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Semi-Empirical Calculations on Methyl Substituted Aromatics

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The C–H and C–C types of hyperconjugation model calculated by the PPP VE SCF ASMO CI method are presented for toluene, *t*-butylbenzene, anilinium ion, and N-trimethyl anilinium ion. In addition a calculation was made for the anilinium ion, treating it as a perturbed toluene molecule and deriving the perturbation from potentials calculated from single center wavefunctions for CH_4 and NH_4^+. The spectroscopic results of these calculations are in good agreement with experiment. However, it is concluded that for electrophilic reactions the experimental reactivities of the anilinium ion and the N-trimethyl anilinium ion should be explained not by the reactivity indices but rather by the external influences of the approaching electrophile.

Die C–H- und C–C-Hyperkonjugation wurde mit Hilfe der PPP VE SCF ASMO CI Methode für Toluol, *t*-Butylbenzol, das Anilinium- und N-Trimethylaniliniumion berechnet. Außerdem wurde eine Rechnung für das Aniliniumion als gestörtes Toluol durchgeführt, wobei die Störung von Potentialen hergeleitet wurde, die von Einzentrum-Wellenfunktionen für CH_4 und NH_4^+ erhalten worden waren. Die spektroskopischen Resultate dieser Berechnungen befinden sich in guter Übereinstimmung mit dem Experiment. Andererseits ergibt sich, daß für elektrophile Reaktionen die experimentellen Reaktivitäten des Anilinium- und des N-Trimethylaniliniumions nicht durch die Reaktivitätsindizes, sondern durch äußere Einflüsse des sich annähernden Agens erklärt werden sollten.

Les modèles d'hyperconjugaison de type C–H et C–C sont calculés par la méthode PPP VE SCF ASMO CI pour le toluène, le *t*-butylbenzène, l'ion anilinium et l'ion N-triméthyl anilinium. De plus, un calcul de l'ion anilinium a été effectué en le considérant comme une molécule de toluène perturbée où la perturbation est obtenue à partir de fonctions d'onde monocentriques de CH_4 et NH_4^+. Ces calculs fournissent des résultats spectraux en accord avec l'expérience. Cependant, pour les réactions électrophiles, il semble que les réactivités expérimentales de l'ion anilinium et de l'ion N-triméthyl anilinium ne doivent pas être expliquées à l'aide des indices de réactivité mais plutôt par les influences externes des réactifs électrophiles.

1. Introduction

The methyl substituted aromatic compounds and their analogues e.g. toluene, t-butylbenzene, anilinium ion, N-trimethyl anilinium ion, are important in chemistry not only in their own right but also because of their relation to the theory of hyperconjugation [1]. In this paper we will deal with calculations of the electronic structures of these compounds using the PPP SCF ASMO CI method [2, 3] in which not all the valence electrons are included.

Bishop and Craig [4] have treated the inductive effect of the NH_3^+-group in Ph-NH_3^+ as a perturbation to benzene having determined the potential form of the NH_3^+-group from the Hamiltonian of the central force problem. The application of this idea to other compounds [5–7] has opened a promising way to carry out calculations on substituted unsaturated compounds within the framework of the conventional π-electron approximation. Using this treatment, one may be able to take the standpoint that the wavefunctions of the CH_3- and the NH_3^+-group can be derived from single center wavefunctions of CH_4 and NH_4^+. If we can reasonably apply the potentials determined by these single center wavefunctions to the compounds with which we are concerned, the somewhat simple treatment described in Sect. 3 will become advantageous in comparison with other methods [8–10, 33, 34] involving all the valence electrons.

In the subsequent sections, the discussion is developed as follows:

i) An outline of the hyperconjugation model [1] for toluene and the anilinium ion is given within the framework of the VE SCF MO approximation [11] based upon the Pariser-Parr-Pople method. For the calculation of electronic spectra, all the singly excited configurations are taken into consideration. Although there have been several discussions on the relative importance of hyperconjugative and inductive effects in toluene [12], the inductive effect is not explicitly introduced in this work.

ii) Some consideration is given as to whether or not the MO's of the anilinium ion can be described by the perturbation of the potential difference between the NH_3^+-group and the CH_3-group to the MO's of toluene, using spherical single center wavefunctions for CH_4 and NH_4^+ to evaluate this potential difference. This model will be interesting as the inductive effect should be taken into account for the anilinium ion. In this sense, this could be called a joint inductive hyperconjugative model with toluene as the reference compound.

iii) Using the hyperconjugation model of i), a simplified treatment for systems such as t-butylbenzene and N-trimethyl anilinium ion is made.

