

# All valence electron calculations on the electronic structure and spectra of some $\alpha$ -substituted toluenes

\*J. BÁNKI and <sup>b</sup>Á. I. KISS

<sup>a</sup>Department of Organic Chemistry, Slovak Technical University,  
880 37 Bratislava

<sup>b</sup>Department of Physical Chemistry, Technical University,  
1521 Budapest

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The electronic structure and spectra of toluene, benzyl fluoride, benzyl alcohol, and benzylamine have been studied by the CNDO/S method. The calculated singlet transition energies, ionization potentials, and dipole moments are in good accordance with the experimental values. The variations in charge densities correspond to the inductive effect of the substituent.

Электронная структура и электронные спектры толуола, бензилфторида, бензилового спирта и бензиламина исследовались методом CNDO/S. Вычисленные синглетные переходные энергии, потенциалы ионизации и дипольные моменты хорошо сходятся с полученными данными измерения. Изменения в плотности заряда отвечают индукционному воздействию заместителя.

The interaction between molecular fragments having  $\pi$  orbitals separated by a tetrahedral carbon atom is a problem of general interest, both from theoretical and experimental points of view. The  $\alpha$ -substituted toluenes seem to be appropriate model systems for such investigations. Recently, *ab initio* calculations [1] were performed for these molecules dealing with the ground state properties. It seems to be interesting to study the electronic spectra, too. All valence electron approximation is accessible for this purpose. A limited number of works were reported: CNDO/S calculation of toluene and benzyl fluoride was performed by Jaffé *et al.* [2, 3].

In this paper a more detailed investigation of the electronic structure and spectra by the CNDO/S method is reported for toluene and  $\alpha$ -substituted toluenes containing first-row elements.

## Method of calculation

Benzyl fluoride, benzyl alcohol, and benzylamine were considered as model compounds. The calculations were performed using the original form of the CNDO/S method [4]. For the bond distances and angles Pople's standard values [5] were used. The parameters for the fluorine atom are those presented by Zahradník and Čársky [6], all other atomic and bond parameters are those given by Del

*Bene and Jaffé* [2, 4]. The two centre repulsion integrals were evaluated by the *Mataga—Nishimoto* approximation [7]. In the configuration interaction (CI) treatment the 30 lowest singly excited configurations were included as in the original form of this method [2, 4].

The investigation of the microwave spectrum of toluene shows that the barrier to internal rotation is very low ( $58.35 \text{ J mol}^{-1}$ ) [8]. Two molecular forms of toluene were considered in the calculation in order to investigate the effect of the relative position of methyl hydrogens. The two forms (*A* and *B*) are shown in Fig. 1. In forms *A* and *B* the interplanar angle  $\varphi$  between the benzene ring and the  $\text{C}_{ar}\text{C}_{me}\text{H}$  plane is  $60^\circ$  and  $30^\circ$ , respectively.

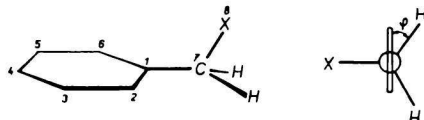


Fig. 1. Investigated molecular forms: *A*:  $\text{X} = \text{H}$ ,  $\varphi = 60^\circ$ ; *B*:  $\text{X} = \text{H}$ ,  $\varphi = 30^\circ$ ; *C*:  $\text{X} = \text{F}$ ,  $\text{O}(\text{H})$ ,  $\text{N}(\text{H}_2)$ ,  $\varphi = 60^\circ$ .

Thus far the molecular geometry and the stable molecular form of the investigated compounds have not been determined experimentally. *Ab initio* calculations [1] show that the orthogonal form ( $\varphi = 90^\circ$ ) of ethylbenzene and benzylamine has smaller energy than the *cis* form ( $\varphi = 0^\circ$ ) because of some steric repulsion, the *cis* form is obtained, however, as more stable with benzyl alcohol and benzyl fluoride.

Experimental data concerning the most stable conformation are available only for the benzyl halides. Electron diffraction measurement is available for benzyl chloride [9], the interplanar angle being  $\varphi = 67.5^\circ$ . The rotational angle calculated from polarization and polarizability data is about  $60^\circ$  for benzyl chloride, bromide, and iodide [10]. In the present calculation the rotational angle was set  $60^\circ$  for all the three toluene derivatives considered (form *C* in Fig. 1).

