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Molecular orbital study on the OH stretching frequency of the phenol dimer and its cation

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Abstract. Ab initio calculations were performed to investigate the structure and bonding of the phenol dimer and its cation, especially the OH stretching frequencies. Some stable structures of the phenol dimer and its cation were obtained at the Hartree–Fock level and were found to be in agreement with predictions based on spectroscopic investigations. In these dimers the phenol moieties are bound by a single OH$\cdots$O hydrogen bond. The hydrogen bond is much stronger in the dimer cation than in the neutral dimer. The calculated binding energy of the phenol dimer in the most stable structure was 6.5–9.9 kcal/mol at various levels of calculation, compared with the experimental value of 5 kcal/mol or greater. The binding energy of the phenol dimer cation is more than 3 times (24.1–30.6 kcal/mol) as large as that of the neutral dimer. For the phenol dimer the OH stretching frequency of the proton-accepting phenol (PAP) is 3652 cm^{-1} and that of the proton-donating phenol (PDP) is 3516 cm^{-1}; these are in agreement with observed values of 3654 and 3530 cm^{-1}, respectively. For the phenol dimer cation the OH stretching frequency of the PAP is 3616–3618 cm^{-1} in comparison with an observed value of 3620 ± 3 cm^{-1}. That of the PDP in the dimer cation is calculated to be 2434–2447 cm^{-1}, which is 1210–1223 cm^{-1} lower than that of the bare phenol. The large reduction in the OH stretching frequency of the PDP in the phenol dimer cation is attributed to the formation of a stronger hydrogen bond in the cation than in the neutral dimer.

Key words: Molecular orbital calculation – Phenol dimer – Phenol dimer cation – Hydroxyl stretching frequency – Hydrogen bond

1 Introduction

With the advance of spectroscopic techniques in recent years, hydrogen-bonded clusters and their ions have received much attention. Observation of the OH stretching vibration is very important to the study of hydrogen-bonded clusters because this vibration is the most sensitive probe of hydrogen-bond formation. Several experimental techniques, including rotational coherence spectroscopy, IR spectroscopy of supersonic jets, photodissociation spectroscopy, and zero kinetic energy (ZEKE) photoelectron spectroscopy, are very useful for predicting geometrical structures and for performing vibrational analysis of hydrogen-bonded complexes. The data from such experiments also help to elucidate the nature of the interaction between π-electron systems belonging to aromatic rings.

The phenol dimer is one of the prototype systems for investigating the structural consequences of the interplay between aromatic–aromatic and hydrogen-bonding interactions. The structure and vibrational frequencies of the phenol monomer have been well characterized [1, 2, 3, 4, 5, 6, 7, 8]. On the other hand, there are few investigations of the phenol cation [9, 10, 11, 12]. Using a mass-selected multiphoton ionization technique, Fuke and Kaya [13] first suggested that the phenol dimer is bound by an OH$\cdots$O hydrogen bond with an asymmetric conformation of the phenol moieties: one moiety is a proton-accepting phenol (PAP) and the other is a proton-donating phenol (PDP). Hartland et al. [3] observed the stimulated Raman spectra of jet-cooled phenol dimer and found OH stretching frequencies at around 3650 and 3530 cm^{-1} for the PAP and PDP moieties, respectively. Connell et al. [14] used rotational coherence spectroscopy to measure the rotational constants of the phenol dimer and reported a structural analysis. They also suggested that the phenol dimer is bound by a single OH$\cdots$O hydrogen bond with nonequivalent and nonplanar geometrical structures of the phenol moieties. Recently, Ebata et al. [15] observed IR and Raman spectra of the phenol dimer in supersonic jets and suggested the same geometrical confirmation. They found that the OH stretching frequencies of the

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PAP and PDP are redshifted by 3 and 127 cm^{-1}, respectively, from that of bare phenol (3657 cm^{-1}).

Sagarik and Asawakun [16] used ab initio calculations to examine the equilibrium structure of the phenol dimer. The binding energy of the phenol dimer in the most stable equilibrium structure was reported to be 7.48 kcal/mol. Of the different structures they reported, structures A, B, and F [16] seem to be most common in experimental studies [17].

