Orbital
The Electronic Journal of Chemistry

ISSN 1984-6428
ONLINE
www.orbital.ufms.br

| Vol 2 | | No. 1 | | January-March 2010 |

Full Paper

Excitation and ionization energies of substituted anilines calculated with density functional theory

Yuji Takahata[a,b], Alberto dos S. Marques[a], Luiza G. Pereira[a]*

[a]School of Engineering, Amazonas State University, Av. Darcy Vargas, 1200, Parque 10 - CEP 69065-020, Manaus, Amazonas, Brazil.
[b]Department of Chemistry, University of Campinas-UNICAMP, Cidade Universitária Zeferino Vaz, CEP 13084-862 , Campinas, São Paulo, Brazil.

Received: 15 December 2009; accepted: 24 April 2010. Available online: 03 May 2010.

ABSTRACT: *Valence electron singlet excitation energies (VEExE), valence electron ionization energies (VEIE), core electron binding energies (CEBE), and non-resonant X-ray emission energies of substituted anilines and related molecules were calculated using density functional theory (DFT). The energy calculations were done with TZP basis set of Slater Type Orbitals. PW86x-PW91c, turned out to be the best XC functional among eight functionals tested for time dependent DFT (TDDFT) calculation of the singlet excitation energies of the substituted anilines. Using the XC functional, average absolute deviation (AAD) from experiment was 0.223 eV for eighteen cases with maximum absolute deviation of 0.932 eV. The valence electron ionization energies of the substituted benzenes were calculated by ΔSCF method with PW86x-PW91c. AAD from experiment was 0.21 eV. The CEBEs were calculated with the previously established method, named as scheme 2003. ΔCEBE(SMS),, sum of mono substituted (SMS) CEBE shift, and mutual interference effect (MIE) were defined and their values were calculated. Magnitude of MIE provides the degree of mutual interference between two substituents in a phenyl ring. Average absolute value of MIE was ca. 0.1 eV for the three isomers of phenetidine. Using the calculated valence electron ionization energies and the core electron binding energies of one of the phenetidines, some X-ray emission energies were calculated.*

Keywords: *singlet excitation energy; ionization energy; CEBE; Density Functional Theory; substituted anilines*

Introduction

Accurate theoretical calculation of electronic spectra helps in understanding and interpreting experimentally observed ones. The density functional theory has been widely *used to calculate not only ground state energy of systems but also transition energies*

---

[*] Corresponding author. E-mail: taka@iqm.unicamp.br

through the use of the time dependent density functional theory. When one uses DFT and TDDFT, one has to choose appropriate exchange and correlation functional to get the best possible results. There is no universal exchange and correlation functional that serves for any situation. Very recently, Jacquemin et al. [1] published results of an extensive TDDFT benchmark study for singlet-excited states using a very extended set of organic molecules testing 29 functionals of five major categories: LDA, GGA, meta-GGA, GH, and LCH. With the optimal functionals, they obtained mean absolute deviations smaller than 0.25 eV. PBE0 and LC-**ω**PBE(20) [2], for instance, provided a mean absolute error of 0.14 eV for the 228 states related to neutral organic dyes. The electronic spectrum of molecules has a strong multideterminantal nature. Transition wavelengths to excited-states presenting a doubly excited character or a significant charge-transfer nature are traditionally poorly estimated. Recently long-range-corrected hybrids (LCH) have been developed to correct this deficiency [3]. Mirashi et al. [4] obtained experimental electronic absorption spectra of some substituted anilines in vapor phase and polar and non-polar solvents. Jana and Ganguly observed UV absorption and emission spectra of *o*-, *m*-, and *p*-phenetidines (Figure 1 A-C) in non-polar and hydrogen bonding solvents at room temperature (liquid state solvent) [5]. UV photoelectron spectra (UPS) of substituted benzenes (Figure 1 D, E) were observed by Klasinc et al. [6].

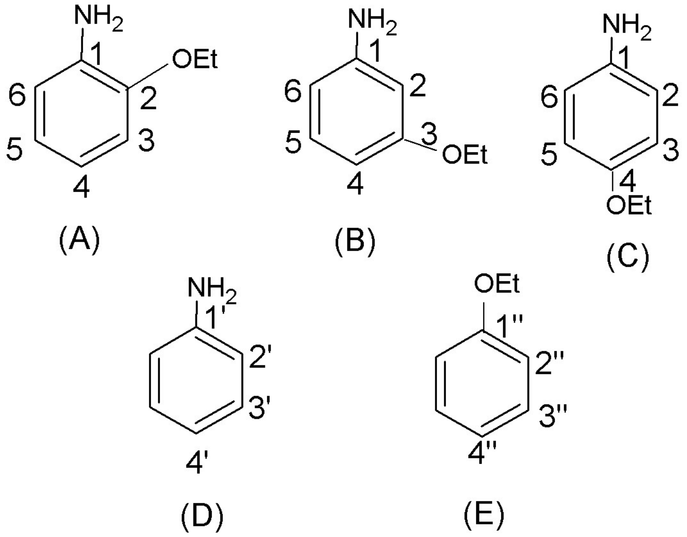

Figure 1. (A) *o*-phenetideine, (B) *m*-phenetidine, (C) *p*-phenetidine, (D) aniline, (E) ethoxybenzene.

