Substituent Effects on the Hydrogen Bonding between 4-Substituted Phenols and HF, H_2O, NH_3

CHENG, Yu-Hui[a] (程宇辉) **FU, Yao**[a] (傅尧) **LIU, Lei**[a] (刘磊) **GUO, Qing-Xiang**[*,a,b] (郭庆祥)

[a] *Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China*

[b] *National Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, Gansu 730000, China*

Density function theory UB3LYP/6-31 + g(d) calculations were performed to study the hydrogen bonds between *para*-substituted phenols and HF, H_2O, or NH_3. It revealed that many properties of the non-covalent complexes, such as the interaction energies, donor-acceptor distances, bond lengths and vibration frequencies, showed well-defined substituent effects. Therefore, from the substituent effects not only the mechanism of a certain non-covalent interaction can be better understood, but also the interaction energies and structures of a certain non-covalent complex, which otherwise might be very hard or resource-consuming to estimate, can be easily predicted.

Keywords non-covalent interaction, hydrogen bonding, substituent effect, density function theory

Introduction

The concept of substituent effects has been widely used for many years in chemistry and related areas such as biomedical science, agriculture chemistry and toxin research. Studies on the substituent effects have greatly helped us in understanding and predicting chemical properties and mechanisms.[1] Nevertheless, it should be mentioned that almost all the former studies on the substituent effects have been focusing on covalently bonded systems, whereas little has been known so far about the substituent effects on the non-covalent interactions.[2]

Recently, the substituent effects in supramolecular systems attracted our interest. In particular, the substituent effects in cyclodextrin as well as cyclobis(paraquat-*p*-phenylene) inclusion complexation have been studied in our laboratory.[3-7] Remarkably, It was found that not only good substituent effects could be observed in these systems, but also the substituent effects could be used to clarify the detailed mechanism of supramolecular recognition.

Nevertheless, it is worthy to note that unlike covalent systems supermolecules usually show complicated or even non-linear substituent effects.[8] The behavior is presumably due to the fact that too many different types of interactions are simultaneously involved there. As the experimental methods should have trouble in separating the effect exerted by every single interaction, theoretical studies become necessary if a better understanding of mechanistic supramolecular chemistry is aimed. Toward this end, a series of theoretical studies on the substituent effects on non-covalent interactions has been initiated, associated with the substituted alkenes, phenolates and phenoxyl radicals.[9-12] In this paper we report the substituent effects in hydrogen bonds between substituted phenols and HF, H_2O or NH_3.

Method

All the calculations were performed with Gaussian 98 program package.[13] Geometry optimization was done with density functional theory method at UB3LYP/6-31 + g(d) level for both the monomers and complexes. Frequency calculations were also performed at UB3LYP/6-31 + g(d) level, which confirmed that all the optimized structures corresponded to true minima as no negative vibration frequency was found. Interaction energy was computed as difference in energy between the complex and the sum of isolated monomers, and basis set superposition error (*BSSE*) was corrected by the counterpoise procedure of Boys and Bernardi.[14] The interaction energies were also corrected with the zero-point energies calculated at UB3LYP/6-31 + g(d) level.

Results and discussion

The key structural parameters including the Y···H distances, O—H bond length, O—H···Y angles and O—H stretching vibration frequencies of the optimized X—C_6H_4—OH···YH_n (Y = F, O, or N) complexes are listed in Table 1.

* E-mail: qxguo@ustc.edu.cn; Fax: 86-551-3606689.

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Table 1 Y···H distances (10^{-1} nm), H—O bond length (10^{-1} nm), O—H···Y angles (°), and Y—H stretching vibration frequencies (cm^{-1}) of the optimized X—C_6H_4—OH···YH_n(Y = F, O or N) complexes