2. The C–H Hyperconjugation Model

The coordinate system of the CH_3-group in toluene is chosen as shown in Fig. 1. If we designate the relevant ligand orbitals of the CH_3-group, respectively, as, a, b, and c, the following equivalent bond orbitals can be formed from the symmetry group orbitals of the three ligands and the $2s$ and $2p$ orbitals of C.

$$\begin{aligned}
\xi_\sigma &= N_x\left\{\lambda_x(\sqrt{3}\cdot 2s - 2p_x) + \frac{1}{\sqrt{3(1+S)}}(a+b+c)\right\} \\
&\equiv N_x\{\lambda_x(\sqrt{3}\cdot 2s - 2p_x) + \chi_1^\sigma\}, \\
\xi_{\bar\pi} &= N_y\left\{\lambda_y\cdot 2p_y + \frac{1}{\sqrt{2(1-S)}}(b-c)\right\} \\
&\equiv N_y\{\lambda_y\cdot 2p_y + \chi_1^{\bar\pi}\}, \\
\xi_\pi &= N_z\left\{\lambda_z\cdot 2p_z + \frac{1}{\sqrt{6(1-S)}}(2a-b-c)\right\} \\
&\equiv N_z\{\lambda_z\cdot 2p_z + \chi_1^\pi\},
\end{aligned} \tag{1}$$

where N's and λ's are normalization factors and S is the overlap integral between ligand orbitals. With the numbering of the atoms as in Fig. 2, one of these bond

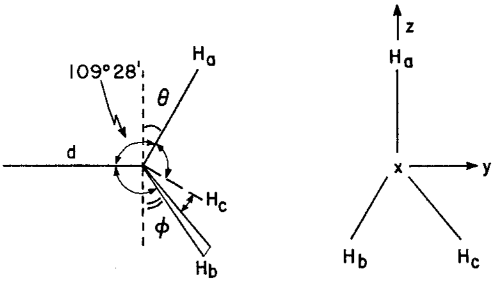

Fig. 1. The Cartesian coordinates of CH_3-group, the ring lies in the xy plane

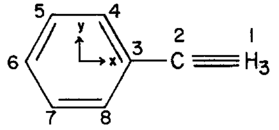

Fig. 2. The numbering and geometry of Ph–CH_3

orbitals, ξ_π may be considered to participate in the π-electron conjugated system as

$$\begin{aligned}\phi_i &= \sum_{p=3}^{8} c_{ip}\chi_p + c'_{i2}\xi_\pi \\ &= \sum_{p=3}^{8} c_{ip}\chi_p + c'_{i2}\{N_z\lambda_z \cdot 2p_z + N_z\chi_1^\pi\} \equiv \sum_{p=1}^{8} c_{ip}\chi_p \,.\end{aligned} \tag{2}$$

The MO's of toluene and the anilinium ion are therefore constructed from Eq. (2). $1s$ AO's are adopted for the ligand orbitals.

The LCAO SCF method, following Roothaan [15] gives the familiar equation:

$$\sum_q c_{iq}(F_{pq} - S_{pq}E_i) = 0\,, \tag{3a}$$

where

$$F_{pp} = \alpha_p + \tfrac{1}{2}P_{pp}(pp\,|\,pp) + \sum_{q\neq p} P_{qq}(pp\,|\,qq)\,, \tag{3b}$$

$$F_{pq} = \beta_{pq} - \tfrac{1}{2}P_{pq}(pp\,|\,qq)\,, \tag{3c}$$

$$P_{pq} = 2\sum_i C_{ip}C_{iq}\,. \tag{3d}$$

This requires the evaluation of one center and two center Coulomb repulsion integrals $(pp\,|\,pp)$ and $(pp\,|\,qq)$ $(p, q \neq 1)$ with respect to real $2p\pi$ AO's and the method we use is given in the appendix and follows the work of Pariser and Parr [2] and Mataga and Nishimoto [16]. In these calculations the ionization potential and electron affinity of carbon and nitrogen are determined by the Z-dependent formula of Matsuoka and I'Haya [17].

