one of the substituent effects of chlorine atoms on the bond lengths is the shortening of the C−O bonds. The average length of the C−C bonds and that of the C−H bonds slightly shorten in the case of *cis-m*-CP, *trans-m*-CP, and *p*-CP. The $O-H_1$ bond of *cis-o*-CP slightly lengthens owing to the hydrogen bonding. The empirical rules for benzene ring deformations[7,8] are the following: As a general rule, a chlorine atom tends to broaden the angle $\beta$ by 1.9° and a functional group OH tends to broaden the angle α by 0.2° (see Figure 1); the bond lengths *a*, *b*, *c*, and *d* lengthen or shorten. As seen from Table 1, the bond angle $\beta$ of every monochlorophenol is larger than the corresponding bond angle of phenol. The bond angles α of *cis*- and *trans-m*-CP are also larger than the bond angle $C_2-C_1-C_6$ of phenol. The inconsistency with the empirical rule for the bond angle α in the case of *cis*- and *trans-o*-CP may be explained by the broadening of the angle $\beta$ neighboring to the angle α. It seems that the accuracy of the present results is not sufficient to examine whether the empirical rule for the angle α applies in the case of *p*-CP. It does not contradict the empirical rule that the bonds *c* and *d* shorten in the case of *cis-m*-CP, *trans-m*-CP, and *p*-CP. *cis*- and *trans-o*-CP are exceptional with respect to the bonds *c* and *d*.

Among the monochlorophenols, *cis-o*-CP has the longest O−H bond, the shortest C−O bond, and the largest C−O−H bond angle. The O−H bond lengths of monochlorophenols except for *cis-o*-CP are almost the same and are slightly shorter than those of *cis-o*-CP. The C−Cl bond is longest for *cis-o*-CP and is shortest for *trans-o*-CP. This shows that *trans-o*-CP has the strongest C−Cl bond and *cis-o*-CP has the weakest one among the monochlorophenols. The charge on the $H_1$ atom is largest for *cis-o*-CP among the monochlorophenols. Consider a cutoff criterion for hydrogen bonding[22] such that the distance between two atoms must be smaller than a sum of van der Waals radii (in units of Å), $W_H + W_{Cl} - 0.3$ Å. We have $W_H = 1.50$ Å for hydrogen and $W_{Cl} = 1.95$ Å for chlorine.[23] The distance H···Cl in *cis-o*-CP is 2.486 Å, much smaller than the above sum. This is consistent with the fact that a hydrogen bond exists between the $H_1$ and Cl atoms in *cis-o*-CP.

The interaction between the lone-pair electrons of a chlorine atom and those of an oxygen atom may be important in the case of *trans-o*-CP, because the distance Cl···O in *trans-o*-CP, 2.930 Å, is smaller than the sum of van der Waals radii, 3.6 Å. As to the bond angle $C_6-C_1-O$, *trans-o*-CP has the largest value among the six molecules. This shows that the chlorine and oxygen atoms in *trans-o*-CP repel each other. The $C_6$ and O atoms of *trans-o*-CP have negative charges smaller than the other five molecules, and its $C_1$ atom has a positive charge larger than the $C_1$ atoms of the other five molecules. The above repulsion is considered to make $E_{el}$ highest among the monochlorophenols, as seen from Table 4.

The total electronic energies $E_{el}$ and zero-point corrections $E_{zp}$ obtained with CAS(10,8)/6-31G(d) are given in Table 4. The values of $E_{el+zp} = E_{el} + E_{zp}$ show that each cis isomer is more stable than its trans isomer in the $S_0$ states. The difference in $E_{el+zp}$ between *cis*- and *trans-o*-CP is 0.004 02 hartree = 10.6 kJ/mol. The population ratio at 298 K calculated by using this value is 0.014, fairly close to a value, 0.018, determined from NMR data.[22] Shin et al.[4] has given a slightly larger value, 13.68 kJ/mol. It is difficult to arrive at a definite conclusion. The calculated difference in $E_{el}$ between the *cis*- and *trans-m*-CP is very small, so that their relative stability is sensitive to the zero-point correction.