X	X—C_6H_4—OH···FH				X—C_6H_4—OH···OH_2				X—C_6H_4—OH···NH_3			
	F···H	H—O	∠O—H···F	ν_{O-H}	O···H	H—O	∠O—H···O	ν_{O-H}	N···H	H—O	∠O—H···N	ν_{O-H}
Para substituted phenols												
C_2H_5	1.970	0.973	159.52	3718.2	1.864	0.980	170.55	3575.7	1.861	0.991	169.45	3331.9
C≡CH	1.946	0.973	166.60	3711.7	1.847	0.981	171.36	3553.1	1.854	0.994	177.74	3289.3
CF_3	1.936	0.974	166.85	3705.8	1.836	0.981	175.73	3543.8	1.829	0.996	169.71	3252.4
CH_3	1.974	0.973	158.78	3718.6	1.863	0.980	170.44	3576.1	1.862	0.991	169.57	3333.7
CH = CH_2	1.956	0.973	161.33	3712.9	1.852	0.980	168.59	3558.8	1.848	0.993	169.98	3300.0
CHO	1.930	0.974	168.35	3703.1	1.828	0.982	173.02	3528.3	1.822	0.997	169.40	3232.0
Cl	1.948	0.973	166.66	3715.9	1.846	0.981	170.48	3556.3	1.852	0.993	177.64	3297.0
CN	1.930	0.974	170.23	3703.8	1.825	0.982	172.21	3525.1	1.818	0.997	169.87	3224.2
$COCH_3$	1.939	0.974	166.14	3704.3	1.835	0.982	175.10	3540.3	1.832	0.995	169.46	3257.8
$CONH_2$	1.944	0.973	165.95	3708.3	1.838	0.982	172.01	3541.9	1.836	0.995	169.31	3270.8
COOH	1.932	0.974	169.01	3704.3	1.834	0.982	174.90	3538.7	1.87	0.996	169.83	3245.0
F	1.951	0.973	166.63	3720.9	1.851	0.980	171.03	3566.4	1.851	0.992	169.52	3312.4
H	1.961	0.973	161.29	3716.3	1.860	0.980	169.95	3570.3	1.856	0.992	169.54	3320.0
$N(CH_3)_2$	1.996	0.972	154.07	3725.2	1.874	0.979	171.79	3590.9	1.875	0.990	169.66	3363.7
NH_2	1.991	0.972	154.31	3724.7	1.871	0.979	171.24	3590.4	1.87	0.990	169.87	3361.0
NO_2	1.923	0.974	171.61	3698.7	1.816	0.983	173.27	3511.6	1.805	0.999	170.05	3186.2
OCH_3	1.975	0.972	159.56	3721.8	1.864	0.979	170.34	3583.1	1.866	0.990	169.54	3346.2
OH	1.970	0.972	160.90	3724.0	1.862	0.979	170.75	3580.8	1.864	0.991	168.86	3341.1
SH	1.954	0.973	162.06	3712.1	1.846	0.981	172.26	3555.6	1.842	0.994	169.82	3287.1
Meta substituted phenols												
C_2H_5	1.973	0.973	159.15	3718.5	1.860	0.980	170.51	3573.2	1.860	0.991	169.64	3330.4
C≡CH	1.953	0.973	164.77	3714.1	1.852	0.980	169.92	3561.8	1.848	0.993	169.30	3300.9
CF_3	1.940	0.973	166.98	3712.1	1.838	0.981	174.89	3549.4	1.835	0.995	169.35	3269.8
CH_3	1.972	0.973	159.66	3718.3	1.862	0.980	170.37	3573.6	1.860	0.991	169.74	3329.5
CH = CH_2	1.959	0.973	161.29	3715.2	1.854	0.980	172.35	3567.3	1.855	0.992	169.59	3316.8
CHO	1.943	0.973	166.36	3712.9	1.840	0.981	169.95	3548.0	1.841	0.994	168.92	3284.9
Cl	1.947	0.973	166.61	3714.3	1.847	0.981	170.44	3555.2	1.840	0.994	169.50	3281.6
CN	1.936	0.973	166.68	3708.8	1.832	0.982	170.84	3537.9	1.828	0.995	169.42	3255.0
$COCH_3$	1.951	0.973	163.44	3713.9	1.848	0.980	171.12	3556.9	1.848	0.993	168.70	3300.2
$CONH_2$	1.954	0.973	161.48	3713.0	1.848	0.981	170.48	3556.6	1.847	0.993	168.82	3299.1
COOH	1.943	0.973	166.28	3713.5	1.844	0.981	170.48	3553.2	1.843	0.993	169.45	3290.3
F	1.947	0.973	166.54	3714.6	1.849	0.981	170.19	3557.7	1.840	0.994	169.51	3287.0
H	1.961	0.973	151.29	3716.3	1.860	0.980	169.95	3570.3	1.856	0.992	169.54	3320.0
$N(CH_3)_2$	2.001	0.972	152.89	3722.5	1.869	0.979	172.22	3584.7	1.867	0.990	170.13	3346.5
NH_2	1.986	0.973	154.41	3722.0	1.863	0.980	170.66	3576.9	1.861	0.991	170.02	3333.0
NO_2	1.927	0.973	170.20	3708.7	1.827	0.982	172.88	3531.4	1.824	0.996	168.98	3244.6
OCH_3	1.963	0.973	161.27	3718.1	1.860	0.980	173.16	3575.1	1.858	0.992	169.40	3328.2
OH	1.962	0.973	162.02	3717.2	1.858	0.980	170.14	3569.2	1.855	0.992	169.49	3319.6
SH	1.958	0.973	162.27	3715.2	1.852	0.980	169.90	3561.3	1.848	0.993	169.49	3301.7

