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Semi-empirical Parameters in π-Electron Systems

II. Hyperconjugation

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Semi-empirical parameters for the determination of the mesomeric effect of a methyl group are evaluated in the Pariser-Parr-Pople approximation. The hetero-atom model is used for the description of the methyl group. The parameter scheme is applied in a study of the electronic structure of methylsubstituted ethylenes, benzenes, and butadienes. A refinement of the method is suggested, in which both the bonding and the anti-bonding quasi π orbital of the methyl group are used as basis orbitals.

In a previous paper (hereafter referred to as I) [1] a method for the determination of semi-empirical parameters within the framework of the zero differential overlap (ZDO) approximation was discussed. A critical examination has shown that the ZDO assumptions are essentially equivalent with a second order approximation in the overlap integral between neighbouring atoms.[2] In order to be consistent with this approximation the parameter W_μ was made dependent on the environment of the carbon atom μ. A model was proposed in which all one-center and two-center nearest neighbour integrals were determined from a set of eight parameters, yielding the one- and two-electron integrals as linear functions of the internuclear distance between neighbouring carbon atoms. The ionization potentials and singlet-singlet transitions of benzene, ethylene, and butadiene were used to evaluate the parameters. The parameter scheme thus obtained, was tested in a study of the π-electron systems of a series of pure hydrocarbons. The results were in good agreement with experiments, and indicated that an extension of the method to molecules containing hetero-atoms might be possible.

This paper deals with an attempt to apply the methods discussed in I to evaluate semi-empirical parameters for the methyl group and its interaction with the π electrons of unsaturated hydrocarbons.

Essentially three ways of treating hyperconjugation with semi-empirical methods have been proposed. Mulliken *et al.*[3] suggested a model, in which the methyl group was treated like a modified vinyl group, in which the carbon atom contributed a normal π orbital to the system, and the hydrogens a quasi π orbital formed as a linear combination of hydrogen 1s orbitals of proper symmetry. Since the overlap integral between the carbon π orbital and the 1s orbitals is large, this model cannot be applied within the framework of the ZDO approximation. Wheland and Pauling[4] proposed a model, which only considered the inductive effect and did not take into account the conjugation between the methyl group and the π-electron network. In the formalism adopted here, this model corresponds to an increased value of W_μ for the carbon atom, to which the methyl group is attached, while the resonance integral is put equal to zero. This model cannot explain all the effects of methylation. It would, as an example, predict equal π-electron spectra for benzene and hexamethylbenzene.

The model applied in this study is the hetero-atom model proposed by Matsen.[5] The two electrons from each of the methyl groups, which interact with the π-electron system, are supposed to be situated in a molecular orbital of the following type

$$\chi = a_1 \pi_C + a_2(2h_1 - h_2 - h_3) \tag{1}$$

where π_C is the π orbital of the methyl carbon, and h_1, h_2, and h_3 are hydrogen 1s orbitals. The orbital χ is added to the basis system. Polarization effects are not included, but the coefficients a_1 and a_2 are supposed to be independent of the type of substitution. It is thus possible to determine semi-empirical parameters for the orbital χ, and its interaction with the carbon atom, to which the methyl group is attached. The ionization potentials and singlet-singlet transitions of the methylsubstituted ethylenes have been used for this purpose. The parameter scheme, thus obtained, has been tested in a study of methyl-substituted benzenes and butadienes, for which rather accurate experimental data are available. The results for the electronic spectra of the benzenes indicate, that a refinement of the theory, in which the anti-bonding orbital χ^* is allowed to interact with the excited π orbitals, might be possible.

SEMI-EMPIRICAL PARAMETERS

The general scheme for the evaluation of semi-empirical parameters was treated in I. In this section the additional parameters necessary for the treatment of the methyl group will be discussed. Some minor changes of the numerical values for the parameters reported in I occur, since a different method has been used for the calculation of Coulomb integrals between non-neighbouring atoms.