## Results and discussion

### Electronic transitions

The calculated spectral data for the six lowest energy transitions of the  $\text{C}_6\text{H}_5\text{CH}_2\text{X}$  ( $\text{X} = \text{H}$ ,  $\text{F}$ ,  $\text{OH}$ ,  $\text{NH}_2$ ) molecules are given in Table 1, together with experimental data on the energies of the highest intensity band maxima and the energy and oscillator strength of the 0—0 band for the first transition.

The ultraviolet spectra have benzenoid character: the bands characteristic of benzene appear slightly modified by a weak substituent effect. The substituent is exerting primarily inductive and also hyperconjugative effect. The position of the experimental 0—0 band of the lowest energy transition [12] shows that the transition energy of the  $\text{C}_6\text{H}_5\text{R}$  molecules decrease in the order



This means that the +I effect of the  $\text{CH}_2\text{X}$  substituent decreases with the increasing -I effect of the group X. The ionization energy of the lone electron pairs of the heteroatom is relatively high; the first two ionization processes of

Table 1

## Spectral data

Molecule	Calculated				Experimental <sup>a</sup>		
	<i>E</i> (eV)	<i>f</i>	Transition	Contribution	<i>E</i> <sub>max</sub> (eV)	<i>E</i> (O—O) <sup>c</sup> (eV)	<i>f</i> (O—O) <sup>c</sup>
Toluene	4.592	0.006	-1 1*	0.751	4.732	4.617	0.0031
			-2 2	0.645			
	5.825	0.041	-1 2	0.812	5.961		
			-2 1	0.566			
	6.349	0.009	-2 4	0.711			
			-1 4	0.655			
	6.552	0.000	-3 1	0.974			
			-3 2	0.211			
	6.579	1.022	-2 1	0.651	6.560		
			-2 2	0.470			
	6.603	1.085	-2 2	0.589			
			-1 1	0.515			
Benzylamine	4.580	0.007	-1 1	0.744	4.796	4.620	0.0030
			-2 2	0.628			
	5.785	0.057	-1 2	0.811			
			-2 1	0.511			
	6.278	0.062	-3 2	0.797			
			-5 2	0.372			
	6.416	0.197	-3 1	0.699			
			-5 1	0.454			
	6.596	0.710	-2 2	0.628			
			-1 1	0.506			
	6.620	0.953	-2 1	0.743			
			-1 2	0.531			
Benzyl alcohol	4.600	0.004	-1 1	0.724	4.805 <sup>b</sup>	4.624	0.0030
			-2 2	0.635			
	5.838	0.037	-1 2	0.784	5.961		
			-2 1	0.556			
	6.461	0.096	-3 2	0.814			
			-4 2	0.374			
	6.565	0.764	-2 2	0.667	6.560		
			-1 1	0.573			
	6.614	0.872	-2 1	0.716			
			-1 2	0.523			
	6.655	0.067	-3 1	0.853			
			-5 1	0.448			
Benzyl fluoride	4.623	0.001	-1 1	0.523	4.805	4.628	0.0034
			-1 2	0.512			
	5.878	0.024	-1 2	0.566			

Table 1 (Continued)

Molecule	Calculated				Experimental <sup>a</sup>		
	$E(\text{eV})$	$f$	Transition	Contribution	$E_{\text{max}}(\text{eV})$	$E(\text{O—O})^c(\text{eV})$	$f(\text{O—O})^c$
			-1 1	0.559			
	6.463	0.035	-3 2	0.766			
			-3 1	0.546			
	6.595	0.890	-2 2	0.661			
			-1 1	0.571			
	6.626	0.734	-2 1	0.623			
			-1 2	0.498			
	6.694	0.384	-4 1	0.663			
			-4 2	0.386			

a) The experimental data refer to cyclohexane solution

b) From [11].

c) From [12].

\* Figures -1, -2, etc. denote the occupied orbitals starting with HOMO, 1, 2, etc. stand for the unoccupied orbitals starting with LUMO

benzyl halides originate from  $\pi$  electrons [13] whilst  $n$ -electron excitations do not occur in the near ultraviolet region.