There are few experimental investigations of the phenol dimer cation. From ZEKE photoelectron spectroscopy, Dopfer et al. [18] suggested that a structural change is induced upon ionization of the phenol dimer. The interaction between the phenol moieties is thought to be enhanced in the ionic dimer, indicating a significant strengthening of the hydrogen bond (shortening of the bond length) on ionization. Sawamura et al. [19] and Fujii et al. [20] observed IR and electronic spectra of the phenol dimer cation and suggested that the PDP moiety acts as the charged moiety. They observed the OH stretching frequency of the PAP at 3620 ± 3 cm^{-1} and were puzzled by the disappearance of distinct bands due to the OH stretching in the PDP moiety in the region 3600–3000 cm^{-1}. Ohashi et al. [21] performed photodissociation spectroscopy of the phenol dimer cation and discussed the structure of the dimer cation on the basis of electronic spectra. The OH stretching of the PDP in the dimer cation has not yet been observed experimentally. The absence of this band in experimental observations has received considerable attention in the literature [5, 19, 20, 21].

In this article, we report the optimized structures, binding energies, and OH stretching frequencies of the phenol dimer and its cation. To the best of our knowledge, this is the first theoretical investigation of the OH stretching frequencies of the phenol dimer and its cation. We report a very small OH stretching frequency of the PDP in the phenol dimer cation, which has not yet been identified in experimental studies.

2 Method of calculations

Ab initio Hartree–Fock (HF) calculations were performed for the phenol monomer and dimer and for their cations using the GAMESS system [22]. We used the basis set of (73/7) given by Huzinaga et al. [23] for C and O, which was decontracted to (721/52), and the double-zeta basis set of Dunning [24] for H. The structure of the phenol monomer and its cation are shown in Fig. 1.

For the phenol dimer, we considered four structures: herringbone, parallel displaced, two T-shaped structures. The first three are the same as the A, B, and F structures considered by Sagarik and Asawakun [16], respectively. In this article, we denote these structures as A, B, and C, respectively (Figs. 2, 3, 4a). In structure C, the OH of the PDP is directed toward the center of the PAP ring, where the hydrogen bond is formed between the OH group and the π electrons of the PAP; we denote this as an OH···X hydrogen bond, where X means the center of the phenyl ring. The fourth structure is similar to C, but the directions of the OH bend and the phenyl ring of the PDP are opposite to those of structure C. This structure is denoted as D hereafter (Fig. 5a).

Starting from these four structures, we optimized the phenol dimer and its cation at the HF level. We used full a optimization technique, i.e., all bond lengths and angles were optimized, while Sagarik and Asawakun [16] kept the structure of the phenol moieties fixed during geometry optimization. Connell et al. [14] performed a structural analysis, while specifying a linear hydrogen bond between the phenol moieties. The binding energies of the neutral phenol dimer and its cation for the four optimized structures were determined from HF, second-order Møller–Plesset perturbation theory (MP2), and complete-active-space self-consistent-field (CASSCF) calculations. The MP2 calculations included correlation of all the π electrons and the CASSCF calculations were performed with an active space of 12 (for the neutral dimer) or 11 (for the dimer cation) electrons in ten orbitals. We performed the counterpoise correction for the basis set superposition error (BSSE) [25, 26] to obtain the binding energies at the HF, CASSCF, and MP2 levels. The vibrational analysis was carried out at the HF level to obtain the OH stretching frequencies.