For the ligand orbitals, (which will be referred to as the pseudo hydrogen atom orbitals) these integrals $(p, q = 1$ or $q \neq 1, p = 1)$ are reduced by using the Mulliken approximation [18]

$$(11\,|\,11) = \tfrac{1}{2}(aa\,|\,aa) + \tfrac{1}{2}(aa\,|\,bb)\,, \tag{4}$$

$$(11\,|\,pp) = \tfrac{1}{6}\{4(aa\,|\,pp) + (bb\,|\,pp) + (cc\,|\,pp)\} \tag{5}$$

where

$$(aa|bb) = (1s_a 1s_a | 1s_b 1s_b) \tag{6}$$

$$(aa|pp) = \cos^2\theta (1s_a 1s_a | 2p_{\sigma p} 2p_{\sigma p}) + \sin^2\theta (1s_a 1s_a | 2p_{\pi p} 2p_{\pi p}), \tag{7a}$$

and

$$(bb|pp) = \cos^2\phi (1s_b 1s_b | 2p_{\sigma p} 2p_{\sigma p}) + \sin^2\phi (1s_b 1s_b | 2p_{\pi p} 2p_{\pi p}). \tag{7b}$$

For the non-nearest neighbours of the CH_3-group, the following approximation is made:

$$(aa|pp) \doteqdot (1s_a 1s_a | 2p_{\pi p} 2p_{\pi p}), \tag{7c}$$

and

$$(bb|pp) \doteqdot (1s_b 1s_b | 2p_{\pi p} 2p_{\pi p}). \tag{7d}$$

The θ and ϕ are, respectively, the angle between the bond a and the z-axis, and the angle between bond b and the z-axis (see Fig. 1).

The integrals of Eq. (4) are calculated analytically. Therefore, the ionization potential of the pseudo hydrogen atom is Z-dependent in our work. It was necessary to do this in order to obtain the correct ortho-para charge distribution.

The integrals of Eq. (7) are estimated, following Pariser and Parr, at an atomic separation smaller than 2.8 Å by using the quadratic extrapolation equation given in the appendix. When the one center repulsion integral over $1s$ AO is calculated analytically, this approximation will become better than the Mataga-Nishimoto scheme, in which the curve of $(1s1s|2p2p)$ improperly increases at small atomic separations. At an atomic separation greater than 2.8 Å, the integrals of Eq. (7) are calculated analytically.

Using the Goeppert-Mayer-Sklar potential [19] the core Coulomb integrals α_p for the real $2p\pi$ AO's ($p \neq 1$) are written as,

$$\begin{aligned} \alpha_p = &- I_p - (n_p - 1)(pp|pp) - \sum_{q \neq p} n_q (pp|qq) \\ &- \sum_{q \neq p} (U_q^0 : pp) + (U_{H_3}^+ | pp), \end{aligned} \tag{8}$$

where I_p is the ionization potential of atom p and n_p is the number of π electrons contributed to the system. On the other hand, the Coulomb integral for the pseudo π type group orbital χ_1^π is given by

$$\begin{aligned} \alpha_{\chi_1}^\pi &= \langle \chi_1^\pi(1) | T(1) + U_{H_3}^+ + \sum_{p \neq 1} U_p^{+n} p(1) | \chi_1^\pi(1) \rangle \\ &= \langle \chi_1^\pi(1) | T(1) + U_{H_3}^+(1) | \chi_1^\pi(1) \rangle \\ &\qquad - \sum_{p \neq 1} n_p (pp | \chi_1^\pi \chi_1^\pi) - \sum_{p \neq 1} (U_p^0 : \chi_1^\pi \chi_1^\pi). \end{aligned} \tag{9}$$