The calculated values of dipole moment $\mu$ are a little larger than experimental values[43−47] (see Table 5). The error of the calculated value of $\mu$ for *p*-CP is 12%, and that for phenol is 23%. The average of the calculated values of $\mu$ for *cis*- and *trans-o*-CP is 2.43 D, close to the experimental value. This agrees with the well-known fact that *o*-chlorophenols exist as a mixture of *cis*- and *trans-o*-CP.[48,49]

**TABLE 4: Total Electronic Energies $E_{el}$ and Zero-Point Corrections $E_{zp}$ for the $S_0$ States of Phenol and Monochlorophenols Obtained Using the HF/6-31G(d) and the CAS(10,8)/6-31G(d) Methods (in hartree)**

| | *cis-o*-CP | *trans-o*-CP | *cis-m*-CP | *trans-m*-CP | *p*-CP | phenol |
|---|---|---|---|---|---|---|
| HF:[a] $\Delta_{el}$ | −0.45868 | −0.45416 | −0.45796 | −0.45786 | −0.45747 | −0.55806 |
| $E_{zp}$ | 0.09182 | 0.09165 | 0.09158 | 0.09154 | 0.09157 | 0.10054 |
| CAS:[a] $\Delta_{el}$ | −0.53182 | −0.52734 | −0.53084 | −0.53076 | −0.53071 | −0.63055 |
| $E_{zp}$ | 0.09139 | 0.09093 | 0.08989 | 0.08984 | 0.08983 | 0.09854 |

[a] We have $E_{el} = \Delta_{el} - 764$ for monochlorophenols, and $E_{el} = \Delta_{el} - 305$ for phenol; the scaling factor for zero-point corrections is $\lambda = 0.8953$.

**TABLE 5: Dipole Moments (in D) in the $S_0$ and $S_1$ States Obtained Using the CAS(10,8)/6-31G(d)**

| | | *cis-o*-CP | *trans-o*-CP | *cis-m*-CP | *trans-m*-CP | *p*-CP | phenol |
|---|---|---|---|---|---|---|---|
| $S_0$ | calc | 1.38 | 3.48 | 0.85 | 3.40 | 2.37 | 1.50 |
| | exp | 2.19[a] | | | | 2.11 (±5%)[b] | 1.224 (±1%)[c] |
| $S_1$ | calc | 1.36 | 3.41 | 0.71 | 3.32 | 2.23 | 1.55 |

[a] The experimental values were taken from ref 43. [b] References 44 and 45. [c] References 42 and 46.

**TABLE 6: Bond Lengths (in Angstroms) and Bond Angles (in Degrees) for the $S_1$ States of Monochlorophenols and Phenol Obtained Using the CAS(10,8)/6-31G(d)**

