ON THE PARAMETRIZATION FOR THE METHYL GROUP
IN THE SEMIEMPIRICAL PARISER-PARR-POPLE METHOD
WITH APPLICATION TO TOLUENE AND MESITYLENE

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It is known that the conjugation of the C-H σ bonding electrons of a methyl
group with the π -electron system of an unsaturated molecule may be simulated
in two distinct ways. The group may be considered either as a triple bonded
$-C\equiv H_3$ species (1) or as a pseudoheteroatom (2).

In the former the H_3 entity is regarded as a pseudoatom having three orbitals
and three electrons. The orbitals are formed from linear combinations of the
three hydrogen 1s orbitals :

$$\Psi_1 = \frac{1}{\sqrt{3}} (s_A + s_B + s_C) \; ; \; \Psi_2 = \frac{1}{\sqrt{6}} (2s_A - s_B - s_C) \; ; \; \Psi_3 = \frac{1}{\sqrt{2}} (s_B - s_C)$$

These functions are mutually orthogonal if overlap integrals are neglected.
Ψ_1 has no node and can form a σ bond with the adjacent carbon. Ψ_2 and Ψ_3
have the symmetry of a pair of p orbitals, one beeing orthogonal to and the
other coincident with the main π -electron system.

Table 1.
Parameter values proposed by Inuzuka (3) and Morita (4)

"atom"	I (ev)	(ev)
C (Me)	- 14.61	11.67
H_3	- 8.80	8.43

Matsen (2) and Stevenson have introduced the concept of the methyl group as
a pseudoheteroatom which contributes a pair of electrons to the π- system.
In this model, we assume that the electrons in a methyl group behave as a
single electron pair on a single atom.

We considered this latter model and applied it to toluene and mesitylene.
We found that the accordance between the theoretical and experimental UV
electronic transitions of these molecules was good for the following values
of the parameters :

$I_{CH_3} = -29$ ev ; $\gamma_{CH_3} = 10$ ev ; $\beta_{(CH_3)-C} = -5$ ev for a distance of 1.5 Å.

We may notice that the value found for I_{CH_3} is almost exactly twice that given for the carbon of the methyl group in Table 1.

The results for the two molecules studied are the following ones :

Table 2.

Molecule	Orbital jump	Theoretical ΔE (ev)	Experimental ΔE (ev) ; (5)
Toluene	$\varphi_4 \longrightarrow \varphi_5$	4.743	4.72
	$\varphi_4 \longrightarrow \varphi_6$	5.951	5.96
Mesitylene	$\varphi_6 \longrightarrow \varphi_7$	4.699	4.67
	$\varphi_6 \longrightarrow \varphi_8$	5.867	5.83

The configuration interaction included the two highest occupied orbitals and the two lowest empty ones.

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