The object of the present work is to calculate valence electron singlet excitation energies, valence electron ionization energies, core electron binding energies, and non-resonant X-ray emission energies of some of the substituted anilines and related molecules using density functional theory. First, we search for an appropriate exchange and correlation functional to calculate singlet excitation energies of the substituted anilines. The calculated excitation energies are compared with the observed ones. The selected exchange-correlation functional is used to predict gas phase excitation energies of the phenetidines and analyze their observed UV spectra in non-polar solvent [5]. Second, Valence electron ionization energies of some substituted benzenes are calculated and compared with the observed ones [6] in order to evaluate accuracy of the calculation. Third, core electron binding energies of the three isomers: o-, m-, and p-phenetidines (Figure 1 A, B, C) are calculated. CEBE is a convenient physical quantity to study substituent effect [7, 8]. Finally, transition energies corresponding to non-resonant X-ray emission of the phenetidines are calculated using the VEIEs and CEBEs.

Material and Methods

Method of calculation

Geometry optimization of the ground state neutral molecules was performed with GAUSSIAN program package [9], using the Hartree-Fock (HF) method with the basis set known as 6-31G(d). The optimized geometries were used for all the energy calculations. All the energy calculations were done using the Amsterdam Density Functional (ADF) program [10]. In all the ADF calculations, basis set used was triple-zeta polarized (TZP) Slater type basis set. The TZP basis set consists of two 1s Slater type orbital (STOs), three 2s and 2p STOs and one 3d STO. For calculation of the excitation energies, we used time-dependent DFT. Eight typical exchange-correlation (XC) energy functionals available in the ADF package were chosen and tested for calculation of the excitation energies of the substituted anilines. They are listed bellows:

(1) BP86: this is equivalent to Becke(exchange) [11] + Perdew (correlation) [12] together.

(2) PW91: this is equivalent to PW91x [13] + PW91c [13] together.

(3) mPBE: this is equivalent to mPBEx [14] + PBEc [15] together.

(4) PW86x [16] + PW91c.

(5) BLYP: this is equivalent to Becke (exchange) + LYP (correlation) [17].

(6) OLYP: this is equivalent to OPTX (exchange) [18] + LYP (correlation).

(7) LB94: this refers to the XC functional of Van Leeuwen and Baerends [19].

(8) SAOP: the statistical average of orbital potentials [20, 21].

The first six functionals, (1) – (6), are Generalized Gradient Approximation (GGA) type and the last two, (7) and (8), are asymptotically correct XC potentials.

The core electron binding energies (CEBEs) of carbon atoms in the phenetidines were calculated using density functional theory with Scheme 2003 [22].

ΔE_{KS} (PW86-PW91)/TZP + C_{rel}//HF/6-31G*. (Scheme 2003)

ΔE_{KS} (= CEBE) is the difference in the total Kohn-Sham(KS) energies calculated by Amsterdam Density Functional for the core-ionized cation and for the neutral parent molecule. The TZP basis set was found to be the most cost effective resulting average absolute deviation from experiment of 0.16 eV for 59 CEBE cases. STO´s are especially suited to represent inner core electronic structure. The functional combination is the Perdew-Wang 1986 exchange functional [16] and the Perdew-Wang 1991 correlation functional [23]. The relativistic corrections [24] can be estimated by an empirical equation 1,

$$C_{rel} = KI_{nr}^{N} \tag{1}$$

where I_{nr} is the non relativistic CEBE and C_{rel} is the relativistic correction. When both C_{rel} and I_{nr} are in eV, K = 2.198×10^{-7} and N = 2.178. In case of carbon atom, C_{rel} takes the value 0.05 eV. Substituent effect of a ring carbon atom in substituted benzene is estimated by CEBE shift (ΔCEBE) which is defined as,

$$\Delta\text{CEBE (substituent effect)}$$

$$= \text{CEBE (C atom in Ph-X)} - \text{CEBE (C atom in Ph-H)} \tag{2}$$

The vertical, valence electron ionization energies were calculated with almost the same method as the Scheme 2003, namely the ΔSCF method. Only difference is that the relativistic correction, C_{rel}, was not included for the calculated valence electron IEs.

