Theoret. chim. Acta (Berl.) 5, 95—101 (1966)

Calculations on the Electronic Spectra of Anilino, Phenoxyl and Benzyl Radicals

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Received February 18, 1966

The electronic spectra of benzyl, anilino and phenoxyl have been calculated, using two well known SCF–MO methods. Good agreement is found with experiment in all instances. However, the calculations still cannot explain the red shift produced by the addition of an extra electron to benzyl.

Die Elektronenspektren des Benzyl-, Anilino- und Phenoxylradikals sind mit Hilfe zweier wohlbekannter SCF–MO-Methoden berechnet worden. Die Übereinstimmung mit den Experimenten ist überall gut. Die Rechnungen können jedoch nicht die Rotverschiebung erklären, die beim Hinzufügen eines Elektrons zum Benzylradikal erzeugt wird.

On calcule les spectres électroniques des radicaux benzyle, anilino et phénoxyle par deux méthodes SCF–MO bien connues. L'accord avec l'expérience est bon partout. Cependant, ces calculs n'expliquent pas l'effet bathocrome de l'addition d'un électron au benzyle.

A. Introduction

The π-electronic spectrum of benzyl radical has been investigated experimentally by PORTER and LAND [1] using flash photolysis techniques, and has also been the subject of many theoretical studies [2, 3, 4]. A new π-π^* electronic transition has recently been reported by PORTER and SAVADATTI [5].

However, the π-electronic spectra of the isoconjugate radicals anilino and phenoxyl, although now experimentally well known, [1], have not been studied by theoretical methods.

Because of uniform electron density in the ground and some excited states, in the neglect of differential overlap approximation in the benzyl radical, there is no first order inductive effect on the transition energies on hetero substitution within the simple Hückel MO method, but only a second order inductive effect and a conjugation effect due to changes in resonance interaction between the hetero atom and the ring. The simple Hückel MO picture, therefore, affords an understanding of the rough location of the absorption bands in the benzyl radical isoconjugate series, and the striking changes in intensity of the first absorption band on heterosubstitution.

However, when electron interaction is explicitly included, the perturbation on heterosubstitution can no longer be identified as an inductive perturbation, but instead, the perturbation consists of one-electron operator perturbations and two-electron operator perturbations. Hence, it would be interesting to study the π-electronic spectra of benzyl radical isoconjugate series, using more refined theoretical methods, to see whether such similarity in π-electronic spectra, and relative intensities of the band strengths are theoretically anticipated.

In the present paper, we report the results of calculations of π-electronic spectra of anilino, and phenoxyl and also benzyl for comparison, using two well known semi empirical molecular orbital (MO) methods, i. e. Pariser-Parr configuration interaction method [6] and self consistent MO method with configuration interaction [7]. We show that the calculated transition energies agree well with experiment in most cases. The position of the new bond in the benzyl spectrum is calculated accurately, and compares very well with the rather extended calculations of BERTHIER [4].

The calculations predict the location of the corresponding transition in anilino and phenoxyl whilst at present no experimental results are available to test the correctness of our predictions. For completeness, we predict the positions of all other bands up to 7 eV for the three radicals.

It is also well known that, when an electron is added to benzyl, the energy of the first band is predicted to increase by about 6000 cm^{-1} [2] whereas in fact it decreases by 7000 cm^{-1} [8]. We have also calculated the π-electronic spectrum of benzyl anion using two different methods, which are the analogues of the two methods used for the calculations on the radicals. Our results show that the energy of the band is still predicted to increase, but only by about 1000 cm^{-1}.

B. Description of Calculations

I. Open shell molecules

Two formally similar calculations were performed on the radicals, viz:

1. In the first calculation, one electron (Hückel) orbitals were chosen as basis functions, and the set of all possible doublet singly excited states, together with the ground state function, was used in a configuration interaction calculation, to give a description of the different states of the radicals. A secular determinant of order 25 was solved in each case, in the usual manner.

Labelling the singly occupied orbital in the ground state as n, doubly occupied orbitals a and m, and an unoccupied orbital as x, we used basis functions described by the normalized Slater determinants (2):

$$\psi_0 = \| a\bar{a} \ldots m\bar{m}\, n \|$$
$$\psi_{n\to x} = | a\bar{a} \ldots m\bar{m}\, x |$$
$$\psi_{a\to n} = | a\bar{n} \ldots m\bar{m}\, n |$$
$$\psi_{a\to x} = \frac{1}{\sqrt{2}} \{ | a\bar{x} \ldots m\bar{m}\, n| + | x\bar{a} \ldots m\bar{m}\, n | \}$$
$$\psi'_{a\to x} = \frac{1}{\sqrt{6}} \{ 2 \, | ax \ldots m\bar{m}\, \bar{n} | - | a\bar{x} \ldots m\bar{m}\, n | + | x\bar{a} \ldots m\bar{m}\, n | \} .$$

These basis state functions are eigenfunctions of S_z and S^2.

