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Semi-empirical Parameters in π-Electron Systems. XIV. Parameters for the Methoxy and Ethyl Groups

GERMUND HÖJER, SARA MEZA-HÖJER and FERNANDO GAYTAN

División de Estudios Superiores de la Facultad de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, México 20, D.F.

The parametrization of the methoxy and ethyl groups for the modified PPP method originally proposed by Roos and Skancke has been analysed. From the basic assumptions of the method it is found that the method should be able to distinguish between the methoxy group and the hydroxy group, which was treated in an earlier paper, while it cannot always account for the experimentally observed differences between methyl- and ethyl-substitution. Ionization potentials and electronic spectra of substituted benzenes are presented.

INTRODUCTION AND DETAILS OF THE CALCULATIONS

Some years ago Roos and Skancke [1] proposed a systematic way to parametrize the PPP method on the basis of an analysis of the ZDO approximation by Fischer-Hjalmars.[2] This work has been extended to include various heteroatoms and substituents in conjugated systems.[1–14] Later on Roos [15,16] generalized the method to metal complexes and Sundbom and Henriksson applied it to the interpretation of the electronic spectra of metal-organic complexes (copper and iron) with very good results.[17–19]

In Refs. 3 and 7 the methyl and hydroxy groups were parametrized. In some vanadium-porphyrins, which the present authors are studying now, the porphin ring has methoxy and ethyl groups as substituents. To include these groups in this method one can think of two different ways. Either one can try to build them with the existing parameters for $-CH_3$ and $-OH$, just adding the missing ones, or one can treat them as complete groups. The way to include these two new groups in the method is determined by the following experimental findings. The ionization spectra and the UV absorption spectra of substituted benzenes show a strong similarity between methyl- and ethyl-substitution and between hydroxy- and methoxy-substitution. The exchange of a hydrogen atom for a methyl group leads only to a small modification of the inductive and mesomeric effects of the original group. In our model this means that the original oxygen π-orbital in the hydroxy or the pseudo π-orbital in the methyl group is perturbed by this exchange. How this affects the original $-OH$, respectively $-CH_3$, parameters is discussed below. But first we want to make a remark about an alternative approach to our problem. One could try the hypothesis, that the methoxy group contributes to the π-system a real π-orbital on the oxygen atom *and* a pseudo π-orbital on the methyl group with a total of four electrons. That would imply a hyperconjugation effect across the $O-CH_3$ bond. Some preliminary tests on anisole along this line gave very unsatisfactory results and clearly demonstrated that this second approach is unrealistic.

Fischer-Hjalmars [2] showed, that in the formally orthogonalized atomic orbital basis the core parameter W_μ is local to the first order in the overlap while $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$ are local to the second order (we use the notations of Ref. 1). For that reason Roos and Skancke made W_μ dependent on the nearest neighbours while the other parameters were directly transferable. In the discussion of the various param-

eters we let χ stand for the π-orbital of the substituent in question. Going from $-OH$ to $-OCH_3$ and from $-CH_3$ to $-C_2H_5$ should then be accomplished by reoptimizing W_χ in the first place. The one-center integral $\gamma_{\chi\chi}$ has previously been estimated from atomic spectral data or from the assumed form of χ. In this case it is very difficult to say how χ is modified by changing a hydrogen atom for a methyl group in the substituent. We will return to this problem later on. Experiments with this parameter show, that the results are very insensitive to reasonable variations in the value of $\gamma_{\chi\chi}$. The two-center integrals $\gamma_{\chi C}$ and $\beta_{\chi C}$ have been obtained in the earlier papers by fitting to experimental data on a few standard molecules. In this case we do not have enough data to make a least squares fit for W_χ, $\gamma_{\chi C}$ and $\beta_{\chi C}$. But $\gamma_{\chi C}$ and $\beta_{\chi C}$ are local to the second order and should not vary by a change in the environment of χ, unless χ is strongly affected by this change. Again the results vary rather slowly with these two parameters. And at last $\Delta W_C(\chi)$, which is the correction to W_C due to χ as nearest neighbour to C, depends only on χ and not on the environment of χ. This analysis turns out to hold quite well for the hydroxy-methoxy case as our results will show in the next section.