According to eqn. (6a) in I the parameter W_μ for an $sp^2\pi$-hydridized carbon atom is made dependent on the type of nearest neighbours to atom μ, by the introduction of a new parameter ΔW_μ. This equation may, when more than one type of neighbouring atoms are considered, be rewritten in the following more general form

$$W_\mu = W_0 + \sum_{\nu=1}^{3} \Delta W_\mu(Q_\nu) \tag{2}$$

where W_0, as before, is the IP of the methyl radical and $\Delta W_\mu(Q_\nu)$ is the change in W_μ, when one of the hydrogens is replaced by another type of neighbour. The atoms Q_ν can, in the case treated in this paper, be of three types, a hydrogen atom (in which case ΔW_μ is zero), a $sp^2\pi$-hybridized carbon atom, or the methyl group treated as a hetero atom. The second case was treated in I, where $\Delta W_\mu(C_\nu)$ was taken as a linear function of the internuclear distance between the carbon atoms μ and ν. The parameter $\Delta W_\mu(CH_3)$ introduced here will, however, be supposed to have the same value for all types of methyl substitution considered. This parameter is a measure of the inductive effect of the methyl group.

The core diagonal matrix element α_χ for the methyl orbital χ may be rewritten in the following way

$$\alpha_\chi = W_\chi - \nu_{\chi\chi} - \sum_\nu \gamma_{\chi\nu} - \sum_{\chi' \neq \chi} 2\ \gamma_{\chi\chi'} \tag{3}$$

this introducing a new parameter W_χ for the orbital χ. The indices ν and χ' refer to carbon π orbitals and orbitals of type (1) from the other methyl groups, respectively. The parameter W_χ should be of the same order of magnitude as minus the first ionization potential for methane, 12.99 eV.[6] Minor deviations from this value may occur, due to polarization effects and differences in the penetration part of α_χ.

The pseudo one-center two-electron integral $\gamma_{\chi\chi}$ for the orbital χ is hard to estimate. A determination of this parameter requires knowledge of the detailed structure of χ. Such an investigation has been made by Fischer-Hjalmars,[7] who has suggested the value 10.01 eV, which has been used in this work. It should be emphasized that the results are unsensitive to minor changes in this parameter.

The Coulomb intergrals $\gamma_{\chi\nu}$ between the orbital χ and the π orbital of the carbon atoms ν have, as in I, been divided into two groups. The integral $\gamma_{\chi\mu}$, where μ is the carbon atom to which the methyl group is attached, is left as an empirical parameter. A simple interpolation formula was used in I for the calculation of Coulomb integrals between non-neighbouring atoms. This technique gave results in good agreement with other methods for carbon-carbon interactions. It has been found, however, that this method is rather unsensitive to differences in the orbital exponents, as compared to other methods.[20] A different approach, the hard sphere approximation suggested by Parr,[8] has therefore been applied in this work. A recalculation of the parameters reported in I has been made with the use of this method. The new parameters are presented in Table 1. A comparison between the values given here and those

Table 1. Semi-empirical parameters for unsaturated hydrocarbons, with the hard sphere approximation.

$\gamma_{\mu\mu} = 11.97$ eV	$\beta_0 = -2.42$ eV	$W_0 = -9.84$ eV
$\gamma_0 = 6.91$ eV	$\delta_\beta = 3.05$ eV/Å	$\Delta W_0 = 0.07$ eV
$\delta_\gamma = -3.99$ eV/Å		$\delta = 9.22$ eV/Å

of Table 1 in I shows, that the different method for the evaluation of non-neighbour Coulomb integrals will have only a minor effect on the parameters for unsaturated hydrocarbons.

In order to obtain the integrals $\gamma_{\chi\nu}$, and $\gamma_{\chi\chi'}$ the orbital χ was replaced by two tangent spheres with the tangent point in the plane of the carbon skeleton, on the middle of the normal from the plane of the hydrogens to the carbon atom of the methyl group. The diameter of the spheres was chosen to be 1.76 Å, calculated from the one-center integral $\gamma_{\chi\chi}$. The corresponding diameter for a carbon π orbital is 1.47 Å.

Thus four empirical parameters are introduced for the description of the mesomeric effect of the methyl group, namely, $\Delta W_{\mu}(CH_3)$, W_{χ}, $\gamma_{\chi\mu}$ and the resonance integral $\beta_{\chi\mu}$. These parameters have been estimated in a calculation of ionization potentials (IP) and transition energies of a set of standard molecules. The methylsubstituted ethylenes have been chosen for this purpose.