Table 1. *Parameters used in the calculations. All in electron volts* (eV)

γ_{ij}	$j \backslash i$	1	2	3	4	5
benzyl	1	11.400	7.297	5.459	3.784	3.361
	2		11.400	7.297	5.459	4.898
anilino	1	12.799	7.591	5.533	3.798	3.366
phenoxyl	2	14.657	8.538	5.918	3.945	3.496

$\beta_{CC} = -2.395$ eV $\quad \beta_{CN} = -2.576$ eV $\quad \beta_{CO} = -3.000$ eV

$\delta\omega_N = -1.677$ eV $\quad \delta\omega_0 = -3.449$ eV

Matrix elements between the states were obtained by standard techniques.

The values of the parameters h and k needed to generate Hückel basis orbitals for this calculation were $h = 0$, 0.5, 1.0 and $k = 1$, 0.8, 0,8 for benzyl, anilino and phenoxyl respectively, as recommended by STREITWIESER [9].

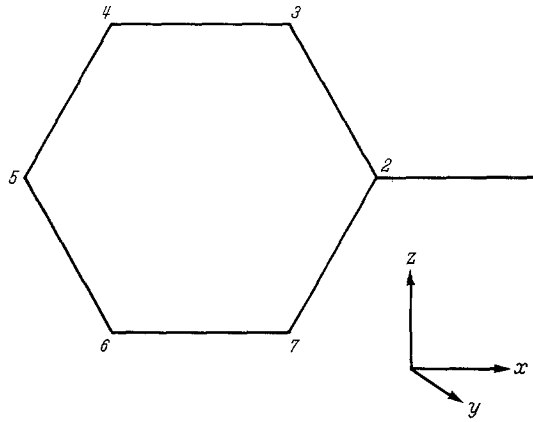

Fig. 1. Numbering of the atoms in the radicals. Introduction of coordinate system

Table 2. *Self Consistent field* MO's

Benzyl energy (eV)	1	2	3	4	5	Symmetry
14.468	.1547	−.4276	.3984	−.3983	.3982	b_2
11.333	−.2733	.5633	−.2296	−.3023	.5656	b_2
11.128	.0000	.0000	.5000	−.5000	.0000	a_2
5.700	.8960	.0000	−.2776	.0000	.2075	b_2
0.270	.0000	.0000	.5000	.5000	.0000	a_2
0.068	−.2732	−.5631	−.2296	.3024	.5657	b_2
−3.069	.1546	.4276	.3985	.3982	.3981	b_2
Anilino energy (eV)	**1**	**2**	**3**	**4**	**5**	**Symmetry**
14.397	.1461	−.4331	.4020	−.3960	.2928	b_2
11.260	−.2455	.5632	−.2324	−.3049	.5733	b_2
11.035	.0000	.0000	.5017	−.4983	.0000	a_2
5.128	.8907	−.0499	−.2833	.0075	.2087	b_2
0.196	.0000	.0000	−.4983	−.5017	.0000	a_2
0.006	−.3068	−.5611	.2229	.2999	.5572	b_2
−3.141	−.1723	−.4218	−.3930	−.4003	−.4038	b_2
Phenoxyl energy (eV)	**1**	**2**	**3**	**4**	**5**	**Symmetry**
14.319	.1809	−.4580	.4017	−.3836	.3748	b_2
11.210	−.2772	.5521	−.1983	−.3200	.5787	b_2
10.833	.0000	.0000	−.5042	.4598	.0000	a_2
4.887	.8236	−.0957	−.3488	.0141	.2623	b_2
0.222	.0000	.0000	−.4958	−.5042	.0000	a_2
−0.125	−.3962	−.5381	−.1759	.3106	.5465	b_2
−3.209	.2349	.4321	.3829	.3922	.3965	b_2

The one center coulomb integrals γ_{ii}, together with the one and two center core terms $\delta\omega_i$ and β_{ij} needed for benzyl and anilino, were those used by PEACOCK and McWEENY [*10*], whilst for phenoxyl, SIDMAN's [*11*] values were suitably scaled to make allowance for the different one center coulomb integral used for carbon.

Otherwise, the two center coulomb repulsion integrals needed in the calculations were obtained by well known methods due to PARISER et al. [*6*]. For clarity, the parameters are given in Tab. 1.