According to Table 1, the O—H···X bond angles are mostly around 170°, showing that all the hydrogen bonds are reasonably strong. The X···H distances decrease in the order F···H > O···H ≥ N···H, indicating that the strength of the hydrogen bonding should increase in the order of F···H—O < O···H—O < N···H—O. In agreement with this, the O—H bond lengths in the phenols are found to increase in the order of F···H—O < O···H—O < N···H—O. This is also consistent with the increasing red shift of the O—H vibration frequencies in the order of F···H—O < O···H—O < N···H—O. Clearly, from HF to H_2O to NH_3, the basicity of the hydrogen bond acceptor becomes stronger and therefore, the corresponding charge transfer from the lone pair of the hydrogen bond acceptor to the

O—H antibonding orbital becomes more significant. This stronger charge transfer results in stronger hydrogen bonding interaction, longer O—H bond, and larger red shift of O—H vibration.[15]

Remarkably, in addition to the above qualitative rationalization the several physicochemical properties are actually found to have excellent correlations with each other. In details, the O—H bond lengths in the complexes are found to correlate with the F···H, O···H and N···H distances very well (Fig. 1). The negative slopes indicate that the longer the O—H bond is, the stronger the hydrogen bond. Similarly, the O—H bond lengths are also found to correlate excellently with the O—H stretching vibration frequencies (Fig. 2). The negative slopes of the regressions indicate that the longer the O—H bond is, the weaker the O—H bond.

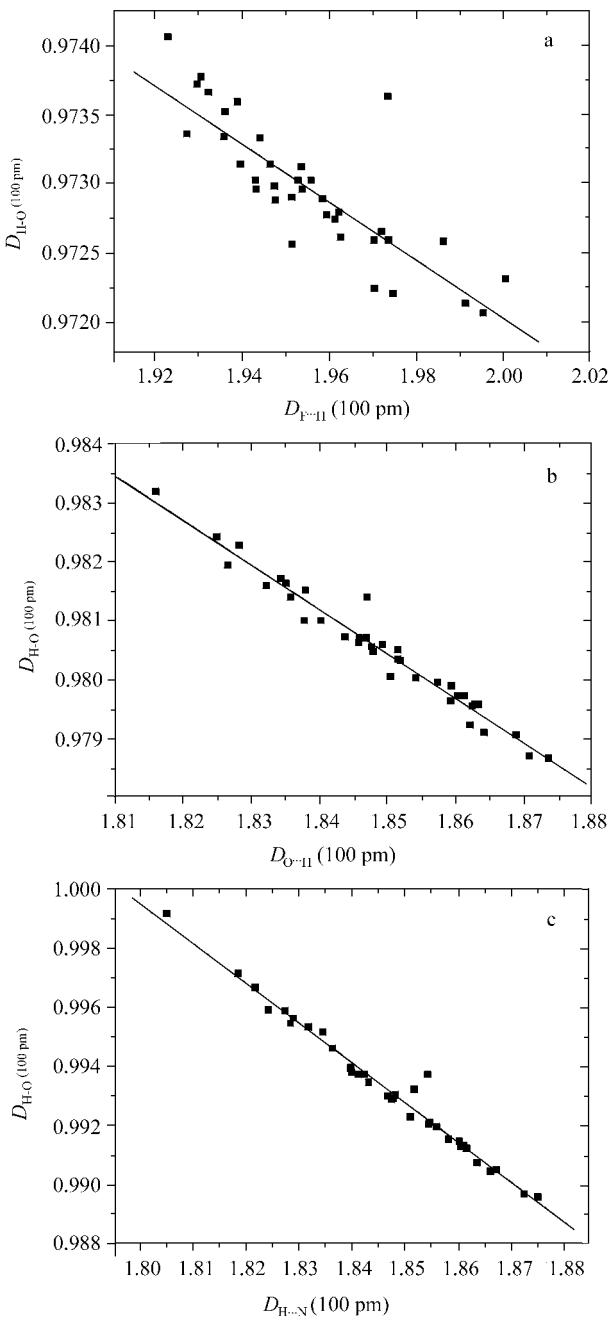


Fig. 1 Correlations between O—H bond lengths with F···H, O···H and N···H distances. (a) $D_{F-H} = 1.014 - 0.021D_{F\cdots H}$ ($r = -0.832$, $N = 38$); (b) $D_{O-H} = 1.120 - 0.075D_{O\cdots H}$ ($r = -0.982$, $N = 38$); (c) $D_{N-H} = 1.241 - 0.134D_{N\cdots H}$ ($r = -0.989$, $N = 38$); r: correlation coefficient, N: number of samples.