METHYLSUBSTITUTED ETHYLENES

The electronic spectra of the methylsubstituted ethylenes have been reported by several authors.[9-11] The most complete data are those given by Jones and Taylor.[9] Their results have been used in this investigation. Ionization potentials measured by photoionization (PI) have been reported by Turner.[6] Corresponding electron impact (EI) data can be found in the compilation of Field and Franklin.[12] Photoionization data have been used here for the determination of the parameters, in accordance with the experimental data used in I.

The carbon skeleton of the molecules has been assumed to be planar with all angles equal to 120°. The same value, 1.337 Å, as in ethylene, has been used for the double bond distance. This is in agreement with the results, which predict almost no change of the length of the double bond for the substituted molecules. The methyl group has been treated as tetrahedral with a carbon-hydrogen distance of 1.09 Å, and a carbon-carbon distance of 1.52 Å.

The semi-empirical parameters have been determined through a least square fit to the IP values and singlet-singlet transition energies. The obtained parameters are reported in Table 2. The observed and calculated IP values and transition energies are given in Table 3. The agreement between the calculated IP values and the PI data is good except for 2-methylpropene. The difference between the PI and EI value is, however, substantially larger in this case than for the other molecules. The PI value might therefore be questioned.

Table 2. Semi-empirical parameters for the methyl group.

$\Delta W_{\mu}(CH_3) = 0.50$ eV

$W_{\chi} = -12.02$ eV

$\beta_{\chi\mu} = -1.38$ eV

$\gamma_{\chi\mu} = 5.70$ eV

$\gamma_{\chi\chi} = 10.01$ eV

Table 3. Ionization potentials and transition energies for the methylsubstituted ethylenes.

	IP eV			ν cm^{-1}	
	calc.	obs.[a]	obs.[b]	calc.	obs.[c]
Propene	9.79	9.73	9.80	58460	58100
trans-2-Butene	9.17	9.13	9.29	56620	56200
cis-2-Butene	9.17	9.24	9.32	56620	57500
2-Methylpropene	9.28	8.95	9.35	57350	53100
2-Methyl-2-butene	8.69	8.80	8.80	55780	56300
2,3-Dimethyl-2-butene	8.21	8.30	—	54990	53500

[a] Photoionization data, Ref. 6.
[b] Electron impact data, Ref. 12.
[c] Ref. 9.

Table 4. Ionization potentials for methylsubstituted benzenes and butadienes.

	calc.	obs.[a]	obs.[b]	obs.[c]
Benzene	9.25	9.25		9.60
Toluene	8.84	8.84	8.81	9.23
	9.19	9.15		
	11.80	11.17		
o-Xylene	8.60	8.56	8.56	8.88
	8.97	(9.01)		
	11.56	10.89		
m-Xylene	8.64	8.55	8.59	8.88
	8.94	(9.0)		
	11.42	10.90		
p-Xylene	8.47	8.44	8.44	8.78
	9.13	(9.4)		
	11.38	10.89		
1,2,3-Trimethylbenzene	8.53			8.67
1,2,4-Trimethylbenzene	8.30			8.55
1,3,5-Trimethylbenzene	8.58		8.41	8.64
1,2,3,4-Tetramethylbenzene	8.22			
1,2,3,5-Tetramethylbenzene	8.20			8.47
1,2,4,5-Tetramethylbenzene	8.06		8.05	8.50
Pentamethylbenzene	8.02		7.92	8.30
Hexamethylbenzene	7.97		7.85	
1-*cis*-3-Pentadiene	8.60	8.68		
1-*trans*-3-Pentadiene	8.59	8.68		
2-Methyl-1,3-butadiene	8.85	8.86		
2,3-Dimethyl-1,3-butadiene	8.72	8.72		

[a] Ref. 6; [b] Ref. 15; [c] Ref. 16.

The transition energies are also in good agreement with experiment, except for 2-methylpropene. The large shift of the $\pi \rightarrow \pi^*$ transition for this molecule, as compared to ethylene, reported by Jones and Taylor, is in accordance with the value given by Gary and Pickett.[13] It is also in agreement with the spectra of other 1,1′-dialkylethylenes.[9] Carr and Stücklen,[10] however, found the absorption maximum of this transition in the region 56 000—57 000 cm^{-1}. There is no reliable choice of the semi-empirical parameters, which gives such a large difference between the transition energies of 2-methylpropene and the 2-butenes, as has been reported by Jones and Taylor.

