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THEORETICAL VS. EXPERIMENTAL IR FREQUENCY SHIFTS UPON π -HYDROGEN BONDING: COMPLEXES OF SUBSTITUTED PHENOLS WITH HEXAMETHYLBENZENE*

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The quality of theoretical prediction of O-H stretching frequency shifts upon π -hydrogen bonding is analyzed for series of ten complexes between monosubstituted phenols and hexamethylbenzene. Computed O-H frequencies from density functional theory computations at B3LYP/6-311++G(2df,2p) were compared with literature spectroscopic data. The results reveal that the applied theoretical method predicts with an excellent accuracy the O-H frequency shifts [$\Delta\nu(\text{OH})$] upon π -hydrogen bond formation. Comparisons with analogous theoretical and experimental data for benzene complexes with substituted phenols reveal the magnitude of the methyl groups' hyperconjugative effects on interaction energies and frequency shifts. The induced by phenol substituents variations in bonding energies and $\Delta\nu(\text{OH})$ are rationalized using theoretically evaluated and experimental parameters.

Key words: π -hydrogen bonding; hexamethylbenzene; substituted phenols; O-H frequency; DFT computations

INTRODUCTION

Vibrational spectroscopy has provided rich experimental information on hydrogen bonding [1–5]. This method has also been instrumental in studies of π -hydrogen bonds [6–8]. The advances of computational quantum chemistry have opened possibilities for gaining deeper insights into the nature of this type of noncovalent interactions that are of key importance in biology, chemistry, and materials science [9–14]. The present study aims at examining properties for series of complexes of hexamethylbenzene with monosubstituted phenols by a combined application of computational and spectroscopic data. The O-H stretching frequency shifts upon complex formation provide an excellent basis for quantifying the effects of structural variations on the processes. The experimental data considered in the present research are taken from the work of Seguin et al. [15]. Our principal interest was in examining how well theoretical computations employing the widely applied B3LYP func-

tional will perform in evaluating properties of the studied complexes. We also focus on analyzing the effects of substituents in the phenolic aromatic ring. By comparisons with previously obtained analogous computational and spectroscopic data for benzene [16], the role of the methyl hyperconjugative effects in hexamethylbenzene on the strength of π -hydrogen bonding is also assessed.

The usual interpretation of substituent effects in the proton-accepting aromatic ring considers their electron withdrawing and releasing effects on the π -electron system [17–19]. An alternative interpretation emphasized the direct interaction between the polar aromatic substituents and the approaching proton-donating molecule [20, 21]. Sherill et al. [21–23] and Lee et al. [24] have shown by using symmetry adapted perturbation theory (SAPT) [25] computations that the ratio between attractive (electrostatic, dispersion, induction) and repulsive (exchange) terms defines the effects of aromatic substituents.

Recent vibrational Stark spectroscopy studies of Saggi, Levinson and Boxer [26, 27] on the π -

*Dedicated to academician Bojan Šoptrajanov on the occasion of his 80th birthday

hydrogen bonded complex of phenol and benzene revealed a dominant role of the electrostatic interaction energy in complex formation. The experimentally determined electrostatic interaction energy compared well with the theoretically derived from DFT computations. Vibrational echo spectroscopy study on the same interaction revealed that the time constant of the complex was only 8 picoseconds [28, 29]. In a previous work, we presented results from an IR spectroscopic and theoretical investigation for a series of 20 π -hydrogen-bonded complexes of monosubstituted phenols and benzene [16]. Correlation analyses employing a number of experimental and theoretical quantities revealed a dominant role of the acidity of the proton donating phenols on complexation energies. Banerjee and Chakraborty [30] reached similar conclusions in their study of complexes of fluorosubstituted phenols with benzene. Zhou et al. [31] conducted a detailed theoretical study of the various geometries of phenol-benzene π -hydrogen bonded complexes.

In the present research, we examine the interaction of ten monosubstituted phenols with hexamethylbenzene. As mentioned, the selected molecules provide a possibility for analyzing the role of methyl hyperconjugative effects on the complex formation. In this respect, it was also of interest to assess how well different theoretical approaches will quantify the expected increased electron density over the aromatic ring in hexamethylbenzene. The theoretical analysis is validated by comparisons with the experimental IR O-H frequency shifts upon π -hydrogen bonding as determined by Saguin et al. [15] for CCl_4 solutions.