Results and Discussion

Valence Electron Excitation Energy

The valence electron singlet-singlet (singlet) excitation energies of seventeen substituted anilines in isolated form were calculated using the eight different XC functionals. There are two or three observed bands reported for each molecule [4]. When the observed lowest energy band is compared with the calculated one, there is no ambiguity in assignment. However, there are ambiguities in assigning the second and higher energy bands comparing calculated spectra. This is the reason why we compare theory with experiment for only the lowest excitation band. In Table 1, the calculated lowest excitation energy of each molecule is compared with the corresponding experimental value obtained in gas phase [4].

Average absolute deviations (AADs) obtained from the total of 17 molecules are listed. They lie between 0.2 and 0.3 eV. The lowest AAD value, 0.223 eV was obtained with the PW86x-PW91c functional. The 2nd, 3rd, and 4th lowest AADs are 0.227 eV, 0.229 eV, and 0.230 eV that were obtained with BP86, mPBE, and PW91, respectively. The three AADs are very close to each other. The largest AAD obtained among the eight XC functional tested is 0.298 eV, which was obtained with OLYP. The two asymptotically correct XC potentials, SAOP and LB94, resulted AADs of 0.272 eV and 0.288 eV that belong to the worst three results among the eight XC functionals tested. Maximum absolute deviation (MAD) is listed in the last line of the table. MADs resulted from meta-nitroaniline, m-$O_2NC_6H_4NH_2$, for all the eight XC functionals were tested. The MADs are as large as ca. 0.9 eV or more. Absolute deviation from experiment for *para*-nitroaniline is ca. 0.5 eV which is also large. The eight XC functionals failed to calculate accurate excitation energies of the nitroanilines. If AADs are calculated with only 14 compounds excluding the three nitroanilines (**15, 16, 17**), The AAD of PW86x-PW91c drops from 0.223 to 0.146 eV (The second line from the bottom in Table 1). This is a substantial improvement. AAD reduces substantially when the nitroanilenes are excluded for all the remaining cases as shown in Table 1 In the case of LB94, AAD drops from 0.288 eV with nitroanilines to 0.141 eV without the three nitro compounds. The difference is quite substantial. LB94 results accurate excitation energies for substituted anilines except for the nitroanilines, for which it fails badly. We conclude that the best XC functional is PW86x-PW91c. BP86, mPBE, and PW91 are almost as good as the best one. It is interesting to note that PW86x-PW91c is also the best XC functional for calculating CEBE [22]. Singlet excitation energies corresponding to the first transition band of *o*-, *m*-, and *p*-phenetidines, in vacuum, were calculated using PW86x-PW91c (the second column in Table 2).

Since observed UV absorption spectra of the molecules were measured in cyclohexane [5], the calculated transition energies cannot be compared directly with the observed ones. Relation between excitation energies in vacuum (or in gas phase), ΔE(vacuum), and the one in a solvent, ΔE(solvent), can be given by eq. 3:

$$\Delta E(vacuum) = \Delta E(solvent) + WD \qquad (3)$$

where WD stands for solvent effect.

Mirashi et al. [4] observed UV absorption spectra of *o*-, *m*-, and *p*-methoxyanilines in vapor as well as in cyclohexane. Average solvent effect of 0.116 eV, WD in eq. 3, of these three compounds in cyclohexane was obtained. Since methoxyaniline and phenetidine (ethoxyaniline) are very similar molecules, one can assume that solvent effect of phenetidines can be approximated by that of methoxyanilines. With the calculated ΔE (Vacuum)s and the solvent effect, 0.116 eV, one can estimate transition energies of the three phenetidines in cyclohexane using eq.3. The resultant values are listed in the 3rd column of Table 2.   The last column lists observed

Table 1. Evaluation of the eight exchange-correlation functionals for calculation of the lowest excitation energies, in eV, of the substituted anilines.