For the ethyl group the situation is more complicated. Experimentally it is found, that ethylbenzene has a lower ionization potential (IP) and a smaller red shift of the ^1L_b band with respect to benzene than methylbenzene. Apparently the method cannot reproduce both these properties at the same time. We will discuss several points connected with this problem. Diminishing the absolute value of W_χ lowers the IP but increases the red-shift at the same time. The first observation we want to make is that, the method gives a too low transition energy for the ^1L_b band in benzene, 39.2×10^5 m^{-1} compared to the experimental value of 39.5×10^5 m^{-1}. Roos used methyl-substituted ethylenes to determine the methylparameters. The calculated energy of the ^1L_b band in toluene comes out right on the observed value. This means, however, that the calculated red shift of toluene (and also for the other methyl-substituted benzenes) is too small if we take the calculated spectra of benzene as standard. In this sense the value obtained for ethylbenzene is better though the absolute value of the transition energy is off compared to the experimental one. Secondly, looking at the suggested form of the π-orbital of the methyl group, one should expect the replacement of one of the hydrogens for a $-CH_3$ to affect to a greater extent the form of the orbital and thus the parameters of this group, than in the hydroxy-methoxy case, where the π-orbital is the oxygen $2p_z$ orbital. In the ethyl group it is not unreasonable to think that the π-orbital partly spreads into the CH_3 group. CNDO calculations [20] do show such a shift in the highest occupied π-orbital in ethylbenzene. The size of the shift depends on the conformation. It is only a few percent for the case with the ethyl group in the benzene plane, while it is quite large when the group is rotated out of the plane. This discussion suggests, that the π-orbital of the ethyl group is a little more diffuse and centered further away from the ring than the methyl π-orbital. That should lead to poorer overlap with the ring, which means a numerically smaller beta value for the bond and smaller repulsion integrals, both $\gamma_{\chi\chi}$ and $\gamma_{\chi C}$. The effect on ΔW (χ) is not so obvious from the change in χ. Variations along these lines were not able to lower the IP and the red shift at the same time. The last point we want to make is that the rotational barrier in ethylbenzene is very small. Experimentally it has been estimated to be around 5.4 kJ/mol.[21] Both *ab initio* [22] and CNDO [20] predict a barrier of about 8.4 kJ/mol and the conformation with the ethyl out of the benzene plane as the most stable one. In this conformation the strict symmetry separation of σ and π breaks down. It is not surprising then that the parametrization, which does not take into account σ-π-mixing, cannot completely reproduce the experimental results. A detailed study of the difference between methyl- and ethyl-substitution is really beyond the limits of the applicability of the π-electron theory.

GEOMETRY

The same geometries have been used as for the corresponding hydroxy- and methyl-substituted molecules. This is very reasonable as neither the hydroxy [7] nor the methyl param-

Table 1. Comparison of calculated and experimental ionization potentials (eV).

Molecule	Calc.	Symmetry (for C_{2v})	Observed Adiabatic	Vertical
Benzene [a]	9.25	a_2, b_1	9.25 [f]	9.40 [h]
Phenol [b]	8.45	b_1	8.46 [f]	8.75 [h]
	9.14	a_2	9.34 [f]	9.45 [h]
Anisole	8.20	b_1	8.20 [f]	8.54 [h]
	9.12	a_2	9.10 [f]	9.37 [h]
1,2-Dimethoxybenzene	7.77			
	8.53			
1,3-Dimethoxybenzene	7.88			
	8.34			
1,4-Dimethoxybenzene	7.61	b_1		7.90 [h]
	9.00	a_2		9.19 [h]
1,4-Bromohydroxybenzene [c]	8.43	b_1		8.52 [h]
1,4-Bromomethoxybenzene	8.22	b_1		8.49 [h]
	9.06	a_2		9.65 [h]
p-Methoxybenzaldehyde	8.55	b_1		8.87 [h]
	9.66	a_2		9.77 [h]
	9.98	n		
Benzaldehyde [d]	9.44	b_1	9.46 [f]	9.80 [h]
	9.71	a_2		10.00 [h]*
	10.10	n		
Toluene [e]	8.84	b_1	8.84 [f]	8.9 [h]
	9.19	a_2	9.15 [f]	9.13 [h]
Ethylbenzene	8.77	b_1	8.77 [g]	
	9.18	a_2		
1,2-Diethylbenzene	8.50			8.91 [i]
	8.92			
1,3-Diethylbenzene	8.54			8.99 [i]
	8.88			
1,4-Diethylbenzene	8.36	b_1		8.93
	9.11	a_2		

[a] Ref. 1. [b] Ref. 7. [c] Ref. 9. [d] Ref. 14. [e] Ref. 3. [f] Ref. 24. [g] Ref. 25. [h] Ref. 26. [i] Ref. 27, electron impact data.
* Estimated by us from the unresolved first band in Fig. 11, Ref. 26. The Refs. 24 and 26 refer to photoelectron spectroscopy data.

eters [3] are distance dependent. A change in the distance ring-substituent would only affect the coulomb integrals between the substituent and its non-nearest neighbours with very small influence on the final results.

RESULTS AND DISCUSSION

The parameter W_χ was optimized by fitting the first IP and the first transition in anisole and ethylbenzene to experimental data. The other parameters retained their values (from $-OH$ and $-CH_3$) in agreement with the analysis above.