No attempt was made to fit the spectra by varying parameter sets, as it is our belief that this procedure invalidates an otherwise powerful theoretical method.

2. In the second calculation, open shell SCF–MO's were calculated, using the method first proposed by ROOTHAAN [*7*], and adapted for π-electron systems by ADAMS and LYKOS [*12*], using the same parameters as before. The SCF–MO's are given in Tab. 2, together with their symmetries under the group C_{2v}. Some confusion has arisen in the past, concerning the labels of the orbitals, due to different definitions of the symmetry planes of the molecule. The plane σ_v is in the plane of the molecule, whilst σ_v' is perpendicular to the plane of the molecule, an orbital of b_2 symmetry being symmetric to reflection in this plane.

It was shown by POPLE [*2*] that for a neutral or radical alternant hydrocarbon having the same number of mobile (π) electrons as conjugated centers that the MO's and their eigenvalues have the usual "pairing" properties, even on an SCF basis. The SCF–MO's of benzyl pair, as expected, whilst on adding a small perturbation at position 1 (i. e. going along the series), the pairing property is destroyed.

The calculation then proceeded as in (*I.* 1.) above. It should be noted that, since we are dealing with open shell systems, the SCF ground state function still interacts with singly excited configurations built out of electron excitation to virtual SCF–MO's like $\psi'_{a\to x}$.

II. Closed shell calculation

1. Hückel orbitals were used as basis functions to build up configurations, and all singly excited configurations were used in a configuration interaction calculation leading to a secular determinant of order 13. The method has been too well documented recently to make further repetition necessary [*16*].

2. SCF–MO's were calculated using the method due to POPLE [*13*], and configuration interaction was allowed between all singly excited states, as in (*II.* 1.). All the calculations reported were programmed for the University of Sheffield I.C.T. "Mercury" computer.

C. Results and Discussion

The new band of benzyl at 4.78 eV identified by PORTER and SAVADATTI [*5*] is calculated to appear at 4.72 eV (SCF) or 4.96 (Hückel CI). The transition is mainly a mixture of $\psi_{2\to 4}$ and $\psi_{4\to 6}$, and has symmetry $B_2 \to B_2$, the ground state wavefunction being B_2. The analogous bands are predicted to be at 4.94 (Hückel) or 4.72 (SCF) for anilino, and 4.76 (Hückel) or 4.71 (SCF) for phenoxyl and are both $B_2 \to B_2$ symmetry. From the symmetries of the first two observed transitions which have been reported in the literature it is clear that the first two observed bands of benzyl, experimentally observed at 2.75 eV and 3.88 eV, are the

Table 3. *Results of configuration interaction calculation on radicals. Term values in* eV. I → J *denotes a singly excited configuration, in the usual manner. M^2 being the sqare of the modulus of the transition moment vector $\vec{M} = (M_x, M_y, 0)$.*

Benzyl term	Benzyl main contrib.	Benzyl Symm	Benzyl M^2	Anilino term	Anilino main contrib.	Anilino Symm	Anilino M^2	Phenoxyl term	Phenoxyl main contrib.	Phenoxyl Symm	Phenoxyl M^2
					Hückel Basis Set						
2.69	$3 \to 4;\ 4 \to 5$	A_2	.0275	2.75	$4 \to 5;\ 3 \to 4$	A_2	.0215	2.86	$4 \to 5;\ 3 \to 4$	A_2	.5951
3.14	$2 \to 4;\ 4 \to 6$	B_2	.0029	3.22	$2 \to 4;\ 4 \to 6$	B_2	.0149	3.44	$2 \to 4;\ 4 \to 6$	B_2	.1312
4.11	$3 \to 4;\ 4 \to 5$	A_2	.2551	4.19	$3 \to 4;\ 4 \to 5$	A_2	.5018	4.44	$4 \to 5;\ 3 \to 4$	A_2	.1281
4.96	$2 \to 4;\ 4 \to 6$	B_2	.8341	4.94	$2 \to 4;\ 4 \to 6$	B_2	.8145	4.76	$2 \to 4;\ 4 \to 6$	B_2	.3715
5.48	$1 \to 4;\ 4 \to 7$	B_2	.4476	5.34	$1 \to 4;\ 4 \to 7$	B_2	.0256	5.61	$1 \to 4;\ 4 \to 7$	B_2	1.9352
5.49		A_2	.2199	6.35		A_2	.0807	6.85		A_2	.4917
6.71		B_2	.8834	6.84		B_2	.2789	6.92		B_2	.4212
6.96		A_2	.0617	7.24		B_2	1.3981				
					SCF Basis Set						
2.69	$3 \to 4;\ 4 \to 5$	A_2	.0022	2.83	$3 \to 4;\ 4 \to 5$	A_2	.0065	2.46	$4 \to 5;\ 3 \to 4$	A_2	.0003
3.43	$2 \to 4;\ 4 \to 6$	B_2	.0015	3.50	$2 \to 4;\ 4 \to 6$	B_2	.0171	3.43	$2 \to 4;\ 4 \to 6$	B_2	.0428
4.05	$3 \to 4;\ 4 \to 5$	A_2	.3949	4.27	$3 \to 4;\ 4 \to 5$	A_2	.4705	4.16	$4 \to 5;\ 3 \to 4$	A_2	.6265
4.72	$2 \to 4;\ 4 \to 6$	B_2	1.2272	4.72	$2 \to 4;\ 4 \to 6$	B_2	.5291	4.71	$2 \to 4;\ 4 \to 6$	B_2	.2163
5.30	$1 \to 4;\ 4 \to 7$	A_2	.2805	5.52	$1 \to 4;\ 4 \to 7$	B_2	.0968	5.13	$1 \to 4;\ 4 \to 7$	B_2	.3881
5.81		B_2	.0233	6.13		A_2	.2735	5.90		B_2	.060
6.28		B_2	.0761	6.30		B_2	.0767	6.33		A_2	.1177
6.70		B_2	1.7219	6.80		B_2	1.8069	7.06		B_2	1.9881
6.90		A_2	.0216	6.88		A_2	.0019				