			Obs.[4]	**Calc.**							
Order				**1st**	**2nd**	**3rd**	**4th**	**5th**	**6th**	**7th**	**8th**
	Compound	band	Vapour	PW86x-PW91c	BP86	mPBE	PW91	BLYP	SAOP	LB94	OLYP
1	$C_6H_5NH_2$	Lb	4.488	4.503	4.522	4.524	4.513	4.499	4.629	4.454	4.414
2	$C_6H_5CH_3$	Lb	4.679	5.138	5.184	5.186	5.175	5.142	5.183	5.028	5.208
3	C_6H_5OH	Lb	4.851	5.166	5.188	5.190	5.179	5.144	5.216	5.056	5.211
4	$C_6H_5OCH_3$	Lb	4.756	4.771	4.792	4.792	4.785	4.772	4.927	4.751	4.844
5	$C_6H_5NO_2$	CT	5.207	5.293	5.320	5.302	5.309	5.327	5.153	5.545	5.387
6	o-$H_3CC_6H_4NH_2$	Lb	4.54	4.568	4.589	4.577	4.567	4.468	4.681	4.511	4.344
7	m-$H_3CC_6H_4NH_2$	Lb	4.653	4.448	4.469	4.463	4.455	4.437	4.572	4.407	4.353
8	p-$H_3CC_6H_4NH_2$	Lb	4.613	4.381	4.400	4.399	4.390	4.375	4.500	4.334	4.277
9	o-$HOC_6H_4NH_2$	Lb	4.533	4.423	4.496	4.393	4.364	4.204	4.612	4.433	4.060
10	m-$HOC_6H_4NH_2$	Lb	4.463	4.559	4.581	4.577	4.567	4.468	4.691	4.489	4.316
11	p-$HOC_6H_4NH_2$	Lb	4.157	4.335	4.353	4.352	4.345	4.332	4.471	4.331	4.300
12	o-$H_3COC_6H_4NH_2$	Lb	4.451	4.472	4.510	4.471	4.456	4.351	4.625	4.443	4.205
13	m-$H_3COC_6H_4NH_2$	Lb	4.414	4.527	4.550	4.545	4.536	4.493	4.665	4.462	4.331
14	p-$H_3COC_6H_4NH_2$	Lb	4.24	4.073	4.092	4.089	4.083	4.077	4.258	4.101	3.966
15	o-$O_2NC_6H_4NH_2$	Lb	3.501	3.202	3.220	3.217	3.210	3.172	3.118	2.841	3.228
16	m-$O_2NC_6H_4NH_2$	Lb	3.8	2.868	2.891	2.899	2.872	2.849	2.763	2.394	2.917
17	p-$O_2NC_6H_4NH_2$	Lb	4.246	3.720	3.747	3.747	3.731	3.703	3.680	3.406	3.758
AAD(17)	**1** to **17**		0	0.223	0.227	0.229	0.230	0.241	0.272	0.288	0.298
AAD(14)	**1** to **14**		0	0.146	0.155	0.157	0.155	0.163	0.188	0.141	0.245
MAD	m-$O_2NC_6H_4NH_2$			0.932	0.909	0.901	0.929	0.951	1.037	1.406	0.883

Table 2. Singlet excitation energies , in eV, of *o*-, *m*-, and *p*-phenetidines.

	Calc.	**Calc.**	**obs.[5]**
Molecule	vacuum	Solv.Effect (-0.116 eV)	CycloHexane
o-phenetidine	4.455	4.339	4.310
m-phenetidine	4.527	4.411	4.350
p-phenetidine	4.066	3.950	4.080
AAD[a]		0.073	(0)

a. Average Absolute Deviation (AAD)

Table 3. Calculated and observed[6] valence electron ionization energies, in eV, of some substituted benzenes.

Molecule	**PhOMe**		**$PhNH_2$**		**PhMe**		**PhOH**		**$PhNO_2$**		***o*-Phenet[a]**	***m*-Phenet**	***p*-Phenet**
Orbital	**Calc.**	**Obs.**	**Calc.**	**Obs.**	**Calc.**	**Obs.**	**Calc.**	**Obs.**	**Calc.**	**Obs.**	**Calc.**	**Calc.**	**Calc.**
HOMO	8.16	8.39	7.88	8.02	8.84	8.78	9.00	8.61	9.30	9.88	7.22	7.45	7.10
HOMO-1	9.17	9.22	9.09	9.12	9.17	9.00	xxx[b]	9.33	xxx		8.17	7.89	8.80
HOMO-2	10.53		10.42	10.78	11.01	11.45	10.35		10.63	11.03	xxx	9.51	8.94
HOMO-3	10.59		11.14		11.07	11.45	11.58	11.6	10.82	11.16	10.15	10.29	10.25
HOMO-4	11.36	11.06	11.61	11.88	11.53	11.86	11.66	11.6	xxx		10.48	10.41	10.46
HOMO-5	11.59	11.55	12.34	12.48	12.46	12.01	12.01	12.13	12.17		10.94	11.12	10.99
HOMO-6	12.07	12.33	13.18		12.84	13.29	xxx	12.59	xxx		xxx	11.19	11.34
HOMO-7	12.90	12.56	xxx				13.51	13.49	12.92	12.68	11.38	11.37	11.70
HOMO-8	xxx[b]	12.76	13.46						14.17	13.49	12.23	12.07	12.05
HOMO-9	xxx		14.63	14.28					xxx				
HOMO-10	13.85	13.99	xxx						14.66	14.99			
HOMO-11	14.59	14.28	15.90	15.74									
HOMO-12	14.86	14.88	17.70										
HOMO-13	16.20	15.78											
HOMO-14	17.35	17.36											

a. Phenet = Phenetidine

b. xxx indicates that value was not obtained due to non convergence of SCF.

values. The estimated transition energies are close to the observed values. AAD of the estimated values is 0.073 eV.