COMPUTATIONAL METHODS

DFT computations employing the B3LYP functional [32–34] combined with the 6-311++G(2df,2p) [35] basis set for a series of ten hydrogen-bonded complexes between monosubstituted phenols and hexamethylbenzene were performed. All computations employed the Gaussian09 program [36]. The optimized structures were verified to be minima of the potential energy surfaces with the aid of harmonic frequency computations. The interaction energies are corrected for basis set superposition error (BSSE) using the counterpoise procedure [37]. The computations employed the IEFPCM method [38] to simulate the experimental conditions (CCl_4 solvent) of the recorded infrared spectra [15]. A number of theoretical quantities were employed in rationalizing the effects of phenol substituents on interaction energies and shifts of O-H stretching frequencies. These included the

NBO [39] and Hirshfeld [40] atomic charges as well as the electrostatic potential at nuclei (EPN). EPN was first introduced by Wilson in 1962 [41]. In a number of studies from our laboratory, we have established that EPN is a remarkably accurate descriptor of the abilities of specific atomic centers in molecules to form hydrogen bonds [42–47] and also in quantifying chemical reactivity [48–51]. In later years, EPN values have been successfully employed by other authors in examining reactivity trends [52–60]. Politzer and Thruhlar [61] defined the electrostatic potential at nuclei Y (V_Y) by Eqn. (1):

$$V_Y \equiv V(\mathbf{R}_Y) = \sum_{A \neq Y} \frac{Z_A}{|\mathbf{R}_A - \mathbf{R}_Y|} - \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_Y|} d\mathbf{r} \quad (1)$$

In this relationship, the singular term for nucleus Y is excluded. Z_A is the charge of nucleus A at position $\mathbf{R}_A$, and $\rho(\mathbf{r})$ is the electron density function. The electrostatic potential at nuclei is a rigorously defined quantum mechanical quantity.

RESULTS AND DISCUSSION

Figure 1 illustrates the computationally evaluated structure of the complex between phenol and hexamethylbenzene. All ten studied complexes are characterized by a T-shaped structure with nearly perpendicular orientation of the proton donor phenols with respect to the hexamethylbenzene ring (Figure 1). As seen, two π -hydrogen bonds are simultaneously formed. The first is between the phenolic O-H bond and the π -electron system of hexamethylbenzene, while the second involves the *ortho* C-H bond. The O-H $\cdots\pi$ -hydrogen bond is much stronger with distance from the O-H hydrogen to the nearest ring carbon of 2.45 Å. The distance from the C-H hydrogen to the nearest carbon is 2.95 Å. Comparisons with the structure of analogous complexes of substituted phenols with benzene [16], reveals some distinct differences (Figure 1). Although the latter complexes also have T-shaped structure, the O-H and C-H bonds for the lowest energy isomers point toward the middle of the respective closest C-C bonds in the benzene ring (Figure 1). In the complexes with hexamethylbenzene, the two π -hydrogen bonds point toward ring edges (Figure 1).

As emphasized, it was of interest to examine how well the employed B3LYP DFT functional would perform in predicting properties of the investigated π -hydrogen bonded complexes. The availability of experimental $\Delta\nu_{\text{OH}}$ shifts for the systems studied provides an experimental verification of the theoretical results. The variations of C-H stretching

frequencies, participating in π -hydrogen bonding, were only obtained from theoretical computations. These frequency shifts were determined for the respective tetradeutero phenols, in which the C-H

bond participating in complex formation remains undeuterated. The theoretically estimated and experimental [15] frequencies for the studied complexes are shown in Table 1.

Figure 1. Optimized structures of π -hydrogen bonded complexes of phenol with hexamethylbenzene (left, center) and benzene (right) from B3LYP/6-311++G(2df,2p) computations.

Table 1. Interaction energies (kcal/mol) for π -hydrogen bonded complexes, experimental and computed O-H stretching frequency shifts (cm^{-1}), and computed C-H stretching frequencies (cm^{-1}) in substituted phenols and their complexes with hexamethylbenzene from B3LYP/6-311++G(2df,2p) calculations (CCl_4 solvent).