| | *cis-o*-CP | *trans-o*-CP | *cis-m*-CP | *trans-m*-CP | *p*-CP | phenol | |
|---|---|---|---|---|---|---|---|
| | | | | | | calc | exp[a] |
| | | | Bond Lengths | | | | |
| $C_1-C_2$ | 1.436 | 1.431 | 1.431 | 1.429 | 1.429 | 1.431 | 1.443 |
| $C_2-C_3$ | 1.429 | 1.430 | 1.429 | 1.431 | 1.431 | 1.432 | 1.443 |
| $C_3-C_4$ | 1.434 | 1.431 | 1.432 | 1.434 | 1.432 | 1.434 | 1.447 |
| $C_4-C_5$ | 1.431 | 1.432 | 1.433 | 1.431 | 1.430 | 1.433 | 1.447 |
| $C_5-C_6$ | 1.433 | 1.434 | 1.433 | 1.432 | 1.434 | 1.434 | 1.441 |
| $C_1-C_6$ | 1.428 | 1.432 | 1.425 | 1.427 | 1.425 | 1.427 | 1.443 |
| Av. C−C | 1.432 | 1.432 | 1.431 | 1.431 | 1.430 | 1.432 | 1.444 |
| $C_2-X_2$ | 1.737 | 1.074 | 1.072 | 1.074 | 1.074 | 1.075 | |
| $C_3-X_3$ | 1.071 | 1.072 | 1.731 | 1.072 | 1.071 | 1.073 | |
| $C_4-X_4$ | 1.073 | 1.073 | 1.072 | 1.072 | 1.730 | 1.074 | |
| $C_5-X_5$ | 1.072 | 1.071 | 1.072 | 1.730 | 1.071 | 1.073 | |
| $C_6-X_6$ | 1.071 | 1.726 | 1.072 | 1.070 | 1.071 | 1.072 | |
| Av. C−H | 1.072 | 1.073 | 1.072 | 1.072 | 1.072 | 1.073 | |
| $C_1-O$ | 1.345 | 1.345 | 1.350 | 1.350 | 1.349 | 1.352 | 1.257 |
| $O-H_1$ | 0.948 | 0.947 | 0.947 | 0.947 | 0.947 | 0.947 | |
| | | | Distances | | | | |
| $C_1 \cdots C_4$ | 2.853 | 2.849 | 2.843 | 2.843 | 2.813 | 2.835 | |
| $O \cdots X_6$ | 2.564 | 2.948 | 2.567 | 2.580 | 2.567 | 2.570 | |
| $H_1 \cdots X_2$ | 2.498 | 2.298 | 2.331 | 2.318 | 2.316 | 2.311 | |
| | | | Bond Angles | | | | |
| $C_1-C_2-C_3$ | 120.7 | 119.6 | 117.7 | 119.3 | 119.2 | 118.9 | |
| $C_2-C_3-C_4$ | 118.7 | 119.9 | 121.5 | 119.9 | 118.6 | 119.7 | |
| $C_3-C_4-C_5$ | 120.9 | 120.9 | 119.6 | 119.6 | 122.4 | 120.8 | |
| $C_2-C_1-C_6$ | 120.1 | 120.4 | 122.0 | 122.1 | 122.1 | 121.9 | |
| $C_4-C_5-C_6$ | 120.0 | 119.0 | 119.8 | 121.4 | 118.5 | 119.7 | |
| $C_1-C_6-C_5$ | 119.6 | 120.2 | 119.3 | 117.8 | 119.2 | 118.9 | |
| $C_2-C_1-O$ | 122.8 | 121.6 | 121.1 | 121.8 | 121.4 | 121.4 | |
| $C_6-C_1-O$ | 117.1 | 117.9 | 116.8 | 116.2 | 116.5 | 116.7 | |
| $C_1-C_2-X_2$ | 119.7 | 119.6 | 121.6 | 120.2 | 120.5 | 120.3 | |
| $C_1-C_6-X_6$ | 118.5 | 120.3 | 119.0 | 120.4 | 119.3 | 119.1 | |
| $C_3-C_2-X_2$ | 119.6 | 120.8 | 120.7 | 120.6 | 120.3 | 120.8 | |
| $C_2-C_3-X_3$ | 119.9 | 120.0 | 119.2 | 120.3 | 121.3 | 120.1 | |
| $C_3-C_4-X_4$ | 119.1 | 119.8 | 119.5 | 120.7 | 118.7 | 119.5 | |
| $C_4-C_5-X_5$ | 120.0 | 121.2 | 119.8 | 119.3 | 120.1 | 120.1 | |
| $C_5-C_6-X_6$ | 122.0 | 119.5 | 121.7 | 121.9 | 121.5 | 121.9 | |
| $C_1-O-H_1$ | 111.2 | 110.6 | 111.1 | 110.9 | 111.0 | 110.7 | |

[a] The experimental structure data were taken from ref 47.