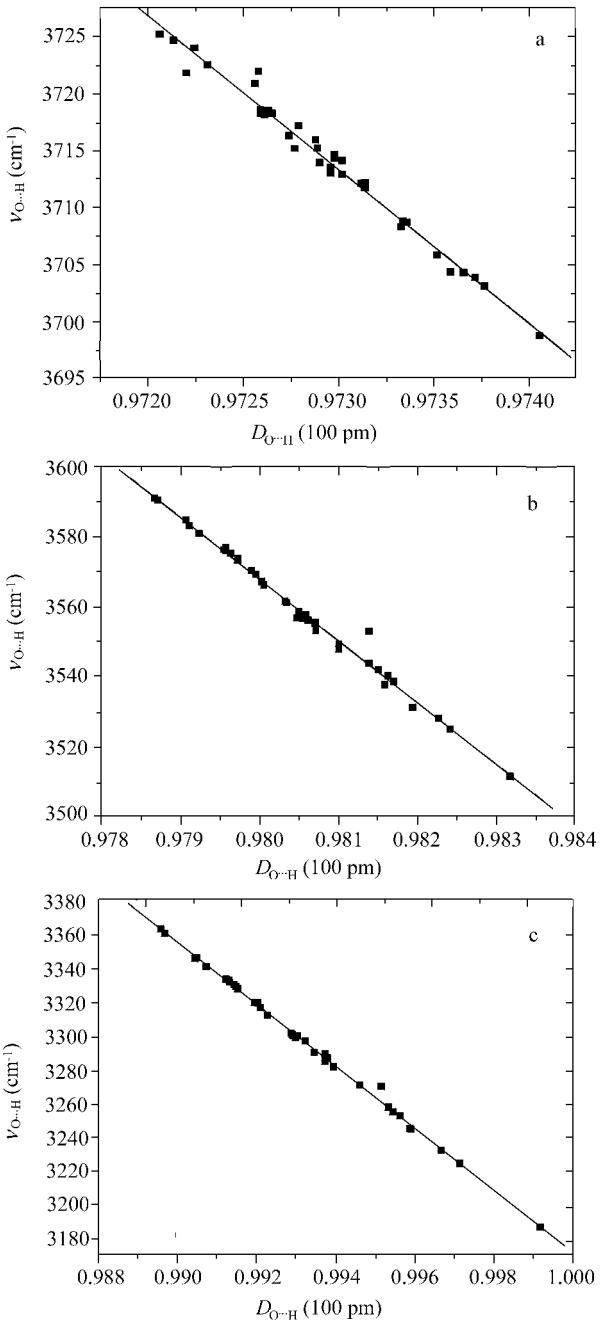
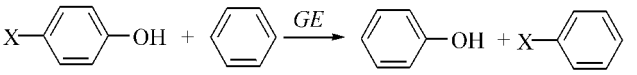


Fig. 2 Correlations between O—H bond lengths with its stretching vibration frequencies. (a) $\nu_{O-H} = 16782.3 - 13431.6D_{O-H}$ ($r = -0.990$, $N = 38$); (b) $\nu_{O-H} = 20749.5 - 17532.3D_{O-H}$ ($r = -0.995$, $N = 38$); (c) $\nu_{O-H} = 21598.6 - 18427.2D_{O-H}$ ($r = 0.999$, $N = 38$); r: correlation coefficient, N: number of samples.

The *BSSE*, interaction energy (ΔE), ground effect (*GE*), and complex effect (*CE*) of every hydrogen bonded complex are summarized in Table 2. Herein, the ground effect and complex effect are defined as the energy changes of the following isodesmic reactions, which reflect the substituent effects on the monomer and complex, respectively (Schemes 1 and 2).

According to Table 2, it is clear that the hydrogen bonding strength increases in the order HF < H_2O < NH_3. In particular, comparing the HF interaction energy (~ 10 kJ / mol) with those of H_2O and NH_3 (20—30 kJ / mol)

Scheme 1 Ground effect



Scheme 2 Complex effect (with HF as an example)

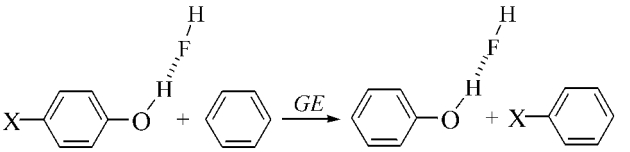


Table 2 *BSSEs*, interaction energies (ΔE), ground effects (*GE*), and complex effects (*CE*) of the hydrogen bonded complexes (kJ/mol)