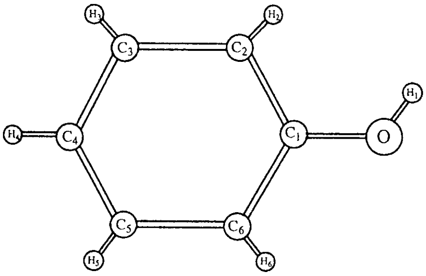

Fig. 1. Geometry of phenol and its cation showing the atom numbering system

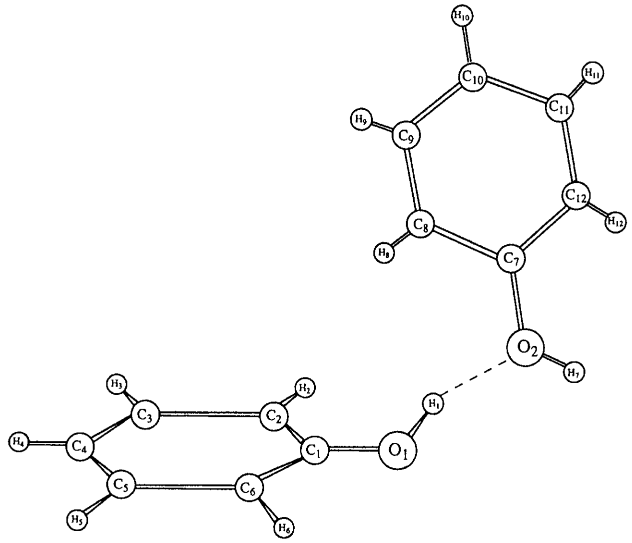

Fig. 2. Optimized structure of the phenol dimer for structure A

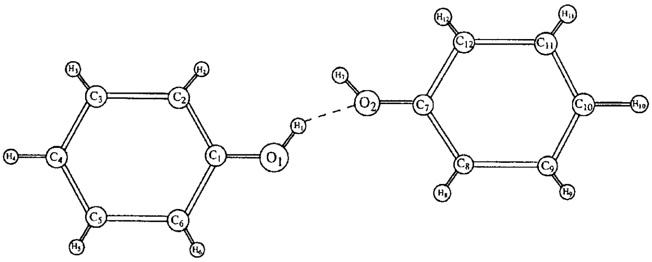

Fig. 3. Optimized structure of the phenol dimer for structure B

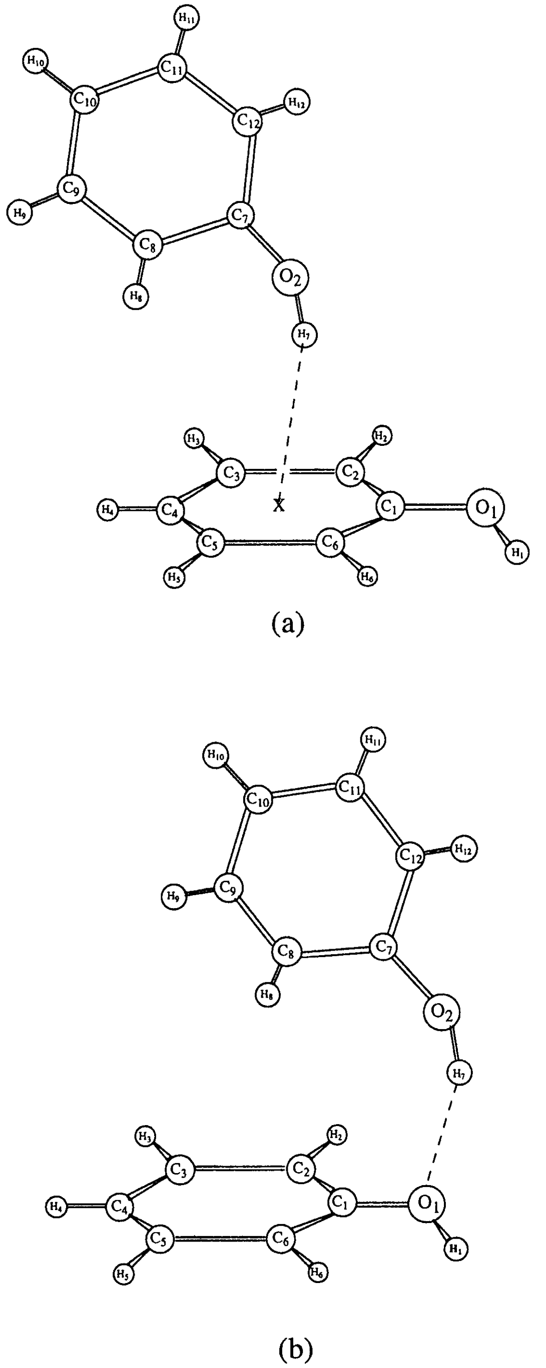

Fig. 4. Optimized structures of **a** the phenol dimer and **b** the phenol dimer cation for structure C

3 Results and discussion

3.1 Phenol and phenol cation

Before examining the phenol dimer and its cation, we first optimized the structure of the phenol monomer and its cation at the HF level and computed the vibrational frequencies. We judged the accuracy of our calculations from a comparison of the calculated structure parameters (Table 1) and selected stretching frequencies (Table 2) of the phenol monomer and its cation with observed values. From Table 1, we see that the O—H_1 bond length of phenol (see Fig. 1 for atom numbering in phenol and its cation) is 0.952 Å in comparison with the observed value of 0.956 Å [2]. The angle C_1—O—H_1 is about 6.4° larger than the observed value of 109°. This appears to be due to the lack of polarization functions in the present calculations. The C_1—O length is only 0.014 Å longer than the observed value. The maximum deviation in other bond lengths from the observed values is 0.011 Å. For the phenol cation, the O—H_1 bond length is consistent with the available theoretical values. A difference of about 10° between other theoretical angles and ours was obtained for the angle C_1—O—H_1; this may also be due to the lack of polarization functions. The other bond lengths and angles are compatible with the available theoretical values.