**B. $S_1$ State.** The bond lengths and bond angles in the $S_1$ states calculated with the CAS(10,8)/6-31G(d) are shown in Table 6. All of the molecules under consideration are almost completely planar in the $S_1$ states. We note that the CIS/6-31G(d) geometry optimization gave an uneven molecular plane for the $S_1$ state of *trans-o*-CP. Electron correlation is essential for the $S_1$ state of *trans-o*-CP.

**TABLE 7: Mulliken Atomic Charges (in Electronic Units) in the $S_1$ State Obtained Using the CAS(10,8)/6-31G(d)**

| | *cis- o*-CP | *trans-o*-CP | *cis-m*-CP | *trans-m*-CP | *p*-CP | phenol |
|---|---|---|---|---|---|---|
| $C_1$ | 0.383 | 0.394 | 0.364 | 0.360 | 0.363 | 0.358 |
| $C_2$ | −0.185 | −0.252 | −0.236 | −0.249 | −0.256 | −0.256 |
| $C_3$ | −0.179 | −0.199 | −0.135 | −0.203 | −0.180 | −0.203 |
| $C_4$ | −0.193 | −0.192 | −0.171 | −0.171 | −0.128 | −0.193 |
| $C_5$ | −0.201 | −0.183 | −0.206 | −0.137 | −0.182 | −0.205 |
| $C_6$ | −0.220 | −0.175 | −0.219 | −0.200 | −0.224 | −0.224 |
| O | −0.746 | −0.725 | −0.740 | −0.739 | −0.739 | −0.744 |
| $X_2$ | −0.011 | 0.201 | 0.221 | 0.201 | 0.203 | 0.193 |
| $X_3$ | 0.228 | 0.209 | −0.002 | 0.212 | 0.229 | 0.201 |
| $X_4$ | 0.211 | 0.210 | 0.228 | 0.228 | 0.000 | 0.200 |
| $X_5$ | 0.209 | 0.227 | 0.212 | −0.003 | 0.229 | 0.201 |
| $X_6$ | 0.225 | 0.023 | 0.224 | 0.242 | 0.226 | 0.216 |
| $H_1$ | 0.478 | 0.463 | 0.460 | 0.460 | 0.460 | 0.456 |

We first study phenol. The CAS(10,8)/6-31G(d) and the CAS(8,7)/6-31G(d,p)[6] give almost the same geometry for the $S_1$ state of phenol. Berden et al.[47] determined the C−C and C−O bond lengths of phenol in the $S_1$ state by analyzing the fluorescence excitation spectra, leaving the other parameters unaffected upon excitation. They noted that their geometry was not unique. The difference in the average C−C bond length of phenol between that of CAS(10,8)/6-31G(d) and the estimation given by Berden et al. is 0.8%, but the difference in the C−O bond length is 7.6%. This large difference in the C−O bond length is thus unimportant. Though the difference in the bond length between CAS(10,8)/6-31G(d) and CAS(8,9)/cc-pVDZ is largest with respect to the C−H bond, it is less than 0.007 Å. The largest difference in bond angles between the two methods is 1.5° for the bond angle $C_3-C_4-C_5$. As for the rotational constants, it is seen from Table 2 that the errors of the calculated rotational constants for phenol are less than 2%.

The substituent effects of chlorine atoms on the C−O bonds, the average length of the C−C bonds, and that of the C−H bonds are qualitatively the same as in the $S_0$ states. *cis-* and *trans-o*-CP are exceptional with respect to the bonds *c* and *d*. The empirical rule of the substituent effect with respect to the bond angle $\beta$ holds true for the $S_1$ states. As to the bond angle $\alpha$, the empirical rule is applicable to *cis-m*-CP, *trans-m*-CP, and *p*-CP. The bond angles $\alpha$ of *cis-* and *trans-o*-CP slightly deviate from the empirical rule, as in the case of the $S_0$ states. The empirical rule for the bond lengths *c* and *d* also hold true for *cis-m*-CP, *trans-m*-CP, and *p*-CP.