X	X—C_6H_4—OH···FH				X—C_6H_4—OH···OH_2				X—C_6H_4—OH···NH_3			
	BSSE	ΔE	*GE*	*CE*	*BSSE*	ΔE	*GE*	*CE*	*BSSE*	ΔE	*GE*	*CE*
						Para substituted phenols						
C_2H_5	1.9	−9.1	−1.6	−1.7	5.9	−17.8	−1.6	−2.0	6.7	−26.5	−1.6	−2.0
C≡CH	2.1	−10.5	1.5	2.8	6.0	−20.7	1.5	4.0	6.0	−27.5	1.5	1.3
CF_3	2.1	−11.5	2.9	5.3	6.0	−23.0	2.9	7.7	6.9	−32.7	2.9	8.8
CH_3	2.1	−8.6	−1.8	−2.3	5.7	−17.6	−1.8	−2.7	6.9	−25.9	−1.8	−2.7
$CH=CH_2$	1.8	−9.7	0.5	0.9	5.9	−19.2	0.5	1.5	7.0	−28.2	0.5	2.0
CHO	2.1	−11.6	5.6	8.2	5.9	−23.7	5.6	11.1	7.1	−33.1	5.6	12.1
Cl	2.2	−10.3	−2.7	−1.4	5.9	−20.8	−2.7	−0.2	7.4	−26.0	−2.7	−3.0
CN	2.1	−12.6	3.3	6.9	6.2	−24.2	3.3	9.6	7.1	−34.4	3.3	11.3
$COCH_3$	2.1	−11.1	4.6	6.7	6.1	−23.2	4.6	9.7	7.1	−31.8	4.6	9.8
$CONH_2$	2.2	−10.8	2.7	4.4	6.1	−22.4	2.7	7.1	7.1	−30.4	2.7	6.5
COOH	2.1	−11.3	5.4	7.7	6.2	−22.2	5.4	9.7	7.3	−31.6	5.4	10.7
F	2.1	−10.0	−5.5	−4.6	6.0	−19.9	−5.5	−3.7	6.9	−28.8	−5.5	−3.4
H	1.8	−9.3	0.0	0.0	6.0	−18.2	0.0	0.0	6.8	−26.9	0.0	0.0
$N(CH_3)_2$	2.0	−8.0	−7.8	−8.9	5.8	−16.2	−7.8	−9.9	6.8	−23.9	−7.8	−10.7
NH_2	2.1	−8.5	−8.4	−9.1	5.9	−16.5	−8.4	−10.2	6.8	−24.6	−8.4	−10.7
NO_2	2.3	−13.5	5.2	9.9	6.2	−25.8	5.2	13.1	7.1	−36.7	5.2	15.3
OCH_3	2.1	−8.7	−6.6	−7.0	6.0	−17.1	−6.6	−7.7	6.8	−25.7	−6.6	−7.8
OH	2.2	−8.8	−7.2	−7.4	6.0	−17.7	−7.2	−7.6	6.8	−26.5	−7.2	−7.6
SH	2.1	−9.9	−1.1	−0.3	5.9	−20.6	−1.1	1.2	6.8	−29.9	−1.1	1.9
						Meta substituted phenols						
C_2H_5	2.0	−8.7	0.6	0.1	5.8	−21.7	0.6	0.2	6.7	−26.4	0.6	0.1
C≡CH	2.1	−10.1	−0.9	0.1	5.9	−23.9	−0.9	1.0	6.8	−29.0	−0.9	1.3
CF_3	2.3	−11.2	−1.1	1.2	6.0	−26.4	−1.1	3.5	6.8	−31.9	−1.1	4.0
CH_3	2.1	−8.7	0.4	0.0	5.7	−21.6	0.4	−0.1	6.9	−26.5	0.4	0.1
$CH=CH_2$	1.8	−9.7	−0.1	0.3	5.9	−22.9	−0.1	0.5	6.8	−27.8	−0.1	0.9
CHO	2.1	−11.1	−1.7	0.4	6.1	−25.4	−1.7	1.7	6.9	−30.7	−1.7	2.2
Cl	2.1	−10.4	−1.0	0.4	6.0	−24.7	−1.0	1.7	6.8	−30.4	−1.0	2.6
CN	2.0	−12.0	−1.7	1.2	6.0	−27.3	−1.7	3.5	6.8	−33.2	−1.7	4.7
$COCH_3$	2.0	−10.6	−1.6	−0.1	5.9	−24.5	−1.6	0.8	6.6	−29.6	−1.6	1.0
$CONH_2$	2.0	−10.4	−1.4	−0.1	6.0	−24.3	−1.4	0.9	6.8	−29.2	−1.4	1.1
COOH	1.9	−10.6	−1.7	−0.5	6.0	−24.7	−1.7	0.7	6.8	−30.1	−1.7	1.5
F	2.1	−10.5	−0.4	1.0	5.9	−24.3	−0.4	2.0	6.9	−30.0	−0.4	2.8
H	1.8	−9.3	0.0	0.0	6.0	−22.3	0.0	0.0	6.8	−26.9	0.0	0.0
$N(CH_3)_2$	2.0	−7.8	2.7	1.3	5.9	−20.0	2.7	0.5	6.7	−24.7	2.7	0.5
NH_2	2.1	−8.5	1.8	1.1	6.0	−20.7	1.8	0.4	5.5	−27.1	1.8	0.7
NO_2	1.8	−12.9	−2.6	1.0	6.1	−28.2	−2.6	3.3	6.9	−34.0	−2.6	4.7
OCH_3	1.8	−9.2	0.5	0.3	5.9	−22.1	0.5	0.2	6.8	−26.8	0.5	0.5
OH	2.2	−9.4	0.6	1.1	5.9	−22.3	0.6	1.0	6.9	−27.5	0.6	1.4
SH	2.0	−9.9	0.8	1.5	5.8	−23.7	0.8	2.4	6.8	−29.0	0.8	2.9

shows that proton-fluorine hydrogen bond is much weaker than the corresponding ones involve oxygen and nitrogen.[16]