Substituent	ΔE	$\nu_{\text{O-H}}$ mon- omer	$\nu_{\text{O-H}}$ complex	$\Delta\nu_{\text{O-H}}$ theor.	$\Delta\nu_{\text{O-H}}$ ^a expl.	$\nu_{\text{C-H}}$ mon- omer	$\nu_{\text{C-H}}$ compl.	$\Delta\nu_{\text{C-H}}$ the- or.
H (phenol)	-1.456	3824	3721	-104	-106	3155	3163	+8
m-CH ₃	-1.265	3824	3726	-99	-102	3157	3161	+3
p-CH ₃	-1.252	3827	3728	-99	-100	3153	3157	+4
m-OCH ₃	-1.244	3825	3723	-102	-105	3162	3168	+6
p-OCH ₃	-1.204	3831	3734	-97	-98	3163	3167	+4
m-N(CH ₃) ₂	-1.215	3828	3737	-92	-97	3177	3180	+2
m-Cl	-1.832	3825	3703	-122	-118	3168	3184	+16
p-Cl	-1.802	3827	3707	-120	-112	3166	3170	+4
p-F	-1.557	3829	3718	-111	-107	3167	3173	+6
m-NO ₂	-2.193	3823	3682	-141	-136	3170	3171	+1
r, plot with $\Delta\nu_{\text{O-H}}$ (theor) ^b					0.976			
r, plot with ΔE ^b				0.985	0.956			

^a From Ref. [15]

^b r, correlation coefficient

The red shifting of O-H stretching frequencies in the hydrogen-bonded complexes is quite significant. The experimental $\Delta\nu(\text{OH})$ from the study of Seguin et al. [15] vary from -98 cm^{-1} to -136 cm^{-1} for the differently substituted phenols (Table 1). It is remarkable that very similar range of variations (from -97 cm^{-1} to -141 cm^{-1}) is predicted

by the B3LYP/6-311++G(2df,2p) computations. Along the entire series of π -hydrogen bonded complexes, the coincidence between theoretical predictions and experiment for the magnitude of frequency shifts is indeed very good. These results illustrate the power of the employed DFT method [B3LYP/6-311++G (2df, 2p)] in evaluating vibra-

tional spectroscopic properties of the studied systems. Figure 2 illustrates the plot between theoretical and experimental $\Delta\nu_{\text{OH}}$.

Figure 2: Plot of theoretically estimated O-H frequency shifts, $\Delta\nu_{\text{O-H}}(\text{theor})$ vs. the experimental $\Delta\nu_{\text{O-H}}(\text{expl})$ (the experimental data are from Ref. [16]).

The dependence is characterized by a good correlation coefficient ($r = 0.976$). It should, of course, be emphasized that the experimental frequencies include anharmonic effects. Thus, the obtained nice correspondence between observed and theoretical (harmonic) $\Delta\nu(\text{OH})$ may be regarded as somewhat fortuitous. Nonetheless, the anharmonic

effects on the O-H stretching frequency are expected to be quite consistent along the investigated series of structurally closely related systems.

The trend for the C-H bond stretching frequency is reverse. For all studied complexes, the theory predicts blue shifts of the respective C-H frequencies upon complexation. These results are in accord with the previously reported data for the complexes of benzene with substituted phenols [16]. The weakening of the O-H bonds and strengthening of C-H bonds is well illustrated by the computed bond lengths (Table 2).

The O-H bonds are clearly elongated upon complexation. Literature studies [62] have shown that the process is accompanied by a transfer of electron density from the proton accepting π -system to the antibonding σ^* X-H orbital of the proton donor resulting in weakening of the bond. This also is reflected in the red-shifting X-H stretching frequency. The blue shifting hydrogen bonding is dominated by dispersive interactions resulting in shortening and strengthening of the respective X-H bonds [23, 62, 63]. Table 2 reveals a satisfactory correlation ($r = 0.966$) between r_{OH} in the formed complexes and energies of hydrogen bonding.

The BSSE corrected interaction energies are also given in Table 1. Satisfactory correlations between ΔE and O-H frequency shifts are obtained (see the correlation coefficients in the last two rows of Table 1).

Table 2. BSSE corrected interaction energies (kcal/mol), O-H ($r_{\text{O-H}}$, Å) and C-H ($r_{\text{C-H}}$, Å) bond lengths for monomeric phenols and for π – hydrogen bonded complexes of phenol and hexamethylbenzene from B3LYP/6-311++G(2df, 2p) computations.