Our calculated frequencies (scaled values) for the stretching modes in phenol and its cation together with the observed values are listed in Table 2. A scaling factor of 0.9069 was determined by a least-squares fit of the calculated stretching frequencies to available observed ones listed in Table 2. The same scaling factor was also used for the phenol dimer and its cation. The calculated OH stretching frequency of the phenol monomer is 3656 cm^{-1}, which is in good agreement with the observed value of 3657 cm^{-1} [3, 4]. The calculated OH stretching frequency (3580 cm^{-1}) of the phenol cation is redshifted by 76 cm^{-1} from that of phenol in comparison to the experimental redshift of 122 cm^{-1}. The redshift of the OH stretching frequency of the phenol cation can be understood by examining the bond lengths and bond orders listed in Table 3. There is a shortening of the C_1—O bond length and an elongation of the O—H_1 bond length due to ionization. The elongation of the O—H_1 bond length decreases the bond order and hence causes the redshift of the frequency. At the same time the C_1—O stretching frequency is blueshifted by about 123 cm^{-1} in comparison to the observed value of 134 cm^{-1}. From a comparison with observed and other calculated frequencies, it can be seen that MP2 overestimates the OH stretch of phenol [7] and underestimates that of the phenol cation [12]. Since we are interested only in OH stretching, we will not discuss the other frequency values.

3.2 Geometry optimization of the phenol dimer and its cation

The four optimized structures for the phenol dimer and its cation are shown in Figs. 2, 3, 4, 5. Selected characteristic bond lengths and angles of these four optimized structures are listed in Table 4. The minimum-energy geometry for the phenol dimer was an OH···O hydrogen-bonded structure, dimer A, with a nonplanar conformation of phenol moieties. The phenol moieties are not equivalent: one acts as the PDP (first ring) and the other as the PAP (second ring) in the hydrogen bond. The O—H bond lengths of the two phenols are almost the same. The $O_1 \cdots O_2$ distance is 2.828 Å and the O_1—H_1—O_2 angle is 176.8°. The O_2—O_1—H_1 angle, which is involved in hydrogen-bond formation, is 1.8° and the angle O_1—O_2—H_7, which is

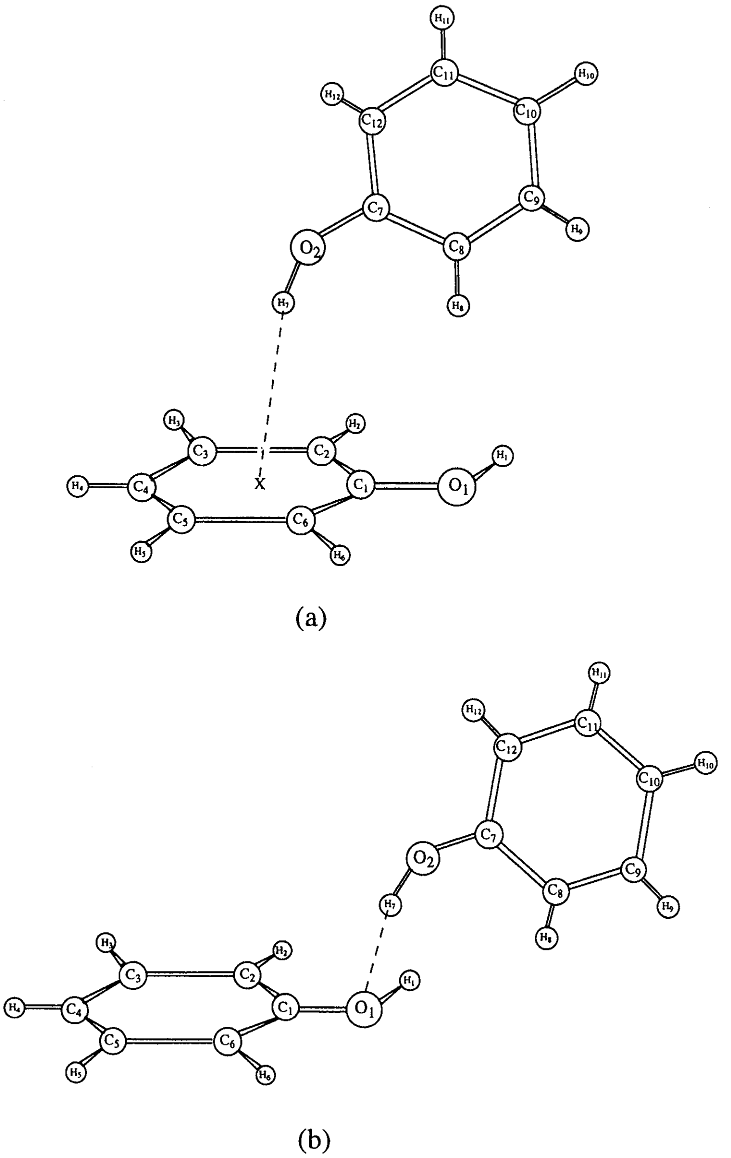

Fig. 5. Optimized structures of **a** the phenol dimer and **b** the phenol dimer cation for structure D