It should be mentioned that *BSSE* has nontrivial effect on the calculated interaction energy. In particular, *BSSE* is as large as about 20% of the interaction energy in F···H—O complexes, about 30% in O···H—O complexes, and about 25% in the N···H—O complexes. Thus, failure to consider *BSSE* may cause significant errors in estimating the hydrogen bonding energy.[17]

From Table 2, it can also be seen that the interaction energy has a good correlation with the F···H—O, O···H—O, or N···H—O distance (Fig. 3), which in consequence means that the interaction energy should also have a good correlation with O—H bond lengths in complexes, and then with O—H stretching vibration frequencies.

Correlations of the interaction energies with the several scales of substituent constants clearly show that σ_p^- is as good as σ_p but much better than σ_p^+ in reflecting the substituent effects (Fig. 4). This finding is reasonable because in complex the proton is shared by the phenolic oxygen and hydrogen bond acceptor. Thereby, the phenolic oxygen should carry some negative charge, which makes σ_p^- and σ_p be good parameters in reflecting the substituent effects.

The negative slopes in the Hammett-type correlations mean that electron-withdrawing substituents increase the interaction energy. This effect is consistent with the expectation because electron-withdrawing substituents should increase phenol acidity. Interestingly, the absolute slope decreases in the order $NH_3 > H_2O > HF$. Therefore, it can be concluded that the substituent effect is stronger as the basicity of the hydrogen bond acceptor increases.

It is worthy to mention that some substituents themselves could interact with NH_3, H_2O or HF to form hydrogen bonds, these interactions slightly affect the hydrogen bonding of the substrates with NH_3, H_2O or HF. In case of H—F···H—OAr complexes, the interaction energies of hydrogen bonding increased by 1.5—1.7 kJ/mol with electron-withdrawing groups, such as COOH and NO_2, and decreased by 0.5—0.6 kJ/mol with the electron-donating groups, such as NH_2 and OH.

Analysis of the ground and complex effects reveals more details about the interaction mechanism. First, as the magnitudes of the ground and complex effect energies are so close to each other, it must be concluded that the substituent effects on the complexes and on the monomers are both important. Second, correlation of the *GE* energies with the *CE* energies shows that the substituent affect the two effects in the same way (Fig. 5a). However, it turns out that the slope increases in the order $HF < H_2O < NH_3$, which means that smaller portion of *CE* is compensated by *GE* when the basicity of the hydrogen bond acceptor is stronger (Fig. 5b). Therefore, it is the *CE* that makes the NH_3 complexes more stable than the HF and then H_2O ones.

