# S.C.M.O. π-Electron Calculations of the Spectra and Ionization Potentials of Some Methyl Substituted Benzenes

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## Introduction

Recently, Lindner and Martensson [1] have presented Pariser, Parr [2] and Pople [3] self-consistent molecular orbital (S.C.M.O.) calculations on some methyl substituted benzenes in which they treated the methyl substituents by a "hyper-conjugative" model. In this treatment, the carbon atom of the methyl group was considered to contribute one π-orbital (and one electron) and the three hydrogens were considered to contribute one "pseudo π-orbital" (and one electron) to the π-system of the molecule. Comparable calculations, using an "inductive" model are presented here.

## Method

The carbon bearing a methyl substituent was treated as having a lower effective nuclear charge than the rest of the carbons in the molecule (i.e. it was assumed that the methyl substituent increased the shielding of the nucleus of the atom under consideration). This decreased nuclear charge was then assumed to decrease the valence state ionization potential (V.S.I.P.) and the one-center two-electron repulsion integral ($\gamma_{11}$) for this center. As previously reported [4, 5], this change was obtained from the change in ionization potential of the methyl radical on successive methyl substitution. The decrease in nuclear charge so obtained was 0.1106 which lead to a decrease of 1.178 eV in the magnitude of the V.S.I.P. and $\gamma_{11}$.

The valence state data in the calculations was from Hinze and Jaffé [6]. The Nishimoto-Mataga integrals approximation was employed [7], while the $\beta_{core}$ terms were estimated from the equation suggested by Flurry and Bell [8]. All $\beta_{core}$ terms were retained in the calculations. The spectral transitions were calculated by a configuration interaction procedure, retaining all singly excited configurations.

## Results

The spectral and ionization potential results are presented in Tab. 1. It is seen that the calculated range of the first spectral transitions is somewhat greater than that found experimentally, while the ionization potential range is somewhat less than found experimentally. It should be emphasized, however, that no spectrally calibrated parameters are used in this work. It is gratifying that the present results

Table 1. *Spectra and Ionization Potentials for Some Methyl Substituted Benzenes*

| Compound[b] | $^1\Delta E_1$[a] | | I.P. | |
|---|---|---|---|---|
| | Calc. | Obs. | Calc.[c] | Obs.[d] |
| Benzene | 4.93 eV | 4.86 eV | 9.97 eV | 9.24[e] |
| Toluene (1) | 4.84 eV | 4.73 eV | 9.66 eV | 8.82[e] |
| $m$-Xylene (1,3) | 4.76 eV | 4.68 eV | 9.51 eV | 8.56[e] |
| Pseudocumene (1,2,4) | 4.66 eV | 4.64 eV | 9.25 eV | — |
| Isodurene (1,2,3,5) | 4.58 eV | 4.63 eV | 9.19 eV | — |
| Pentamethylbenzene (1—5) | 4.49 eV | 4.59 eV | 9.06 eV | 7.85[f] |
| Hexamethylbenzene (1—6) | 4.41 eV | 4.56 eV | 9.05 eV | 7.35[f] |

  [a] Lowest singlet transition. Experimental values are for $\lambda_{max}$ in hydrocarbon solvent from Ref. [13].
  [b] Positions of methyl substituents in parentheses.
  [c] Koopmans' theorem ionization potential.
  [d] Photoionization potential values.
  [e] Ref. [14].
  [f] Ref. [15].

Table 2. *Calculated Total $\pi$-Electron Densities in Some Methyl Substituted Benzenes*

| Compound[a] | $q_1$ | $q_2$ | $q_3$ | $q_4$ | $q_5$ | $q_6$ |
|---|---|---|---|---|---|---|
| Benzene | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Toluene (1) | 0.938 | 1.023 | 0.997 | 1.013 | 0.997 | 1.028 |
| $m$-Xylene (1,3) | 0.935 | 1.056 | 0.935 | 1.040 | 0.994 | 1.040 |
| Pseudocumene (1,2,4) | 0.980 | 0.963 | 1.052 | 0.948 | 1.036 | 1.021 |
| Isodurene (1,2,3,5) | 0.960 | 1.008 | 0.960 | 1.064 | 0.945 | 1.064 |
| Pentamethylbenzene (1—5) | 0.972 | 1.004 | 0.988 | 1.004 | 0.972 | 1.060 |
| Hexamethylbenzene (1—6) | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |

  [a] Positions of methyl substituents in parentheses.

are in better numerical agreement with experiment than those of Ref. [1] where two parameters were calculated from the toluene spectrum.

The charge densities for the molecules under consideration are presented in Tab. 2. Qualitatively, these are in essentially the order that would be expected. No $\pi$-electron dipole moments were calculated, as the validity of these is highly questionable in the light of recent non-empirical calculations on $\pi$-systems [9].

## Discussion

The present work should not be taken as an attempt to disprove the phenomenon of "hyperconjugation". There is no doubt that there are definite interactions between $\pi$-electron systems and attached methyl groups (for example, E.S.R. hyperfine splitting of the signal of $\pi$-electron free radicals by methyl protons [10]). We do, however, feel that most effects can be adequately and more easily described by a simple inductive model. We have previously reported calculations which successfully described the E.S.R. hyperfine splitting by ring protons [4], the ground state basicities [5] and the excited singlet state basicities [11, 12] of the methyl substituted benzenes by using the model reported here. (Actually, a further justification for the inductive model can be obtained from the results of LINDNER and

MÅRTENSSON. By their calculations, only 0.004 of an electron was transferred from each methyl group to the aromatic ring.)

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