not involved in hydrogen-bond formation, is 112.2°. Connell et al. [14] suggested the same structure for the phenol dimer from a rotational coherence spectroscopy analysis. Sagarik and Asawakun [16] also reported the same structure for the minimum-energy geometry of the phenol dimer. A close comparison with their values is not possible because of some constraints imposed in their optimization procedures; however, we can make a comparison with their binding energies. The binding energies calculated at different levels of calculation using the counterpoise correction for BSSE [25, 26] are listed in Table 5. The binding energies of dimer A calculated at the HF, MP2, and CASSCF levels are 6.51, 9.93, and 6.46 kcal/mol, respectively, which agree well with the experimental prediction of 5 kcal/mol or greater [14] and with the theoretical value of 7.48 kcal/mol given by Sagarik and Asawakun [16].

The energy-optimized dimer B, in which the phenol moieties are in the same plane, is shown in Fig. 3. This is also nonequivalently bound by a hydrogen bond. In this case the angle $O_2—O_1—H_1$ involved in the hydrogen-bond formation is 9.3°, which is larger than that of dimer A. The binding energies of dimer B calculated at the HF, MP2, and CASSCF levels are 6.24, 7.38, and 6.21 kcal/mol, respectively, which are slightly smaller than those of dimer A.

The energy-optimized structure of T-shaped dimer C, in which the hydrogen bond is formed between the OH of the PDP and the π system of the PAP is shown in Fig. 4a. The binding energies of dimer C at various levels of calculation are 4.8–6.1 kcal/mol smaller than those of dimers A and B. Sagarik and Asawakun gave a larger binding energy than ours [16] for dimer C. Finally, we optimized dimer D (Fig. 5a), in which the O_1–H_1 bend and the second phenyl ring are in the opposite direction to those of dimer C. The binding energies of dimer D are 0.5–0.8 kcal/mol larger than those of dimer C, but are much smaller than those of dimers A and B. Thus, dimers C and D with an OH$\cdots$X hydrogen bond are less stable for the neutral phenol dimer.

Table 1. Optimized geometry of phenol (*Ph*) and its cation

	PhOH					$(PhOH)^+$		
	Present	Obs[a]	HF[b]	DFT[b]	MP2[b]	Present	HF[c]	DFT[c]
Bond length (Å)								
C_1—C_2	1.383	1.398	1.389	1.410	1.396	1.424	1.436	1.433
C_2—C_3	1.388					1.355	1.364	1.371
C_3—C_4	1.384					1.426	1.424	1.426
C_4—C_5	1.384					1.418	1.418	1.418
C_5—C_6	1.382					1.354	1.369	1.373
C_6—C_1	1.386					1.431	1.438	1.438
C_1—O	1.378	1.364	1.351	1.382	1.372	1.309	1.279	1.313
O—H_1	0.952	0.956	0.943	0.977	0.943	0.960	0.956	0.979
C_2—H_2	1.073	1.076	1.076	1.093	1.082	1.071	1.075	1.087
C_3—H_3	1.072					1.070	1.074	1.085
C_4—H_4	1.071	1.082	1.075	1.092	1.081	1.071	1.073	1.080
C_5—H_5	1.072					1.070	1.073	1.085
C_6—H_6	1.070					1.070	1.074	1.085
Bond angle (degrees)								
C_1—O—H_1	115.4	109.0	110.9	108.1	108.5	121.6	112.0	113.4
C_2—C_1—O	122.8	122.5			122.8	123.2	122.5	122.9
C_6—C_1—O	116.6					115.4	116.1	115.6
C_1—C_2—C_3	119.5					118.9	118.4	118.5
C_2—C_3—C_4	120.5					120.2	120.6	120.1
C_3—C_4—C_5	119.4					120.6	120.7	121.2
C_4—C_5—C_6	120.7					119.7	120.1	119.8
C_5—C_6—C_1	119.5					119.2	118.7	118.8
C_6—C_1—C_2	120.6					121.4	121.4	121.5
C_1—C_2—H_2	120.4					119.9		
C_2—C_3—H_3	119.4					120.4	120.0	120.3
C_3—C_4—H_4	120.3					119.5	119.4	119.3
C_4—C_5—H_5	120.0					119.5	119.8	119.8
C_5—C_6—H_6	121.8					123.2	123.3	122.9

[a] Ref. [2]
[b] Ref. [5] with 6–31 G(d, p) basis set
[c] Ref. [12] with 6–31 G(d) basis set