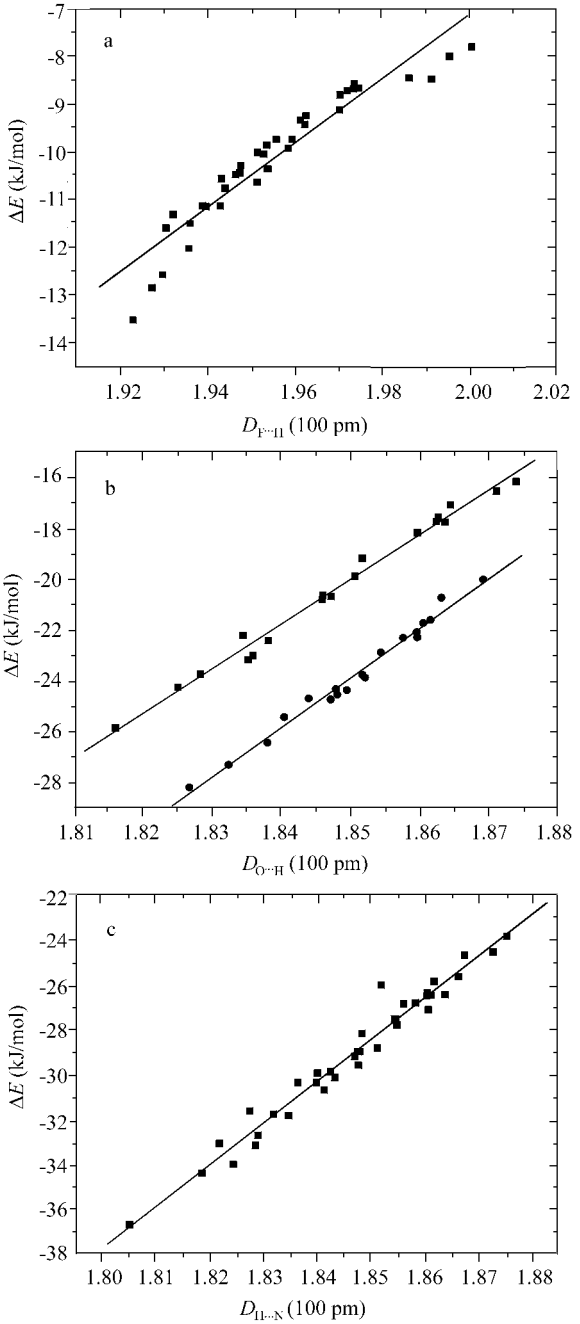


Fig. 3 Correlation between the interaction energy and O—H···F, O—H···O, or O—H···F distances. (a) $\Delta E = -142.1 + 67.5 D_{H\cdots F}$ ($r = 0.949$, $N = 38$); (b) ■ *para* $\Delta E = -343.2 + 174.7 D_{H\cdots O}$ ($r = -0.994$, $N = 19$), ● *meta* $\Delta E = -384.4 + 194.9 D_{H\cdots O}$ ($r = -0.992$, $N = 19$); (c) $\Delta E = -372.6 + 186.0 D_{H\cdots N}$ ($r = 0.983$, $N = 38$); r: correlation coefficient, N: number of samples.

Conclusion

Substituent effects on the hydrogen bonding between phenol and HF, H_2O, NH_3 were studied with density functional theory calculations. A very large number of