Valence Electron Ionization Energy

Since PW86x-PW91c is the best XC functional to calculate the valence electron excitation energies of the substituted benzenes and CEBEs[22], we expect that it can also be a good functional for calculating valence electron ionization energies. The VEIEs were calculated with the ΔSCF method that can be described as following:

ΔE_{KS} (PW86-PW91)/TZP //HF/6-31G(d).

Where ΔE_{KS} (= VEIE), TZP was used for basis set. Geometry was optimized with HF/6-31G(d). Table 3 lists the calculated VEIEs of some substituted benzenes together with observed ones.

In majority of the cases, SCF calculation of cation converged. However, there were cases where SCF did not converge. Non convergence of SCF is indicated by xxx in Table 3. The VEIEs due to only several highest occupied molecular orbitals are listed for the most of the molecules. Assignment of observed UPS bands using the calculated VEIEs involves some ambiguity especially for higher energy bands. There is no ambiguity in assigning the lowest energy PE spectrum band, because it corresponds to ionization from the highest occupied molecular orbital (HOMO). Assignment of the second lowest band is also possible. It involves one level bellow to HOMO (HOMO-1). Table 4 lists the two lowest observed PE bands and the calculated VEIEs due to HOMO and HOMO-1.

Table 4. Calculation of average absolute deviation (AAD) of valence electron ionization energies, in eV, for mono substituted benzenes using only HOMO and HOMO-1.

	Molecule	**Orbital**	**Calc.**	**Obs.[6]**
1	$PhNH_2$	HOMO	7.88	8.02
2		HOMO-1	9.09	9.12
3	$PhCH_3$	HOMO	8.84	8.78
4		HOMO-1	9.17	9
5	PhOH	HOMO	9.00	8.61
6	PhOMe	HOMO	8.16	8.39
7		HOMO-1	9.17	9.22
8	$PhNO_2$	HOMO	9.30	9.88
AAD(1-8)			0.21	0
AAD(1-7)			0.15	0
MAD[a]	$PhNO_2$		0.58	

a. Maximum absolute deviation

Average absolute deviation of the eight cases is 0.21 eV. The maximum absolute deviation is 0.58 eV which is due to $PhNO_2$. If $PhNO_2$ is excluded in the list, AAD becomes

0.15 eV. It is interesting to observe that the AADs of Table 4 is almost identical to those obtained in Table 1 in the column of PW86x-PW91c. The XC functional results AAD of ca. 0.22 eV both in calculation of valence electron excitation energy (Table 1) and ionization energy (Table 4). If the nitro compounds are excluded for the statistics, AADs drop to 0.15 eV in Tables 1 and 4. It is noteworthy the fact that AAD for calculating CEBE with PW86x-PW91c is 0.16 eV [22].

Core electron binding energy

Table 5 lists calculated CEBE, ΔCEBE (eq. 2), in eV, of ring carbons of mono (Ph-X) and *o*-, *m*- and *p*-phenetidines (Figure 1 A-C). Calculated and observed [25] CEBEs, in eV, for C_1, C_2, C_3 and C_4 of Ph-NH_2 are 291.39 (291.29), 289.99 (289.85), 290.17 (290.25), 289.81 (289.85), in which observed values are in parentheses.

Average absolute deviation is 0.09 eV. The calculated CEBEs reproduce the observed values well. We expect similar accuracy to the calculated CEBEs of the remaining molecules in Table 5.Figure 2 shows calculated ΔCEBE of Ph-NH_2 and Ph-OEt.