Table 2. Calculated stretching frequencies (cm^{-1}) of phenol and its cation. Δ is defined as $(\nu_{present} - \nu_{obs}) \times 100/\nu_{obs}$

Mode	PhOH				$(PhOH)^+$			
	$\nu_{present}$	ν_{obs}	Δ(%)	ν_{calc}	$\nu_{present}$	ν_{obs}	Δ(%)*	ν_{calc}
OH stretch	3656	3657[a]	−0.03	3664[c]	3580	3535[f]	+ 1.3	3565[h]
		3656[b]	−0.01	3668[d]				3564[i]
				3882[e]				3453[j]
CH stretch	3072	3087[b]	−0.5		3089			
CH stretch	3058	3070[b]	−0.4		3080			
CH stretch	3043	3063[b]	−0.6		3075			
CH stretch	3035	3049[b]	−0.5		3065			
CH stretch	3023	3027[b]	−0.1		3057			
CC stretch	1634	1610[b]	+1.5		1636	1669[g]	−2.0	
CC stretch	1616	1603[b]	+0.8		1531			
CC stretch	1522	1501[b]	+1.4		1479	1500[g]	−1.4	
CC stretch	1487	1472[b]	+1.0		1428			
CC stretch	1374	1343[b]	+2.3		1362			
CO stretch	1252	1261[b]	−0.7		1375	1395[g]	−1.5	

[a] Ref. [3, 4]
[b] Ref. [1]
[c] Ref. [5] by DFT/6–31 G(d, p) (unscaled value)
[d] Ref. [6] by SCF/6–31 G(d) (scaled by 0.8907)
[e] Ref. [7] by MP2/6–31 G(d, p) (unscaled value)
[f] Ref. [10]
[g] Ref. [9]
[h] Ref. [12] by UHF/6–31 G(d) (scaled by 0.8929)
[i] Ref. [12] by quoted UNO-CAS (scaled using the value of Liu)
[j] Ref. [12] by MP2/6–31 G(d) (scaled by 0.9427)

The optimized structures of the phenol dimer A and B cations are similar to those of the respective neutral dimers A and B; however, the bond lengths and angles of the dimer cation are different from those of the neutral

Table 3. Bond lengths and bond orders of phenol and its cation

Bond	Bond length (Å)		Bond order	
	PhOH	$(PhOH)^+$	PhOH	$(PhOH)^+$
$O—H_1$	0.952	0.960	0.76	0.70
$C_1—O$	1.378	1.309	0.93	1.14

Table 4. Optimized structures of the phenol dimer and its cation

System Structure	$(PhOH)_2$				$(PhOH)_2^+$			
	A	B	C	D	A	B	C	D
Bond length (Å)								
$O_1—O_2$	2.828	2.809	4.199	4.374	2.482	2.492	2.478	2.479
$O_1—H_1$	0.960	0.961	0.952	0.953	1.021	1.019	0.956	0.956
$O_2—H_7$	0.953	0.952	0.953	0.953	0.956	0.953	1.022	1.022
$H_1—O_2$	1.869	1.867			1.461	1.478		
$H_7—O_1$							1.458	1.458
$X—H_7^a$			3.027	3.042				
$C_1—C_7$	4.657	4.802	4.949	4.503	4.172	4.581	4.156	4.221
$C_4—C_{10}$	9.004	9.931	6.768	8.161	7.815	9.804	7.654	8.263
Bond angle (degrees)								
$O_1—H_1—O_2$	176.8	166.0			177.2	172.4		
$O_1—H_7—O_2$							175.4	177.4
$O_2—O_1—H_1$	1.8	9.3			1.7	4.7	117.0	120.8
$O_1—O_2—H_7$	112.2	131.5			117.9	127.9	2.5	1.3
$C1—X—H_7^a$			75.5	77.4				
$X—H_7—O_2^a$			166.4	161.4				
$C_1—O_1—H_1$	116.5	116.8	115.7	115.4	125.4	126.5	115.1	114.8
$C_7—O_2—H_7$	115.0	114.7	115.7	115.6	117.9	113.7	126.1	124.9

[a] X means the center of the phenyl ring

Table 5. Binding energies (kcal/mol) of the phenol dimer and its cation. The counterpoise correction for basis set superposition error are included

Structure	$(PhOH)_2$					$(PhOH)_2^+$		
	HF	MP2	CASSCF	Obs[a]	SA[b]	HF	MP2	CASSCF
A	6.51	9.93	6.46	≥5	7.48	24.45	30.44	26.82
B	6.24	7.38	6.21		6.86	20.93	27.51	22.61
C	1.47	1.25	1.00		5.76	24.60	30.30	26.83
D	2.02	2.00	1.50			24.14	30.58	26.74