Recently Denis and Pullman [14] evaluated semi-empirical parameters for hyperconjugation, using the two atom model of Mulliken *et al.*[3] Even if the two methods are not directly comparable, it is of interest to notice that the parameters obtained in their work are very similar to those obtained here. Thus the inductive effect is in both cases 0.5 eV. The two-electron integrals and resonance integrals are also very similar even if a direct comparison is impossible.

METHYLSUBSTITUTED BENZENES AND BUTADIENES

The parameter set reported in the preceding section has been applied in a study of the electronic structure of a series of methyl-substituted benzenes and butadienes. In these calculations the carbon skeleton was assumed to be planar, with the same bond distances and angles as for the unsubstituted molecules. The carbon-carbon distance to the methyl group was for all cases assumed to be 1.52 Å.

Table 4 gives the calculated and observed ionization potentials. The experimental values have been taken from three sources. The values in column two are photoelectron spectroscopy data reported by Turner.[6] With this technique it is also possible to obtain higher ionization potentials. For toluene and the xylenes three IP values are reported. The photoionization data reported by Viselov [15] are given in the third column. The values in column four are the electron impact data reported by Meyer and Harrison.[16] Their values are considerably higher than those reported by others. Thus they obtained 9.60 eV for the first IP of benzene, to be compared with the value 9.25 eV reported by Turner, which was used in I. To be able to compare the observed shifts in the IP values due to methylation with the calculated shifts, the values given by Meyer and Harrison might be reduced with 0.35 eV, which is the difference between the EI and PI values for benzene.

Calculated and observed transition energies for the four lowest singlet-singlet transitions in the methylbenzenes are given in Table 5. The observed band maxima for the ^1B and ^1L_a systems are from the spectra published by Jones and Taylor.[9] These spectra have, however, been taken in heptane solution. A comparison between the vapour and solution spectra of benzene, published by the same authors, shows that the solvent red shift is around 1600 cm^{-1} for ^1B, and 1700 cm^{-1} for ^1L_a. The band maxima for the methylbenzenes, reported by Jones and Taylor, have been shifted towards the blue the same amount, in order to obtain transition energies corresponding to the vapour phase.

A comprehensive table of observed spectral shifts of the ^1L_b system for substituted benzenes has been published by Petruska.[17] The transition energies given in Table 5 for this band system have been obtained from the table of Petruska, using 39 500 cm^{-1} as the energy of the corresponding band maximum in benzene (*cf.* Table 2 in I).

Table 5. Transition energies for singlet-singlet transitions in methylsubstituted benzenes. All values in cm^{-1}.

	^1B		^1L_a		^1L_b	
	calc.	obs.[a]	calc.	obs.[a]	calc.	obs.[b]
Toluene	55 850 55 650	54 500	49 950	50 000	38 840	38 900
» (with χ^*)	55 650 55 490		49 680		38 760	
o-Xylene	55 270 55 260	53 700	49 280	49 600	38 580	38 700
» (with χ^*)	54 980 54 820		48 800		38 400	
m-Xylene	55 310 55 270	53 100	49 510	48 600	38 660	38 400
» (with χ^*)	55 030 54 780		49 020		38 450	
p-Xylene	56 000 55 370	53 300	49 450	48 600	38 280	38 100
» (with χ^*)	55 450 55 140		48 830		38 220	
1,2,3-Trimethylbenzene	54 740 54 650	52 900	48 800	48 200	38 480	38 200
1,2,4-Trimethylbenzene	55 320 54 940	52 600	48 960	48 100	38 180	37 900
1,3,5-Trimethylbenzene	54 860	52 000	49 210	47 800	38 640	38 000
1,2,3,4-Tetramethylbenzene	54 580 54 330	—	48 430	—	38 150	37 800
1,2,3,5-Tetramethylbenzene	54 660 54 510	51 700	48 610	47 800	38 220	37 700
1,2,4,5-Tetramethylbenzene	55 050 54 790	52 200	48 550	47 600	37 850	37 600
Pentamethylbenzene	54 270 54 210	—	48 170	—	37 960	37 500
Hexamethylbenzene	53 900	—	47 840	—	37 850	—

[a] Ref. 9. (corrected to vapour phase, see text); [b] Ref. 17.