ones which we have calculated at 2.69 eV and 4.11 eV (Hückel) and 2.69 eV and 4.05 eV (SCF).

Similarly, one would expect the first two bands of anilino (experimentally 3.12 eV and 4.04 eV) to be the ones which we have calculated at 2.75 eV and 4.19 eV (Hückel) and 2.83 and 4.27 (SCF), and for phenoxyl, the experimental bands at 3.10 eV and 4.23 eV appear, from symmetry considerations, to be the ones we calculate at 2.86 eV and 4.42 eV (Hückel) and 2.46 eV and 4.16 eV (SCF).

Murrell [*17*] has pointed out that, on passing along the series under consideration, the first weak band 'steals' intensity from the second (strong) band by an inductive perturbation due to the introduction of the heteroatom. This is the reason why the relative intensities of the first two observed bands are 0.01:1; 0.3:1 and 1.0:1 in benzyl, anilino and phenoxyl respectively.

Table 4. *Results for benzyl anion*

	term	type	symmetry
Hückel	2.72	$4 \to 5$	B_1
Basis	4.27	$4 \to 6$	A_1
Set	5.96	$3 \to 6; 2 \to 5$	B_1
	6.26	$4 \to 7$	B_1
	6.56	$3 \to 5; 2 \to 6$	A_1
SCF	3.00	$4 \to 5$	B_1
Basis	4.33	$4 \to 6$	A_1
Set	6.06	$3 \to 6; 2 \to 5$	B_1
	6.26	$4 \to 7$	B_1
	6.61	$3 \to 5; 2 \to 6$	A_1

Our calculations give relative intensities .0428:1, .1078:1, 4.6456:1 (Hückel) and .0056:1, .0140:1, and .0005:1 (SCF) for the three, and so, are seen to agree well with experiment in the Hückel case, but less well in the other case.

However, as was shown by Murrell [*15*] in the closed shell case, the influence of doubly excited configurations, which have not been included in our calculations, may be significant in the intensity calculation.

The results of the calculation on benzyl anion are shown in Tab. 4. It is seen that the energy of the first band as compared to that in benzyl is not right, even though the fit between experiment and prediction is fair. It seems probable that the excess charge in benzyl anion could be responsible for this result, and we are at present repeating the calculation, using the method of Brown and Heffernan [*14*] together with several other ions.

D. Conclusions

We have shown that, using two sophisticated methods for the calculation of π-electronic spectra for open shell molecules, whilst we can calculate the transition energies very well, the calculation of other quantities such as transition moment, is less good, but still qualitatively correct. We have calculated successfully the energy of the new transition of benzyl, and we predict the corresponding transition in anilino and phenoxyl would occur in roughly the same region.

Experimental study in finding the predicted transitions in anilino and phenoxyl would be interesting. However, even with the advanced theories used, we have been unable to explain successfully the red shift in the first band of benzyl, on the addition of an extra electron.

Acknowledgements. We would like to thank the Director of the Computing Laboratory, Sheffield University, for the computing facilities. We also thank Professor C. A. COULSON, F.R.S., and Professor J. N. MURRELL, for valuable discussions.

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