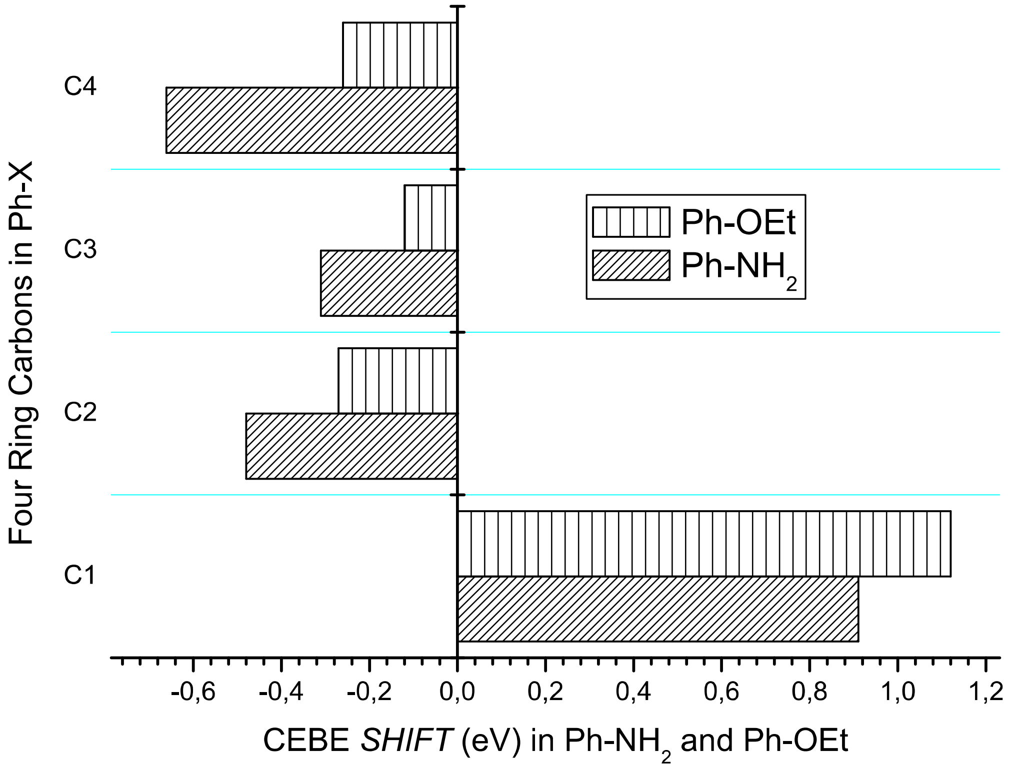

Figure 2. ΔCEBE (eV) of four ring carbons, C_1 = Ipso, C_2 = *ortho*, C_3 = *meta*, and C_4 = *para* in Ph-NH_2 and Ph-OEt.

The ΔCEBEs of the two molecules have negative values at C_2 (*ortho*), C_3 (*meta*) and C_4 (*para*) indicating that NH_2 and OEt are of electron donating. The electron donating power of NH_2 is almost twice as great to that of OEt. We assume that ΔCEBE of the di-substituted (X-Ph-Y) benzenes (Figure 1 A-C) is a consequence of cumulative of two ΔCEBEs of mono-substituted Ph-X (Figure 1 D), mono-substituted Ph-Y (Figure 1 E) and mutual interference effect (MIE). This assumption can be expressed by Eq. 4.

Table 5. Calculated CEBE , ΔCEBE and ΔCEBE (SMS), sum of mono substituted (SMS) CEBE shift, and mutual interference effect (MIE), in eV, of mono (Ph-X) and di-substituted benzene (X-Ph-Y), where X and Y = NH_2 and OEt.

(1)	**(2)**	**(3)**	**(4)**	**(5)**
	CEBE	**ΔCEBE**	**ΔCEBE (SMS)**	**MIE (3)-(4)**
$PhNH_2$				
1	291.39	0.91		
2	289.99	-0.48		
3	290.17	-0.31		
4	289.81	-0.66		
Ph-OEt				
1	291.59	1.12		
2	290.21	-0.27		
3	290.35	-0.12		
4	290.22	-0.26		
o-PHENETIDINE				
1	290.99	0.52	0.64	-0.13
2	291.33	0.85	0.64	0.21
3	289.86	-0.62	-0.58	-0.04
4	289.61	-0.86	-0.79	-0.07
5	289.70	-0.77	-0.79	0.01
6	289.75	-0.73	-0.58	-0.15
AAD[a]				0.10
m-PHENETIDINE				
1	291.19	0.72	0.79	-0.07
2	289.61	-0.86	-0.75	-0.12
3	291.52	1.04	0.81	0.23
4	289.58	-0.90	-0.93	0.03
5	290.01	-0.46	-0.43	-0.03
6	289.61	-0.87	-0.74	-0.13
AAD				0.10
p-PHENETIDINE				
1	291.20	0.73	0.65	0.07
2	289.96	-0.52	-0.60	0.08
3	290.00	-0.48	-0.58	0.10
4	291.02	0.54	0.46	0.08
5	290.00	-0.48	-0.58	0.10
6	289.96	-0.52	-0.60	0.08
AAD				0.09

a. Average absolute deviation

$$\Delta CEBE\ (X\text{-}Ph\text{-}Y) = \Delta CEBE(Ph\text{-}X) + \Delta CEBE(Ph\text{-}Y) + MIE \quad (4)$$

$$\Delta CEBE(SMS) = \Delta CEBE(Ph\text{-}X) + \Delta CEBE(Ph\text{-}Y) \quad (5)$$