The new parameters are

$W_{OCH_3} = -10.42$ eV; $W_{C_2H_5} = -11.18$ eV

As mentioned in the previous section the results for the ethyl group are not entirely satisfactory but we give them for completeness. In the tables we include also some molecules treated in earlier papers in this series to simplify the discussion.

Ionization potentials. The calculated and experimental ionization potentials (IP's) are presented in Table 1. When Roos and Skancke [1] initiated this method only adiabatic ionization potentials were available for the molecules of interest. In the following papers [3–14] this practice was continued for consistency. Experimentally the difference between the adiabatic and vertical IP's is of the order 0.2 to 0.4 eV. Our theoretical values are obtained as usual

Table 2. Calculated and observed electronic transitions in 10^5 m^{-1}.

Theoretical			Compilation by Petruska [23]			Observed					
ν_{max}	$-\Delta\nu$ [a]	f_{calc}	$-\Delta\nu_{0-0}$ [b]	f	solvent	ν_{max}	intensity	ν_{max}	intensity	ν_{max}	intensity
Benzene [c]											
39.17		0.0				39.4	[g]	39.4	$f=0.001$ [h]	39.5	[i]
50.62		0.0				49.8		49.5	0.10	50.6	[j]
56.14		1.19				56.3		54.4	0.69	55.9	[j]
Phenol [d]											
37.89	1.28	0.013	1.74(1.80)	−(0.017)	vap. (iso)	37.02	0.02 [g]	37.2	$\log\varepsilon=3.34$ [k]	36.7	$\log\varepsilon=3.18$ [l]
47.07	3.55	0.158	2.10			46.94	0.132	47.6	3.78	47.0	3.78
53.69	2.45	0.830	1.70			54.04	0.636			52.7	4.70
54.72	1.42	1.036				55.90	0.467				
Anisole											
37.38	1.79	0.019	1.85	0.020	hex	37.02	0.023 [g]	36.90	$a=2200$ [m]	36.90	[n]
45.72	4.90	0.212	3.40			46.62	0.175	45.5			
52.22	3.92	0.576				53.88	0.585				
54.40	1.74	0.922				55.65	0.371				
1,2-Dimethoxybenzene											
36.18	2.99	0.024	2.40	0.028	hex	36.43	$a=3920$ [n]				
43.04	7.58	0.130				44.44	11700				
50.53	5.61	0.946									
50.72	5.42	0.542									
1,3-Dimethoxybenzene											
36.40	2.77	0.015	2.50	0.024	hex	36.64	[n]				
44.18	6.44	0.081									
49.62	6.52	0.962									
49.82	6.32	0.511									
1,4-Dimethoxybenzene											
35.62	3.55	0.054	4.50	0.032	hex	34.60	$a=3010$ [n]				
43.38	7.24	0.337				44.35	8870				
52.31	3.83	0.650									
54.50	1.64	1.010									

Table 2. Continued.

1,2-Dihydroxybenzene [d]									
36.93	2.24	0.017	2.70	0.026	hex	36.05	[n]		
44.79	5.83	0.105	2.80						
52.00	4.14	1.061							
52.36	3.78	0.753							
1,3-Dihydroxybenzene [d]									
37.08	2.09	0.011	2.60	0.022	hex	36.36	[n]		
45.59	5.03	0.067	3.80						
51.53	4.61	1.088							
51.95	4.19	0.736							
1,4-Dihydroxybenzene [d]									
36.54	2.63	0.041	5.40	0.032	hex	34.07	$a=2810$ [n]		
44.97	5.65	0.275				44.54	5180		
53.35	2.79	0.828							
54.66	1.48	1.064							
p-Bromomethoxybenzene									
37.26	1.91	0.000				35.46	$a=1600$ [n]	35.46	$a=1750$ [m]
43.79	6.83	0.342				44.15	14200	44.00	12500
51.35	4.79	0.708							
54.46	1.68	0.935							
p-Bromohydroxybenzene [e]									
37.6	1.57	0.001				35.40	$a=1930$ [n]	35.52	$a=1750$ [m]
44.9	5.72	0.31				44.25	12100	44.64	10000
52.5	3.64	0.88							
54.6	1.54	1.06							
p-Methoxybenzaldehyde									
31.37		0.0							
35.91		0.017							
40.12		0.504							
48.23		0.422							
52.22		0.259							
54.28		0.719							
57.43		0.102							

Table 2. Continued.