The $H_1 \cdots Cl$ distance of *cis-o*-CP is 2.498 Å, smaller than the value of the cutoff criteria for hydrogen bonding. This shows that *cis-o*-CP has a hydrogen bond between Cl and $H_1$ atoms in the $S_1$ state. The $Cl \cdots O$ distance of *trans-o*-CP is 2.948 Å, smaller than the sum of the van der Waals radii. Further, the bond angle $C_6-C_1-O$ of *trans-o*-CP is largest among the six molecules. These suggest that the interaction between the lone-pair electrons of the chlorine atom and those of the oxygen atom is important for *trans-o*-CP, as in the case of the $S_0$ state.

The $S_1 \leftarrow S_0$ excitation leads to the following effects on the geometries and the charge distributions: The C−C bonds lengthen, and the C−H, C−O and C−Cl bonds shorten; the bond angles $C_2-C_1-C_6$ and $C_3-C_4-C_5$ broaden, and the distance $C_1 \cdots C_4$ in each molecule lengthens. The O−H bond length and the bond angle C−O−H are almost invariant. The

**TABLE 8: Pure Electronic Transition Energies $\nu_{el}$ and the Origin Energies of the $S_1 \leftarrow S_0$ Transition $\nu_{el+zp}$ Obtained Using the CAS(10,8)/6-31G(d) (in Units of $cm^{-1}$)**

| | *cis-o*-CP | *trans-o*-CP | *cis-m*-CP | *trans-m*-CP | *p*-CP | phenol |
|---|---|---|---|---|---|---|
| $\nu_{el}$ | 38 676 | 38 337 | 38 224 | 38 212 | 37 966 | 38 470 |
| $\nu_{el+zp}{}^{a}$ | 37 343 | 37 042 | 37 084 | 37 088 | 36 879 | 37 401 |
| $\nu_{el+zp}{}^{b}$ | 37 152 | 36 852 | 36 897 | 36 902 | 36 692 | 37 198 |
| exp | 35 892[c] | 35 702[c] | 35 769 ± 5[d]<br>35 773[c] | 35 889 ± 5[d]<br>35 894[c] | 34 820[e] | 36 348.71 ± 0.01[f] |

[a] The scaling factor for zero-point corrections is 0.8953. [b] The scaling factor is 0.9115 for the $S_0$ state and 0.9035 for the $S_1$ state. [c] References 13 and 15. [d] Reference 16. [e] Reference 11. [f] Reference 47.

charge distributions on the H atoms in the $S_1$ states are nearly the same as those in the $S_0$ states (see Table 7). The effect of the $S_1 \leftarrow S_0$ excitation on the value of $\mu$ is slight (see Table 5). In the case of the $S_1$ state of phenol, it differs from the $S_0$ state that the negative charges at the meta positions are larger than the negative charge at the para position. The negative charge on the carbon atom bonded to a chlorine atom, except for *trans-o*-CP, is smaller by 0.068 (in electronic units) on the average than that on the corresponding carbon atom of phenol. The negative charge on the $C_6$ atom in *trans-o*-CP is smaller by 0.049 than that of phenol. In the case of the $S_0$ states, the decrerase of the negative charge on the carbon atom in a monochlorophenol, except for *trans-o*-CP, is 0.067, compared with that on the corresponding carbon atom of phenol; the decrease of the charge on the $C_6$ atom of *trans-o*-CP is 0.045. Therefore, the substituent effect of a chlorine atom on the carbon atom bonded to it in the $S_1$ state may be approximately the same as that in the $S_0$ state.