[a] Ref. [14]
[b] Ref. [16]

dimers, as seen in Table 4. The dimer cation is also bound by a single OH···O hydrogen bond, with one phenol moiety acting as the PDP and the other as the PAP. In our calculations, the charged moiety appears to be the PDP, which is obviously because the phenol cation is more acidic than neutral phenol. Table 4 shows that the $O_1—O_2$ distance of the dimer A cation is 2.482 Å, which is 0.35 Å shorter than that of neutral dimer A. The $O_1—H_1$ bond length (1.021Å) of the PDP involved in hydrogen-bond formation is longer than the $O_2—H_7$ bond length (0.956Å) of the PAP. Angle $O_2—O_1—H_1$, which is involved in hydrogen-bond formation, is 1.7° and angle $O_1—O_2—H_7$, which is not involved in hydrogen-bond formation, is 117.9°. The calculated binding energies of the dimer A cation are 24.45, 30.44, and 26.82 kcal/mol at the HF, MP2, and CASSCF levels, respectively; these are more than 3 times larger than those of the neutral dimer A. Dopfer et al. [18] suggested that such strong binding occurred in the phenol dimer cation. Re and Osamura [27] also found that the stabilization energy of hydrogen bonding in the phenol–ammonia cation is about 3 times larger than that of the neural complex. In the dimer B cation (Fig. 3), the $O_1—H_1$ distance of the PDP is also longer than the $O_2—H_7$ distance of the PAP. This structure is about 3–4 kcal/mol more stable than the dimer A cation.

In the case of the phenol dimer C and D cations, we finally obtained the optimized structures shown in Figs. 4b and 5b, respectively. These structures are not similar to the corresponding neutral dimer structures, but are very similar to the dimer A cation (Fig. 2) with the PDP and PAP moieties interchanged. The binding energies of the dimer A, C, and D cations are also almost the same. Thus, the dimer with the OH···X hydrogen bond disappears in the phenol dimer cation and the A, C, and D structures are local minima with similar structure parameters and almost the same binding energies.

3.3 OH stretching frequency of the phenol dimer and its cation

The calculated OH stretching frequencies and the IR absorption intensities of the phenol dimer and its cation are shown in Table 6 for different optimized structures. We see that for the minimum-energy phenol dimer A, the OH stretching frequency of the PAP is 3652 cm^{-1}, which is in good agreement with the value of 3654 cm^{-1} observed by Ebata et al. [15]. The OH stretching frequency of the PDP is 3516 cm^{-1} in comparison to the observed value of 3530 cm^{-1} [15]. The OH stretching frequency of the PAP is reduced by 5 cm^{-1} and the hydrogen-bonded OH stretching frequency of the PDP is reduced by 141 cm^{-1} from that of bare phenol (3657 cm^{-1}). Such reductions in the OH vibrational frequency in hydrogen-bond formation generally occur; according to the observation of Ebata et al. [15] the corresponding reductions are 3 and 127 cm^{-1} for the OH vibrations of PAP and PDP, respectively.

For dimer B, the OH stretching frequencies of the PAP and PDP moieties are also consistent with the observed values. For dimers C and D, however, the OH stretching frequency of the PDP is almost equal to that of bare phenol, the reduction is about 11 cm^{-1}; therefore, we conclude that structures C (Fig. 4a) and D (Fig. 5a) with the OH···X hydrogen bond may not be possible geometries for the phenol dimer because the OH stretching frequencies of the PDP are almost the same as in bare phenol and also because of their small binding energies. The IR absorption intensities of the OH stretch of the PAP are slightly larger than that of rare phenol and those of the PDP for dimers A and B are 10 times larger than that of rare phenol.

For the phenol dimer A cation, the OH stretching frequency of the PAP is 3616 cm^{-1}. Structures C and D also have almost the same frequency values. These are in good agreement with the recently observed value of 3620 ± 3 cm^{-1} of Sawamura et al. [19] and Fujii et al. [20]. The calculated OH stretching frequencies are reduced by about 40 cm^{-1} from that of bare phenol. These structures of the phenol dimer cation are responsible for the observed spectra. However, structure B should be ruled out because of the large OH stretching frequency of its PAP, which is almost the same as that of bare phenol. The reduction is only 1 cm^{-1}. Structure B is also unstable by about 4–5 kcal/mol compared with the others.