Where the subscript 1 is used to designate the group orbitals constructed from the hydrogen AO's. The penetration integrals in Eqs. (8) and (9)

$$(U_q^0 : pp) = - \int \chi_p(1)\, U_q^0(1)\, \chi_p(1)\, dv_1 \tag{10}$$

will be neglected throughout these calculations. In Eq. (9), the following operator employed by Morita [20, 21] and Inuzuka [22] is used

$$\begin{aligned} T(1)+U_{\mathrm{H}_3}^{+}(1) = T(1) - \sum_{\mathrm{H}=a,b,c} 1/r_{\mathrm{H}}(1) + J(\chi_1^{\sigma}\chi_1^{\sigma})(1) \\ -\tfrac{1}{2}K(\chi_1^{\sigma}\chi_1^{\sigma})(1) + J(\chi_1^{\bar{\pi}}\chi_1^{\bar{\pi}})(1) - \tfrac{1}{2}K(\chi_1^{\bar{\pi}}\chi_1^{\bar{\pi}})(1)\,, \end{aligned} \tag{11}$$

where J's and K's are Coulomb and exchange type operators. The last term of Eq. (8) is approximated by

$$\begin{aligned} (U_{\mathrm{H}_3}^{+}|pp) &= \int \chi_p(1)\, U_{\mathrm{H}_3}^{+}(1)\, \chi_p(1)\, \mathrm{d}v_1 \\ &= -(U_{\mathrm{H}_3}^{0}:pp) - (\chi_1^{\pi}\chi_1^{\pi}|pp) \doteqdot -(\chi_1^{\pi}\chi_1^{\pi}|pp)\,. \end{aligned} \tag{12}$$

The Hatree-Fock type operator given above in Eq. (11) agrees with the result of Hanazaki and co-workers [23] which allows for random spins.

The ionization potential of the H_3 group is calculated, using the Mulliken approximation, as

$$\begin{aligned} I.P. &= \langle \chi_1^{\pi}(1)|\, T(1) + U_{\mathrm{H}_3}^{+}(1)\,|\chi_1^{\pi}(1)\rangle \\ &= \langle \chi_1^{\pi}(1)|\, T(1) - \sum_{\mathrm{H}=a,b,c} 1/r_{\mathrm{H}}(1)\,|\chi_1^{\pi}(1)\rangle \\ &\quad + J_{\chi_1^{\pi}\chi_1^{\bar{\pi}}} - \tfrac{1}{2}K_{\chi_1^{\pi}\chi_1^{\bar{\pi}}} + J_{\chi_1^{\pi}\chi_1^{\sigma}} - K_{\chi_1^{\pi}\chi_1^{\sigma}} \end{aligned} \tag{13}$$

with the assumption that

$$\{T(1) - 1/r_{\mathrm{H}}(1)\}\,|1s_{\mathrm{H}}(1)\rangle = W_{\mathrm{H}}\,|1s_{\mathrm{H}}(1)\rangle\,. \tag{14}$$

In Calculation A, W_H is taken to be the experimental ionization energy of the 1s hydrogen atom (-13.595 eV) [24]. If we perform the calculation with respect to the H_3 group completely analytically (Calculation B), W_H in Eq. (14) becomes a function of the orbital exponent ζ of the 1s AO.

For the resonance integral between the real $2p\pi$ AO's, the formula of Wolfsberg-Helmholz [25] is adopted,

$$\beta_{pq} = -\frac{K}{2}\, S_{pq}(I_p + I_q)\,, \tag{15}$$

where S_{pq} is the overlap integral between AO's p and q and K is taken to be 0.875 which is close to the value used by I'Haya [17].

The resonance integral $\beta(\mathrm{C}, \mathrm{H}_3)$ between the pseudo hydrogen atom and the carbon atom in the methyl (or ammonio) group is estimated by the approximation:

$$\beta(\mathrm{C}, \mathrm{H}_3)/\beta(\mathrm{C}, \mathrm{CH}_3) \doteqdot S(\mathrm{C}, \mathrm{H}_3)/S(\mathrm{C}, \mathrm{CH}_3)\,, \tag{16}$$

where $\beta(\mathrm{C}, \mathrm{CH}_3)$ is calculated from Eq. (15) and the overlap integral $S(\mathrm{C}, \mathrm{H}_3)$ is given as

$$S(\mathrm{C}, \mathrm{H}_3) = 2/\sqrt{6(1 - S_{\mathrm{HH}})} \cdot (\cos\theta + \cos\phi)\,(1s_{\mathrm{H}}|2p_{\mathrm{C}\sigma})\,. \tag{17}$$