Eq.5 defines sum of mono substituted (SMS) CEBE shift. If MIE=0, one gets ΔCEBE (X-Ph-Y) = ΔCEBE (SMS). According to Eq.4, we can express ΔCEBEs of six ring carbons of *o*-phenetidine, for instance, by following six equations:

$$C_1 = C_{1'} + C_{2''} + MIE_1 \quad (4.1)$$

$$C_2 = C_{2'} + C_{1''} + MIE_2 \quad (4.2)$$

$$C_3 = C_{3'} + C_{2''} + MIE_3 \quad (4.3)$$

$$C_4 = C_{4'} + C_{3''} + MIE_4 \quad (4.4)$$

$$C_5 = C_{3'} + C_{4''} + MIE_5 \quad (4.5)$$

$$C_6 = C_{2'} + C_{3''} + MIE_6 \quad (4.6)$$

In Table 5, ΔCEBE (SMS)s and MIEs corresponding to the Eq. 4.1 to 4.6 are listed in the columns denoted as ΔCEBE (SMS) and MIE for *o*-phenetidine. In a similar manner, ΔCEBE (SMS)s and MIEs for *m*-phenetidine and *p*-phenetidine were calculated and listed in this table.

The value of MIE at C_5 in *o*-phenetidine (Figure 1 A) is 0.01eV. This indicates that mutual interference between the two substituents is almost zero. It may be that the substituent effect of X diminishes that of Y. MIE is as large as 0.21 eV at C_2 in the molecule. This implies that mutual interference between the two substituents is large. MIE is ca. 0.1 eV at every carbon atom in the ring of *p*-phenetidine indicating uniform mutual interference effect of the two substituents. This may be due to a consequence of high symmetry of the molecule. Average absolute values (AAV) of MIE of *o*-phenetidine is 0.10 eV. AAVs for *m*-phenetidine and *p*-phenetidine are 0.10 and 0.09 eV respectively. We conclude that average absolute value of MIE in phenetidines is ca. 0.1eV.

Non-Resonant X-ray Emission

Non-resonant X-ray emission is the result of a valence electron dropping to a core-hole. The energy of the X-ray emission is simply the difference between VEIE(listed in Table 3) and CEBE (listed in Table 5). Table 6 lists some calculated energies, in eV, of the X-ray emission for aniline and phenetidines. Only those that originate HOMO, HOMO-4, HOMO-8 are listed in the table for the sake of brevity. Experimentally, the X-ray emission is related to near edge X-ray absorption fine structure (NEXAFS).

Table 6. Some calculated none-resonant X-ray emission spectra, in eV, of aniline and phenetidines.

Atom	**NEXAFS**		
$PhNH_2$	HOMO	HOMO-4	HOMO-8
1	283.51	279.78	277.92
2	282.11	278.39	276.53
3	282.29	278.56	276.70
4	281.93	278.20	276.35
o-PHENETIDINE			
1	283.77	280.51	278.76
2	284.10	280.85	279.10
3	282.63	279.38	277.63
4	282.39	279.14	277.38
5	282.48	279.22	277.47
6	282.53	279.27	277.52
m-PHENETIDINE			
1	283.74	280.78	279.12
2	282.16	279.20	277.54
3	284.07	281.10	279.44
4	282.13	279.17	277.50
5	282.56	279.60	277.94
6	282.16	279.20	277.54
p-PHENETIDINE			
1	284.10	280.74	279.15
2	282.86	279.49	277.91
3	282.90	279.53	277.95
4	283.92	280.55	278.97
5	282.90	279.53	277.95
6	282.86	279.49	277.91

Conclusion

PW86x-PW91c, is the best XC functional among the eight functionals tested for TDDFT calculation of singlet excitation energy of the substituted anilines. Using the XC functional, average absolute deviation from experiment is 0.223 eV for the eighteen cases with the maximum absolute deviation of 0.932 eV which resulted from *m*-nitroaniline (Table 1). The largest AAD among the eight is 0.298 eV, which resulted from OLYP. Large errors are registered in the three isomers of nitroanilines with all the eight XC functional tested. If the nitroanilines are excluded in the statistics, AADs drop to ca.0.15 eV. Valence electron ionization energies of the substituted benzenes were calculated by the ΔSCF method with PW86x-PW91c. AAD evaluated from eight cases is 0,21 eV which is close to the corresponding value obtained for the calculation of the excitation energy. CEBEs and ΔCEBEs of *o*-, *m*-, and *p*-phenetidines and related mono substituted benzenes were calculated. ΔCEBE(SMS), sum of mono substituted (SMS) CEBE shift and mutual interference effect (MIE) were defined and their values were calculated. The magnitude of MIE provides the degree of mutual interference between the two substituents. Average absolute value of MIE is ca. 0.1 eV for the three isomers. Using the calculated valence electron ionization energies and the core electron binding energies of one of the phenetidines, some X-ray emission energies were calculated.=

The numbers of cases used to evaluate the AADs, 0.223 eV for the valence electron single excitation energies and 0.21 eV for valence electron ionization energies of the substituted anilines are seventeen and eight, respectively. These numbers of the cases are rather limited. The conclusions obtained based upon these numbers may not be very general. However, it is interesting to observe that the values of our two AADs, 0.223 and 0.21 eV, are very close to 0.25 eV that is the AAD obtained by the benchmark study of singlet excitation energies using a very extended set of organic molecules.