Substituent	ΔE	$r_{\text{O-H}}$ reactant	$r_{\text{O-H}}$ complex	$r_{\text{C-H}}$ reactant	$r_{\text{C-H}}$ complex
H (phenol)	-1.456	0.9624	0.9676	1.0835	1.0829
m-CH ₃	-1.265	0.9625	0.9673	1.0833	1.0826
p-CH ₃	-1.252	0.9623	0.9673	1.0836	1.0830
m-OCH ₃	-1.244	0.9622	0.9675	1.0826	1.0820
p-OCH ₃	-1.204	0.9620	0.9669	1.0832	1.0829
m-N(CH ₃) ₂	-1.215	0.9621	0.9667	1.0824	1.0819
m-Cl	-1.832	0.9626	0.9685	1.0828	1.0822
p-Cl	-1.802	0.9624	0.9682	1.0830	1.0825
p-F	-1.557	0.9622	0.9678	1.0828	1.0824
m-NO ₂	-2.193	0.9629	0.9695	1.0828	1.0826
r , plot with ΔE^b		0.819	0.966		

Comparisons of computed hydrogen bonding energies and O-H frequency shifts for complexes of substituted phenols with hexamethylbenzene and with benzene as proton acceptors are presented in Table 3. The experimental and theoretical (using the same level of theory) data for benzene are from our earlier study [16]. These comparisons reveal the effects of methyl hyperconjugation. Much higher hydrogen bonding energies characterize the complexes of phenols with hexamethylbenzene. In the case of the unsubstituted phenol as proton-donating species, the interaction energy is almost twice as high compared to the complex with benzene (Table 3). These observations clearly indicate a substantially increased electron density over the hexamethylbenzene ring, which facilitates the complex formation. Figure 3 compares the theoretically estimated EPN values and Hirshfeld atomic charges

at the aromatic ring carbons in monomeric hexamethylbenzene and benzene. Contrary to expectations, Hirshfeld population analysis shows lower negative charges at the ring carbons in hexamethylbenzene compared to benzene. In contrast, the EPN values provide more accurate picture of the charge distribution in the two molecules. More negative electrostatic potentials at the point of the ring carbons indicates increased negative charges in the neighborhood, in harmony with the expected increased electron density. It should be emphasized that EPN values reflect complex influences of all negative and positive charges in the molecule (see Eqn. 1). Nonetheless, it was clearly demonstrated, that EPN at aromatic ring carbons reflects in a consistent way the effects of substituents in aromatic systems [51].

Table 3. Interaction energies (ΔE , kcal/mol) for π -hydrogen bonded complexes of substituted phenols with hexamethylbenzene and benzene, experimental and computed O-H IR frequency shifts (cm^{-1}) upon complexation from B3LYP/6-311++G(2df,2p) computations and experiment [16].

Substituent	Hexamethylbenzene			Benzene		
	ΔE	$\Delta\nu_{\text{O-H}}$ theor.	$\Delta\nu_{\text{O-H}}$ ^a expl.	ΔE	$\Delta\nu_{\text{O-H}}$ theor.	$\Delta\nu_{\text{O-H}}$ ^b expl.
H (phenol)	-1.456	-104	-106	-0.732	-65	-48
m-CH ₃	-1.265	-99	-102	—	—	—
p-CH ₃	-1.252	-99	-100	-0.845	-65	-45
m-OCH ₃	-1.244	-102	-105	—	—	—
p-OCH ₃	-1.204	-97	-98	-0.653	-60	-47
m-N(CH ₃) ₂	-1.215	-92	-97	—	—	—
m-Cl	-1.832	-122	-118	-1.061	-76	-55
p-Cl	-1.802	-120	-112	-0.970	-72	-53
p-F	-1.557	-111	-107	-0.990	-73	-48
m-NO ₂	-2.193	-141	-136	—	—	—

^a From Ref. [15]

^b From Ref. [16]

Three theoretically evaluated parameters (NBO and Hirshfeld atomic charges, EPN values) were employed in rationalizing the effects of substituents in the proton-donating phenols on the energies of complex formation with hexamethylbenzene. In addition, the experimental pKa values for the different phenols were also considered. In our previous study on complexes between benzene and substituted phenols [16], the phenol pKa acidity constants best described the trend of interaction energy variations. Hydrogen bonding energies, pKa values, and the evaluated theoretical parameters are shown in Table 4. The correlation coefficients for the plots of ΔE with these quantities are given in the last row of Table 4.

Surprisingly, the pKa values do not provide a fully satisfactory description of the observed variations in interaction energies. The two types of atomic charges considered, do not perform well in explaining the trends of changes of π -hydrogen bonding energies. The best obtained correlation is with the EPN values at the phenolic O-H hydrogen in isolated phenols (V_H). The less negative V_H at the O-H hydrogen under the influence of electron-withdrawing substituents (NO₂, Cl, F) corresponds to greater ability of these hydrogen atoms to participate in hydrogen bonding. Inversely, the electron-donating substituents (CH₃, OCH₃) lead to more negative V_H values and lower strength of the formed π -hydrogen bonds. These results confirm the good predictive power of the electrostatic potential at nu-

clei as reactivity descriptor for the hydrogen bonding in series of related molecules [42–46]. The computed electrostatic potential at the O-H hydrogen pro-

vide best description of the ability of the monomeric phenols to form π -hydrogen bond with the hexamethylbenzene π -system.