Theoretical			Compilation by Petruska [23]			Observed					
ν_{max}	$-\Delta\nu$ [a]	f_{calc}	$-\Delta\nu_{0-0}$ [b]	f	solvent	ν_{max}	intensity	ν_{max}	intensity	ν_{max}	intensity
Toluene [f]											
38.84	0.33	0.011	0.61(0.61)	−(0.003)	vap. (iso)						
49.95	0.67	0.018	1.40								
55.65	0.49	1.212	1.40								
55.85	0.29	1.143									
Ethylbenzene											
38.73	0.44	0.012	0.55	0.003	iso						
49.68	0.94	0.032									
55.46	0.68	1.203									
55.69	0.45	1.119									
1,2-Diethylbenzene											
38.41	0.76	0.014	1.03	0.003	iso						
48.81	1.81	0.032									
54.86	1.28	1.209									
54.97	1.17	1.103									
1,3-Diethylbenzene											
38.51	0.66	0.012	1.06	0.003	iso						
49.08	1.54	0.017									
54.81	1.33	1.229									
54.99	1.15	1.114									
1,4-Diethylbenzene											
38.07	1.10	0.043	1.25	0.005	iso						
48.98	1.64	0.081									
55.15	0.99	1.203									
55.80	0.34	1.071									

[a] Frequency shift relative the calculated benzene band. [b] Frequency shift relative the observed benzene band. [c] Ref. 1. [d] Ref. 7. [e] Ref. 9. [f] Ref. 3. [g] Ref. 28, vapour. [h] Ref. 29, hexane. [i] Ref. 30, vapour. [j] Ref. 31, vapour. [k] Ref. 32, cyclohexane. [l] Ref. 29, heptane. [m] Ref. 33, cyclohexane. [n] Ref. 34, MeOH.

as minus the energy of the orbital in question according to Koopmans' theorem. For the comparison theory-experiment the adiabatic IP's or the vertical IP's lowered by the above-mentioned difference should be used.

For the parametrization we used for anisole the adiabatic photoelectron spectroscopy value given by Turner,[24] which is the same reference as was used for the hydroxy group.[7] For ethylbenzene we used the adiabatic spectroscopic value reported by Hammond *et al.*[25]

The degenerate e_{1g} level in benzene is split into b_1 and a_2 in C_{2v} (monosubstitution and *para*-disubstitution). The substitution orbital(s) is (are) of b_1 symmetry and can mix directly with the b_1 orbital of the e_{1g} level and also to a smaller extent with the deeper lying a_{2u} orbital, which also transforms as b_1 in C_{2v} symmetry. The a_2 orbital, which cannot mix directly with the substituent orbital(s), should be less affected by the substitution than the b_1 orbital. The table shows a very good agreement between calculated and experimental data for the first ionization potential b_1. The second ionization potential, which corresponds to the a_2 orbital, requires a comment. The $-CH_3$, $-C_2H_5$, $-OH$ and $-OCH_3$ groups have very small effect on the a_2 level as expected and the agreement between theory and experiment is very good for this band too. It is only in the case of bromosubstitution the method fails to show a fairly strong stabilization of the a_2 level experimentally observed. In all the other cases this level remains very near the e_{1g} level in benzene.

Electronic spectra. The calculated and observed spectra are collected in Table 2. In the cases where we have used Petruska's [23] compilation of the spectra of substituted benzenes for the comparison of theory and experiment, we have assumed that the shifts of ν_{max} are very similar to the shifts in the 0–0 bands given by Petruska. Most of the experimental spectra are taken in solution. Unfortunately this makes the comparison of the effects of the hydroxy and methoxy groups rather difficult as the former group but not the latter one is readily available for hydrogen bonding, solute-solute and when the solvent is an alcohol also solute-solvent. It is quite probable that the solvent shifts (including effects solute-solute) will be different for the two groups. The observed differences are very near the experimental accuracy too. For these reasons the evaluation of the results for the electronic transitions will not be as clear as in the case of the ionization potentials, where the experiments are in the vapour phase.

The calculated positions of the bands are very good. But the methoxy group is always predicted to give larger red shifts than the hydroxy group, while the experimental data do not show a definite trend on that point. The agreement on the variation of the intensities of the bands is very good between theory and experiment. The methoxy group should intensify the ^1L_b and ^1L_a bands and lower the intensity of the ^1B band compared to the hydroxy group.

CONCLUSIONS

The comparison of the hydroxy and methoxy groups and the methyl and ethyl groups provides a good illustration of the consistency in the basic approximations of the method. The reoptimization of W_χ to account for the change from $-OH$ to $-OCH_3$ or from $-CH_3$ to $-C_2H_5$ gave very good results for the prediction of the first IP's while the results were not so conclusive with respect to the electronic spectra. However, this might be related to the fundamental problem of relating theoretical spectra, which correspond really to the vapour phase, and experimental solution spectra. We feel this problem is specially serious for the case $-OH$ and $-OCH_3$. Experimentally $-CH_3$ and $-C_2H_5$ substitutions are very similar and apparently the method cannot account for the fine differences due to the reasons given at the end of the introduction.

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