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A Semiempirical Approach to Hyperconjugation and Application to Toluene, the Xylenes and Mesitylene

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The semiempirical scheme proposed by PARISER, PARR and POPLE (PPP) [*1*] has successfully been applied to many conjugated molecules [*2*]. The fixed formalism to estimate the integrals in the energy-expressions makes the method especially suited for comparison of electronic properties for series of similar molecules.

Many conjugated molecules of great interest in organic chemistry and biochemistry contain substituted groups with σ-electrons which interact with the π-electrons. One frequently occurring example of such a group is the methyl group ($-CH_3$). The methyl group is thought to exhibit both a hyperconjugative [*3*] and an inductive influence on the π-electron system. The question of the relative importance of these two effects is still not settled [*4*].

Earlier theoretical calculations [*3, 5*] on methyl substituted benzene molecules have mainly made use of a simple molecular orbital treatment of the Hückel type [*6*]. Some recent calculations [*4*] by the PPP-method consider the methylgroup as having essentially inductive effect. The methyl group in thymine has been treated in the PPP-scheme with parameter values taken from the Hückel theory [*7*]. ARMSTRONG and PERKINS [*7a*] have treated methylsubstituted organoborons with essentially the same model as used in this paper.

Method

We consider the methyl group as $-C{\equiv}H_3$ [*3*]. In this model there is a diagonal hybridized carbon atom with two σ-bonds and one π-bond to the pseudoatom H_3. Thus we fix the valence ionization potential (I) and the electron affinity (E) for the carbon atom. For the pseudoatom H_3 we estimate the ionization potential as the calculated energy for an electron ascribed to the hypothetical group-orbital with π-symmetry, and moving in an effective field from the three protons and the other two electrons. The remaining two quantities needed, the electron affinity for

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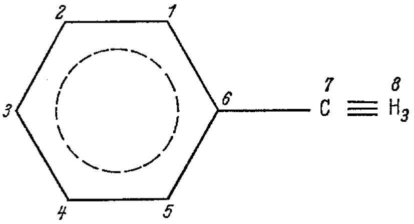

Fig. 1. Numbering system in toluene. Points of substitution: ortho 1.6; meta: 2.6; para: 3.6; mesitylene: 2, 4, 6

H_3 and the parameter $\beta(C{\equiv}H_3)$ are varied to fit the dipole moment and the transition energies for toluene.

For the calculations we used the PPP-scheme as modified by OHNO [8]. The electron repulsion integrals were approximated by OHNO as

$$\gamma_{kl} = (R^2_{kl} + a^2_{kl})^{-1/2} \tag{1}$$

where if Hartree atomic units are used

$$a_{kl}^{-1} = \tfrac{1}{2}(\gamma_{kk} + \gamma_{ll}) \,. \tag{2}$$

R_{kl} is the internuclear distance between atom k and l and

$$\gamma_{vv} = I_v - E_v \,. \tag{3}$$

We have included all singly excited configurations in the configuration interaction treatment. For mesitylene, however, only 26 configurations are considered.

Parameter Values Used

For the benzene ring: $I_C = 11.16$ eV [9], $E_C = 0.03$ eV [9], $\beta_{CC}(1.39\ \text{Å}) = 2.39$ eV [1].

For the methyl group: $I_{H_3} = 9.50$ eV, $E_{H_3} = 0.00$ eV, $\beta_{CH_3}(0.45\ \text{Å}) = 3.0$ eV, $\beta_{CC}(1.51\ \text{Å}) = 1.22$ eV [1]. All angles are assumed to be 120°. Distances are indicated above [10].

Results

For toluene the dipole moment from the π-electrons is calculated to be 0.50 Debye, the moment from the σ-electrons is estimated to be 0.03—0.06 Debye [15]. The experimental value is 0.40 Debye [13].

Table 1. *Calculated and observed energies for methyl substituted benzene*

	Lowest singlet transition (eV)		Ionization potential (eV)	
	Calc.	Obs.	Calc.	Obs.
Benzene	4.97	4.72 [11]	11.30	9.52 [12]
Toluene	4.89	4.64 [11]	11.02	9.23 [14]
o-Xylene	4.82	4.62 [16]	10.86	—
m-Xylene	4.84	4.58 [16]	10.87	—
p-Xylene	4.82	4.55 [17]	10.79	—
Mesitylene	4.87	4.53 [18]	10.80	—

Table 2. *Calculated charge distributions in methyl substituted benzene*

	q_1	q_2	q_3	q_4	q_5	q_6	q_7[a]	q_8[a]
Toluene	1.006	0.999	1.006	0.999	1.006	0.987	1.136	0.860
o-Xylene	0.994	1.006	1.005	1.005	1.006	0.994	1.134	0.862
m-Xylene	1.013	0.987	1.012	0.998	1.012	0.987	1.135	0.861
p-Xylene	1.006	1.006	0.993	1.006	1.006	0.993	1.135	0.861
Mesitylene	1.018	0.986	1.018	0.986	1.018	0.986	1.134	0.862

[a] The charges in the different methylgroups in xylene and mesitylene are the same.

The results as reported in Tab. 1 show that the proposed parameters correctly give the relative influence of the methyl group on the benzene molecule. Orto-xylene does not fit into the relative order, but there we expect steric effects. For mesitylene the configuration interaction treatment was somewhat limited in comparison with the other molecules.

Two gratifying results can be seen in Tab. 2. The electrophilic attack on toluene will be in orto-para position, which is in accordance with experiments. Secondly the relative charge distributions in the methyl groups are in good agreement with the dipole moment for the ($-CH_3$)-group [*13*] and with the chemical reactivity of the H_3-group. Pullman [*5*] and Ladik [*7*] both obtained nearly neutral carbon and hydrogen atoms in the methylgroup. Ladik [*7*] even got a negative charged H_3-group. Armstrong [*7a*] got a positive charged H_3-group. The question of the sign of the dipole moment for toluene seems not to be settled yet. All the calculation mentioned give a dipole moment of the right order of magnitude.

The method of approach seems promising, and it should be possible to extend the use of H_3-pseudoatoms also to other substituent groups as e.g. $(-NH_3)^+$. The model proposed here is now applied to more complicated molecules, the results will be published elsewhere.

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