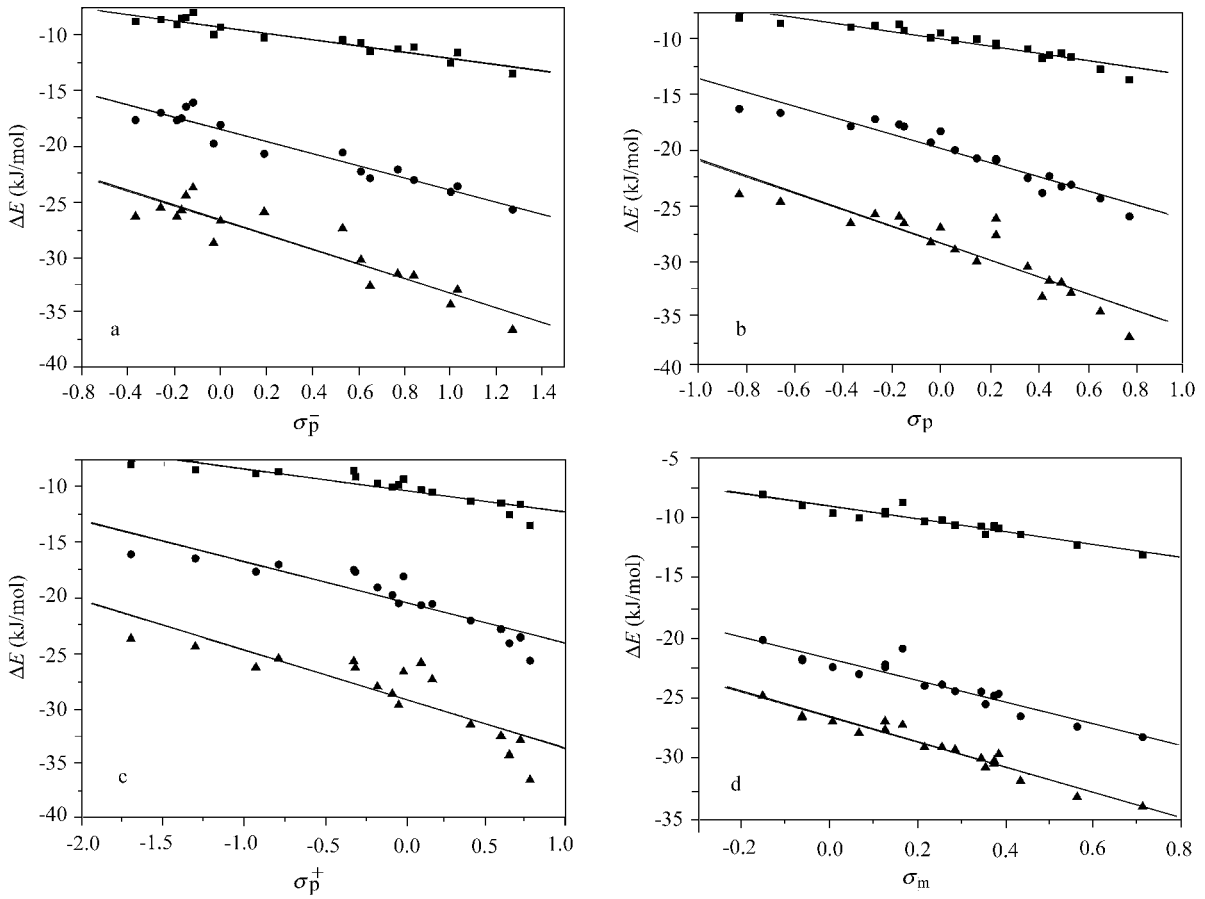


Fig. 4 Correlations of the hydrogen bonding interaction energies with substituent (a) σ_p^-, ■ $\Delta E_{HF} = -9.3 - 2.8\sigma_p^-$ ($r = -0.948$, $N = 17$), ● $\Delta E_{H_2O} = -5.5\sigma_p^- - 18.6$ ($r = -0.958$, $N = 17$), ▲ $\Delta E_{NH_3} = -6.6\sigma_p^- - 27.0$ ($r = -0.921$, $N = 17$); (b) σ_p, ■ $\Delta E_{HF} = -3.2\sigma_p - 9.9$ ($r = -0.941$, $N = 19$), ● $\Delta E_{H_2O} = -6.3\sigma_p - 19.7$ ($r = -0.953$, $N = 19$), ▲ $\Delta E_{NH_3} = -7.4\sigma_p - 28.3$ ($r = -0.941$, $N = 19$); (c) σ_p^+, ■ $\Delta E_{HF} = -1.9\sigma_p^+ - 10.4$ ($r = -0.886$, $N = 17$), ● $\Delta E_{H_2O} = -3.7\sigma_p^+ - 20.7$ ($r = -0.902$, $N = 17$), ▲ $\Delta E_{NH_3} = -4.4\sigma_p^+ - 29.3$ ($r = -0.850$, $N = 17$); (d) σ_m, ■ $\Delta E_{HF} = -5.3\sigma_m - 8.8$ ($r = -0.946$, $N = 19$), ● $\Delta E_{H_2O} = -9.0\sigma_m - 21.6$ ($r = -0.938$, $N = 19$), ▲ $\Delta E_{NH_3} = -10.5\sigma_m - 26.6$ ($r = -0.970$, $N = 19$).

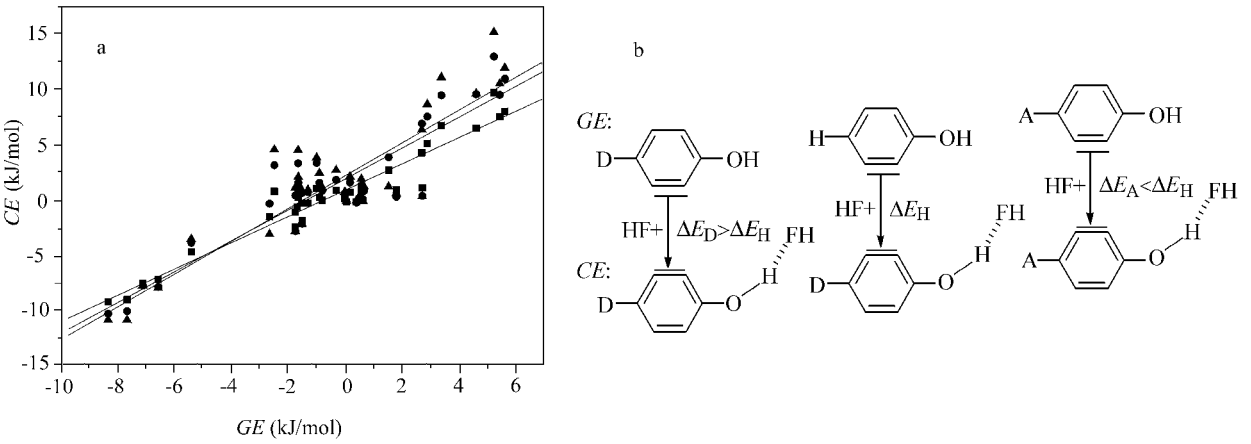


Fig. 5 Correlation between the ground effect and complex effect (a) ■ CE (HF) = 1.185GE + 1.091 (r = 0.956), ● CE (H_2O) = 1.392GE + 2.109 (r = 0.907), ▲ CE (NH_3) = 1.478GE + 2.411 (r = 0.885) and its mechanism (b).

substituents were considered in the study and therefore the research was considerable systematic and detailed in nature. From the study, it was found that many properties of the non-covalent interaction, including the interaction energies, donor-acceptor (host-guest) distances, bond lengths, and vibration frequencies, could show as well-defined substituent effects as normally found for covalent systems. In fact, as the substituent effects were found to be so strong, it was expected that from the substituent studies not only the mechanism of any particular non-covalent interaction could be better understood, but also the interaction energies and structures of any particular non-covalent complex could be easily predicted. This means that substituent effect was indeed a useful, predictive tool to be used in supramolecular chemistry. Clearly, on the basis of the results obtained here for a relatively simple system, we were then able to address more complicated but less understood non-covalent systems in the future.

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