The calculated transition energies for the first two transitions are in good accordance with the experimental values and the substituent shifts are also well reproduced by the calculation. According to the calculation with toluene the upper state of the third and the lower state of the fourth transition have a considerable  $\sigma$  contribution from  $s$  and  $p_y$  orbitals, respectively. The fifth and sixth transitions have predominantly  $\pi$  character. The first five transitions of benzyl fluoride and benzyl alcohol are of  $\pi \rightarrow \pi^*$  type except the third transition the starting level of which has a considerable  $\sigma(p_y)$  component. With benzylamine the third and fourth transitions have  $\sigma(p_x)$  character. After completion of these calculations *Linder et al.* [14] recently stated that the  $\sigma$ -electron delocalization is too large in the CNDO/S method and suggested an improved version of calculation.

### Ionization potentials

The ionization potentials are shown in Table 2. Following the Koopmans theorem the negative orbital energies are considered as calculated values. The order of the first ionization potentials is the same for the calculated and experimental values, the former being somewhat higher. The agreement is the best for the first two ionization potentials of benzyl fluoride. The difference between the calculated values of the two rotamers is very small with toluene, and it is several hundredths of eV with benzylamine.

Table 2

Comparison of calculated data with experimental results

Molecule	Ionization potentials (eV)		Dipole moments $\times 10^{3b}$ (C m)	
	calculated	found [15]	calculated	found [17]
Toluene <i>A</i>	9.43	8.82	1.92	1.43
<i>B</i>	9.43		2.06	
Benzylamine	9.37	8.64	5.26	4.60
Benzyl alcohol	9.51	8.85 <sup>a</sup>	6.09	5.57
Benzyl fluoride	9.96	9.55 <sup>b</sup>	6.39	5.90
	9.86	9.80 <sup>b</sup>		

a) Value for  $C_6H_5CH_2OCH_3$ .<sup>†</sup>

b) Ref. [13].

## Charge densities

The total charges are given for some atoms in Table 3 instead of the ground state charge densities. For all molecules investigated the charge density of the ring atoms decreases in the sequence  $C_2$  ( $C_6$ ),  $C_4$ ,  $C_3$  ( $C_5$ ). A comparison of the different molecules shows that the charge density on all carbon atoms varies for the  $C_6H_5R$  molecules in the sequence  $R = CH_3, CH_2NH_2, CH_2OH, CH_2F$ . It decreases on the ring carbon atoms in *ortho* and *para* positions as well as on the tetrahedral carbon atom, and it increases on the substituted ring carbon atom and, to a smaller extent, in *meta* positions. The negative charge decreases on the carbon atoms in *ortho* and *para* positions and increases in *meta* positions. The positive charge increases on the tetrahedral carbon atom in the given sequence. For a more reliable comparison the total charge of the group X ( $X = NH_2, OH, F$ ) is also given in Table 3. The negative charge on the group X increases in the above sequence. The variation of charges may be ascribed to the inductive effect.

Table 3

Total charges

Molecule	2	4	6	7	CH <sub>2</sub>	X*
Toluene <i>A</i>	-0.0182	-0.0269	-0.0325	-0.0388	-	-
Benzylamine	-0.0369	-0.0289	-0.0327	0.0388	0.0761	-0.0575
Benzyl alcohol	-0.0324	-0.0254	-0.0303	0.0678	0.1225	-0.1166
Benzyl fluoride	-0.0265	-0.0196	-0.0203	0.1201	0.1923	-0.2135

\* X=F, OH, NH<sub>2</sub>.<sup>†</sup>

The charge densities of the two rotamers of toluene are nearly identical, the deviations are in the fourth decimal, therefore only the figures for the form *A* are given in Table 3. The charge densities of the  $\pi(p_z)$  atomic orbitals in toluene are in good accordance with the  $\pi$ -charge densities obtained from PPP calculation [16]. The PPP values are by several hundredths higher.

The charge density is altered in the first excited state primarily on the  $\pi(p_z)$  orbitals of the ring carbon atoms and on the orbitals of the substituent. The values of the total charges show that the carbon atoms in positions 1, 4, and 7 become more positive, and those in positions 2, 3, 5, and 6 more negative.

### Dipole moments

The calculated and experimental dipole moments can be found in Table 2. The agreement is satisfactory, the calculated values being somewhat higher. Both sets of data show the same trend.

The dipole moments of the different conformations are somewhat different. With toluene, form *A* gives a better accordance with the experimental value.

The dipole moments are not so good as those obtained by CNDO/2 calculations.

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