The frequency shift of the OH stretching of the PDP in the dimer cation is the most remarkable feature. The OH stretching frequency of the PDP for dimer cation A was calculated to be 2447 cm^{-1}. Almost the same value has been obtained for structures C and D. The reduction in this hydrogen-bonded OH stretching frequency is 1210–1223 cm^{-1} from that of bare phenol. This is explained by comparing selected bond lengths and bond orders between the phenol dimer and its cation; these are listed in Table 7 for structure A. From the table, the bond lengths as well as the bond orders for O_2—H_7 of the PAP moiety are similar in the neutral and cationic dimers. However, the O_1—O_2 and $H_1\cdots O_2$ distances of the dimer cation decrease by 0.35 and 0.41 Å, respec-

Table 6. OH stretching frequencies (cm^{-1}) and IR absorption intensities of the phenol dimer and its cation. *PAP* denotes the proton-accepting phenol and *PDP* the proton-donating phenol. The numbers in *parentheses* are the IR absorption intensities, which are measured relative to that of the OH stretching of rare phenol

Structure	$(PhOH)_2$				$(PhOH)_2^+$			
	PAP		PDP		PAP		PDP	
A	3652	(1.25)	3516	(10.13)	3616	(2.52)	2447	(57.59)
B	3658	(1.07)	3509	(10.17)	3657	(1.35)	2489	(62.83)
C	3655	(1.13)	3646	(1.93)	3617	(2.57)	2436	(57.36)
D	3652	(1.13)	3646	(2.43)	3618	(2.43)	2434	(60.02)
Obs.	3654[a]		3530[a]		3620 ± 3[b]		–	

[a] Ref. [15]

[b] Ref. [19, 20]

Table 7. Bond lengths and bond orders of the phenol dimer and its cation

Bond	Bond length (Å)		Bond order	
	$(PhOH)_2$	$(PhOH)_2^+$	$(PhOH)_2$	$(PhOH)_2^+$
O_1—O_2	2.828	2.482		
O_2—H_7	0.953	0.956	0.75	0.72
O_1—H_1	0.960	1.021	0.68	0.49
$H_1\cdots O_2$	1.869	1.461	0.001	0.16

tively, compared to those of the neutral dimer, resulting in an elongation of the O_1-H_1 length of 0.06 Å. The $H_1 \cdots O_2$ bond order increases from 0.001 to 0.16 and the O_1-H_1 bond order decreases by 0.19. Thus, the O_1-H_1 bond becomes weaker and the H_1 atom of the PDP moves closer to the PAP and the O_1-O_2 length shortens, resulting in the formation of a stronger hydrogen bond in the cation than in the neutral dimer. The large reduction in the OH stretching frequency of the PDP in the phenol dimer cation can be attributed to the effects of elongation of the O_1-H_1 bond on the formation of a stronger hydrogen bond in the dimer cation than in the neutral dimer. Such strengthening of the hydrogen bond in the dimer cation was suggested by Dopfer et al. [18]. This OH stretching frequency of the PDP has not yet been observed in any spectroscopic studies of the phenol dimer cation. There is also no available theoretical data for comparison. However, Re and Osamura [27] recently reported a large reduction (of about 864–1581 cm^{-1}) in the hydrogen-bonded OH stretching frequency of the cations $[phenol–NH_3]^+$, $[phenol–H_2O]^+$ and $[phenol–(H_2O)_2]^+$ from that of bare phenol due to the formation of a stronger hydrogen bond in the cations. The IR absorption intensities of the OH stretch of the PDP for dimer cations A, C, and D are 23–25 times larger than those of the PAD and almost 60 times larger than that of rare phenol. The present study is the first theoretical report of the OH stretching frequencies of the phenol dimer and its cation. Since there are no data for the hydrogen-bonded OH stretching frequency of the dimer cation, our results may serve for future reference.

4 Conclusions

We investigated possible geometrical structures for the phenol dimer and its cation. The calculated binding energy of the phenol dimer agrees reasonably with experimental and other theoretical values. The calculated binding energies of the dimer cation are about 28 kcal/mol at the MP2 and CASSCF levels; this is more than 3 times larger than in the neutral dimer. Our calculated OH stretching frequencies of the phenol dimer are in agreement with observed values. The OH stretching frequencies (3616–3618 cm^{-1}) of the PAP in the phenol dimer cation are in good agreement with the observed value (3620 ± 3 cm^{-1}). Those of the PDP in the dimer cation are calculated to be 2434–2447 cm^{-1}, which are 1210–1223 cm^{-1} lower than that of bare phenol. The large reduction in the OH stretching frequency of the PDP in the phenol dimer cation can be attributed to elongation of the O—H bond involved in the hydrogen bond on the formation of a stronger hydrogen bond in the cation than in the neutral dimer. These values for the OH stretching frequencies of the PDP in the phenol dimer cation will serve for future reference.

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