**C. Origin Energy of the $S_1 \leftarrow S_0$ Transition.** Table 8 presents the origin transition energies for monochlorophenols and phenol. There has been much interest in the electronic spectra of phenol.[47,50−52] Our result for phenol will be compared with the origin transition energy observed by Berden et al. because of its high resolution. If we assume $\lambda = 0.8953$ for both $S_0$ and $S_1$ states, the error of the origin transition energies $\nu_{el+zp}$ obtained using the CAS(10,8)/6-31G(d) is about 2.9% for phenol, lies between 3.3 and 4.0% for monochlorophenols except for *p*-CP, and is 5.9% for *p*-CP. The reason the error of the result for phenol is small may be that all of the lone pairs of the oxygen atom are included in the calculation. If we use $\lambda = 0.9115$ for the $S_0$ state and $\lambda = 0.9035$ for the $S_1$ state, the errors of $\nu_{el+zp}$ are between 2.3 and 5.4%. Therefore, it will be allowable to use the recommended value of $\lambda$ for both $S_0$ and $S_1$ states. The CAS(8,7)/6-31G(d,p)[6] has given the origin energy of the $S_1 \leftarrow S_0$ transition with an error of 3.0%. The present value of $\nu_{el}$ for phenol is worse by 393 $cm^{-1}$ than the value obtained using the CAS(8,9)/cc-pVDZ.[5] Consider the case of *p*-CP. If we use the CAS(10,8)/cc-pVDZ, it reduces the value of $\nu_{el}$ for *p*-CP by 240 $cm^{-1}$, compared with the value obtained using the CAS(10,8)/6-31G(d). If we adopt the CAS(10,8)/6-31+G(d), it reduces the origin transition energy for *p*-CP by 323 $cm^{-1}$, compared with the present value. If we take into account the value of $\nu_{el}$ obtained using the CAS(10,8)/6-31+G-(d) and the zero-point correction obtained with the CAS(10,8)/6-31G(d), the origin transition energy becomes $\nu_{el+zp} = 36\,556$ $cm^{-1}$. The error of this value is still large, 5.0%. The relatively large deviation from experimental results in the case of *p*-CP might be partly due to some uncertainty involved in UV absorption spectra.

The calculated values of $\nu_{el+zp}$ are in the order of *p*-CP < *trans-o*-CP < *cis-m*-CP < *trans-m*-CP < *cis-o*-CP < phenol, as seen from Table 8. This order is qualitatively consistent with that of the experimental values. The zero-point correction is important in identifying the electronic spectra of monochlorophenols. We note the following: The error of the difference in $\nu_{el+zp}$ between each pair of cis and trans isomers is less than about 0.3% and that between *cis-o*-CP and *p*-CP is about 1.7% in reference to the average of the origin transition energies of the monochlorophenols. Namely, it is possible to identify each isomer within a range of error of about 2% at worst.

## IV. Summary

We have determined the optimized geometries and total energies for the $S_0$ and $S_1$ states of five monochlorophenols and phenol by using the CAS(10,8)/6-31G(d). The calculated geometries are considered to be accurate enough. It has been shown that *cis-o*-CP has a hydrogen bond in both $S_0$ and $S_1$ states. The interaction between the lone pair electrons of chlorine and those of oxygen affects the geometries of *trans-o*-CP for the $S_0$ and $S_1$ states. The substituent effects of chlorine atoms on both the geometries and the charge distributions have been studied in both $S_0$ and $S_1$ states. It is common to all monochlorophenols that the substituent chlorine atom makes the C−O bond shorten and that the empirical rule with respect to the bond angle $\beta$ holds true. *cis-* and *trans-o*-CP are exceptional with respect to the bonds *c* and *d*. The $S_1 \leftarrow S_0$ excitation enlarges the carbon rings and reduces the C−H, C−O, and C−Cl bond lengths. The O−H bond length and the C−O−H bond angle are almost invariant upon excitation. We have obtained a reasonable value for the relative stability of *cis-* and *trans-o*-CP. There is little difference in the relative stability between *cis-* and *trans-m*-CP within the accuracy of the CAS(10,8)/6-31G(d). The errors of the calculated origin transition energies are between 3 and 6%. The increasing order of the calculated origin transition energies of monochlorophenols and phenol is in qualitative agreement with experimental results. Zero-point corrections are essential in the identification of the electronic spectra of monochlorophenols.

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