The agreement between calculated and observed transition energies is satisfactory for the ^1L_b and ^1L_a bands. The spectral shift of the ^1B band is, however, less well reproduced. The calculated frequencies are, in almost all cases, higher than the observed, the difference being larger the larger the frequency is. Thus the mean deviation from experiment for ^1L_b is 300 cm^{-1}, while the corresponding values for ^1L_a and ^1B is 700 cm^{-1} and 2200 cm^{-1}, respectively. A possible explanation of this might be a too small delocalization of the virtual π orbitals onto the methyl groups, obtained with the present

Table 6. Transition energies for singlet-singlet transitions in methylsubstituted butadienes. All values in cm^{-1}.

	calc.	obs.[a]	calc.	obs.[a]
1-*cis*-3-Pentadiene	46 150	47 500	56 730	55 900
1-*trans*-3-Pentadiene	46 310	46 600	56 920	55 500
2-Methyl-1,3-butadiene	46 590	46 400	55 800	55 200
2,3-Dimethyl-1,3-butadiene	47 110	45 500	53 210	54 900

[a] Ref. 9.

method. As an example, the charge delocalized onto the methyl group in toluene, from the six ring orbitals, taken in increasing order of energy, is: 0.394, 0.000, 0.064, 0.000, 0.008, and 0.003 fractions of an electron. Thus the effect of hyperconjugation on the virtual orbitals is negligibly small. The delocalization of these orbitals can, however, be increased, if they are allowed to interact with the anti-bonding methyl orbital χ^*. The effect of incorporating this orbital has been tested in a calculation on toluene and the xylenes. The same two electron and resonance integrals were used for χ^* as for χ in this calculation. The value of W_{χ^*} was estimated to be -0.2 eV, by means of the second transition in methane at 11.8 eV,[18] which is probably a transition of the type $\chi \rightarrow \chi^*$.[19] The incorporation of χ^* into the basis will, as expected, increase the delocalization of the virtual π orbitals. The charge delocalization is thus for toluene changed to: 0.394, 0.000, 0.066, 0.000, 0.020, and 0.017. The calculated transition energies are given in Table 5. The agreement with experiment is now very good for ^1L_a and ^1L_b. The frequencies of the ^1B band is, however, still 1000—2000 cm^{-1} too high. The large shift of this band system is impossible to reproduce with the present method. Consider, as an example, the transition at 55 490 cm^{-1} in toluene. This transition is due to an excitation of an electron from an orbital, which, for symmetry reasons, contains no contributions from the orbital χ and χ^*, to an orbital of the same symmetry type. The effect of the methyl group on this transition is therefore only indirect, through changes in two-electron repulsion integrals. The calculated shift, as compared to benzene, is 500 cm^{-1}, while 1400 cm^{-1} is observed. There is no reliable choice of the parameters, which could abolish this discrepancy. The same conclusion can also be drawn from the results published by Denis and Pullman.[14]

The transition energies of the butadienes are reported in Table 6. The observed data have been taken from the work of Jones and Taylor.[9] The exact locations of the band maxime are difficult to determine, on account of a series of overlapping Rydberg transitions. The agreement between calculated and observed frequencies is, in view of this, satisfactory.

CONCLUSIONS

The extension of the parameter scheme for unsaturated hydrocarbons suggested in I to include the mesomeric effect of the methyl group yields results in good agreement with experiment in most cases. A refinement of the hetero atom model through the inclusion of the anti-bonding orbital χ^* is possible. A detailed treatment necessitates, of course, a recalculation of the parameter set for χ, and also the introduction of new empirical parameters to describe the orbital χ^*. A basis set including both the orbital χ and χ^* is not strictly consistent in the ZDO formalism. This formal inconsistency is, however, not serious for this case, since χ and χ^* are almost orthogonal. The matrix element of the Fock operator between χ and χ^* is also approximately zero, if the orbitals are assumed to be SCF-molecular orbitals for the methyl group. This approach is therefore justified within the ZDO approximation, in contrary to the two atom model. It should, however, be emphasized that the effect of the orbital χ^* is only small. The refinement obtained in this way is therefore in most cases negligible for the semi-quantitative results pursued in semi-empirical calculations.

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