Figure 3: EPN values (top, in atomic units) and Hirshfeld charges (bottom, in electrons) at aromatic ring carbons in hexamethylbenzene and benzene

Table 4. Interaction energies, experimental frequency shifts, electrostatic potential at nuclei (EPN), NBO and Hirshfeld atomic charges at O-H hydrogen atom in substituted phenol monomers from B3LYP/6-311++G(2df, 2p) computations

Substituent	ΔE kcal/mol	$\Delta\nu_{\text{O-H}}^{\text{a}}$ cm^{-1}	V_{H} a. u.	$q_{\text{H}}^{\text{NBO}}$ e	$q_{\text{H}}^{\text{Hirsh}}$ e	$\text{pK}_{\text{a}}^{\text{b}}$
H (phenol)	-1.456	-106	-0.9691	0.4794	0.1746	9.99
m-CH ₃	-1.265	-102	-0.9722	0.4790	0.1738	10.08
p-CH ₃	-1.252	-100	-0.9733	0.4785	0.1731	10.19
m-OCH ₃	-1.244	-105	-0.9705	0.4803	0.1747	9.93
p-OCH ₃	-1.204	-98	-0.9752	0.4780	0.1721	10.21
p-N(CH ₃) ₂	-1.215	-97	-0.9330	0.4868	0.1871	9.88
m-Cl	-1.832	-118	-0.9569	0.4822	0.1791	9.02
p-Cl	-1.802	-112	-0.9580	0.4814	0.1780	9.38
p-F	-1.557	-107	-0.9622	0.4804	0.1762	9.95
m-NO ₂	-2.193	-136	-0.9415	0.4846	0.1833	8.35
r, plot. with ΔE		0.956	0.953	0.732	0.881	0.939

^a From Ref. [15]

^b From Ref. [64]

^c r, correlation coefficient

CONCLUSIONS

Theoretical computations at B3LYP/6-311++G(2df,2p) predict quite accurately O-H stretching frequency shifts induced by π -hydrogen bonding between hexamethylbenzene and a series of substituted phenols. Comparisons with literature theoretical and experimental data for analogous T-shaped complexes of benzene with phenols provide an insight into the effects of methyl hyperconjugation on complex formation. Much stronger complexes with hexamethylbenzene are formed as reflected in computed energies as well as in observed and predicted $\Delta\nu(\text{OH})$ shifts.

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ТЕОРЕТСКИ НАСПРОТИ ЕКСПЕРИМЕНТАЛНИ ПОМЕСТУВАЊА НА ИНФРАЦРВЕНИТЕ ФРЕКВЕНЦИИ ПРИ π -ВОДОРОДНО СВРЗУВАЊЕ: КОМПЛЕКСИ НА СУПСТИТУИРАНИ ФЕНОЛИ СО ХЕКСАМЕТИЛБЕНЗЕН

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Анализиран е квалитетот на теоретското претскажување на поместувањата на О–Н валентните фреквенции при π -водородно сврзување кај серија од десет комплекси помеѓу моносупституирани феноли и хексаметилбензен. Пресметаните О–Н фреквенции со примена на методот на теоријата за функционал од електронската густина на B3LYP/6-311++G(2df,2p) ниво на теорија се споредени со спектроскопските податоци од литературата. Резултатите покажаа дека применетиот теоретски метод со одлична точност ги претскажува поместувањата на О–Н валентните фреквенции [$\Delta\nu(\text{OH})$] при формирање на π -водородно сврзување. Споредувањата со аналогните теоретски и експериментални податоци за бензенски комплекси со супституирани феноли ја даваат големината на хиперкоњугативниот ефект на метилните групи врз интеракционите енергии и фреквентното поместување. Индуцираните (од страна на фенолните супституенти) варирања на енергиите на врските и на $\Delta\nu(\text{OH})$ се рационализирани со користење на теоретски евалуирани како и со експериментални параметри.

Клучни зборови: π -водородно сврзување; хексаметилбензен; супституирани феноли; О–Н фреквенции; DFT пресметки