Acknowledgements

We thank Dr. José Luis de Souza Pio of Amazonas State University. YT expresses his gratitude to Dr. Delano P. Chong for sending a preprint of his work on calculation of transition energies of *p*-nitroaniline. The authors acknowledge Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) of Brazil for research fellowships, 304751/2006-5 for YT and 302440/2005-4 for ADSM. ADSM also thanks Ministério da Ciência e Tecnologia, Conselho Nacional de Desenvolvimento Científico e Tecnológico (MCT/CNPq) for financial support from (553292/2005-6, CT/AMAZÔNIA/MCT/CNPq).

References and Notes

[1] Jacquemin, D.; Wathelet, V.; Perpete, E. A. Adamo, C. *J. Chem. Theory Comput.* **2009**, *5*, 2420.

[2] Vydrov, O. A.; Scuseria, G. E. *J. Chem. Phys.* **2006**, *125*, 234109.

[3] Weintraub, E.; Henderson, T.M.; Scuseria, G. E. *J. Chem. Theory Comput*. **2009**, *5*, 754.

[4] Mirashi, P. L. S.; Varkhede, R. S.; Kunte, R. S. *Indian J. Pure & Appl. Phys*. **1990**, *28*, 565.

[5] Jana, P.; Ganguly, P. *Spectrochimica Acta*, **1993**, *49A*, 1515.

[6] Klasinc, L.; Kovač. B.; Güsten, H. *Pure & Appl. Chem*. **1983**, *55*, 289.

[7] Takahata, Y. *Int. J. Quantum Chem*. **2008**, *108*, 2326.

[8] Takahata, Y.; Marques, A.M.; Custodio, R. *J. Mol. Struct.: THEOCHEM*, http://dx.doi.org/10.1016/j.theochem.2009.09.015

[9] Frisch, M. J.;Trucks, G.W.; Schlegel, H.B.; Gill, P.M.W.; Johnson, B.G.; Robb, M.A.; Cheeseman, J.R.; Keith, T.A.; Peterson, G.A.; Montgomery, J.A.; Ragavachari, K. ; Al-Laham, M.A.; Zakrzewski, V.G.; Ortiz, J.V.; Foresman, J.B.; Cisolwski, J.; Stefanov, B.B.; Nanayakkara, A.; Peng, C.Y.; Ayara, P.Y.; Chen, W. ; Wong, M.W. ; Andres, J.L.; Replogle, E.S; Gomperts, .R. ; Martin, R.L.; Fox, D.J.; Binkley, J.S. ; Defrees, D.J; Baker, J.; Stewart, J.P; Head-Gordon, .M.; Gonzalez, C.; Pople, J.A. Gaussian, Inc.: Pittsburgh, PA,

1995. Gaussian 03, Revision B.05, Gaussian, Inc., Pittsburgh PA, 2003.

[10] ADF Program System, release 2004.01: see http://www.scm.com.

[11] Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

[12] Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

[13] Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Sing, D. J.; Fiolhais, C. *Phys. Rev*. *B* **1992**, *46*, 6671.

[14] Adamo, C.; Barone, V. *J. Chem. Phys.* **1996**, *116*, 5933.

[15] Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

[16] Perdew, J. P.; Wang, Y. *Phys. Rev*. *B* **1986**, *33*, 8800.

[17] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev*. B **1988**, *37*, 785.

[18] Handy, N. C.; Cohen, A. J. *Mol. Phys.* **2001**, *99*, 403.

[19] van Leeuwen, R.; Baerends, E. J. *Phys. Rev. A* **1994**, *49,* 2421.

[20] Schipper, P. R. T.; Gritsenko, O. V.; van Gisbergen, S. J. A.; Baerends, E. J. *J. Chem. Phys*. **2000**, *112*, 1344.

[21] Gritsenko, O. V.; Schipper, P. R. T.; Baerends, E. J. *Chem. Phys. Lett.* **1999**, *302*, 199.

[22] Takahata, Y.; Chong, D. P. *J. Electron Spectrosc. Relat. Phenom.* **2003**, *133*, 69.

[23] Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

[24] Chong, D. P. *J. Chem. Phys.* **1995**, *103*, 1842.

[25] Ohta, T.; Fujikawa, T.; Kuroda, H. *Bull. Chem. Soc. Jpn.* **1975**, 48, 2017.