In evaluating the repulsion integrals we need to know the effective nuclear charge. For the first row atoms, following Brown and Heffernan [11], the effective nuclear charge is written as

$$Z_p = N_p - 1.35 - 0.35\,(\sigma_p + P_{pp})\,, \tag{18}$$

where N_p is the atomic number of an atom p and σ_p is the number of σ-valence electrons on atom p and P_{pp} is the charge density. The effective nuclear charge of the 1*s* AO of hydrogen is given by Slater'srule [26, 27]

$$Z_{1s} = 1 - 0.3\,(K-1)\,, \tag{19}$$

where K is the number of electrons in the K shell. When the pseudo hydrogen atom participates in the conjugated system it contributes one electron. As a result of conjugation it is assumed that the charge distribution P_{11} at the pseudo hydrogen atom will make the effective nuclear charge of the 1*s* AO's obey the following equation

$$Z_{1s} = 1 - 0.3\,(P_{11}-1)\,. \tag{20}$$

Thus, the whole calculation is dependent on the π-electron charge densities.

3. Perturbation Treatment of the Hyperconjugation Model

The Hamiltonian of the anilinium ion may be approximately described by that of toluene plus the potential difference between an ammonium group and a methane group i.e.

$$\begin{aligned}\mathscr{H}(\mathrm{Ph}-\mathrm{N}^+ \equiv \mathrm{H}_3, R') = \mathscr{H}(\mathrm{Ph}-\mathrm{C} \equiv \mathrm{H}_3, R) + \sum_{i\neq 2}^{8} \frac{1}{\varepsilon}\,[V_{\mathrm{NH}_4^+}(\boldsymbol{R}_i' - \boldsymbol{R}_{\mathrm{NH}_3^+}') \\ - V_{\mathrm{CH}_4}(\boldsymbol{R}_i - \boldsymbol{R}_{\mathrm{CH}_3})]\,,\end{aligned} \tag{21}$$

where it may be reasonable to assume that the potential is influenced by the dielectric constant ($\varepsilon = 2.39$ (28)) of the molecular skeleton of toluene. Other values of ε will also be tested in the calculations. R represents the molecular coordinates for toluene, and R' for the anilinium ion.

The potentials of methane and the ammonium ion felt by a π-electron at a distance R_{A} from the centers of the molecules are in the spherical approximation, respectively represented as

$$\begin{aligned}V_{\mathrm{CH}_4}(R_{\mathrm{A}}) &= -6/R_{\mathrm{A}} - \sum_{\mathrm{H}}^{4} 1/R_{\mathrm{HA}} + \int \Psi_{\mathrm{CH}_4}^{*}\left(\sum_{i=1}^{10} 1/R_{i\mathrm{A}}\right)\Psi_{\mathrm{CH}_4}\,\mathrm{d}\tau \\ &\doteqdot -6/R_{\mathrm{A}} - 4/R_{>} + \int \varrho_{\mathrm{CH}_4}(1)\,(1/R_{\mathrm{A}}(1))\,\mathrm{d}v_1\,,\end{aligned} \tag{22}$$

and

$$V_{\mathrm{NH}_4^+}(R_{\mathrm{A}}) \doteqdot -7/R_{\mathrm{A}} - 4/R_{>} + \int \varrho_{\mathrm{NH}_4^+}(1)\,(1/R_{\mathrm{A}}(1))\,\mathrm{d}v_1\,, \tag{23}$$

where Ψ is the spherical single center wavefunction calculated by Bishop [29, 30]:

$$\Psi = |s(1)\,s(2)\,s^*(3)\,s^*(4)\,p_x(5)\,p_x(6)\,p_y(7)\,p_y(8)\,p_z(9)\,p_z(10)|\,. \tag{24}$$

The s, s^* and p are the 1*s*, orthogonalized 2*s* and 2*p* type STO's with noninteger principal quantum numbers. The parameters of these wavefunctions required in our calculations correspond, to $R_{\mathrm{C-H}}$ equal to 2.05 a.u. (1.08 Å) for methane, and to $R_{\mathrm{N-H}}$ equal to 1.95 a.u. (1.02 Å) for ammonium ion. The charge distribution of these molecules is calculated to be

$$\varrho = 2[ss + s^*s^* + p_x p_x + p_y p_y + p_z p_z]\,. \tag{25}$$

In Eqs. (22) and (23), $R_{>}$ means the greater of R_{H} and R_{A}. The potential of NH_4^+ at the points required in our calculation, (Fig. 3) agrees well with the potential

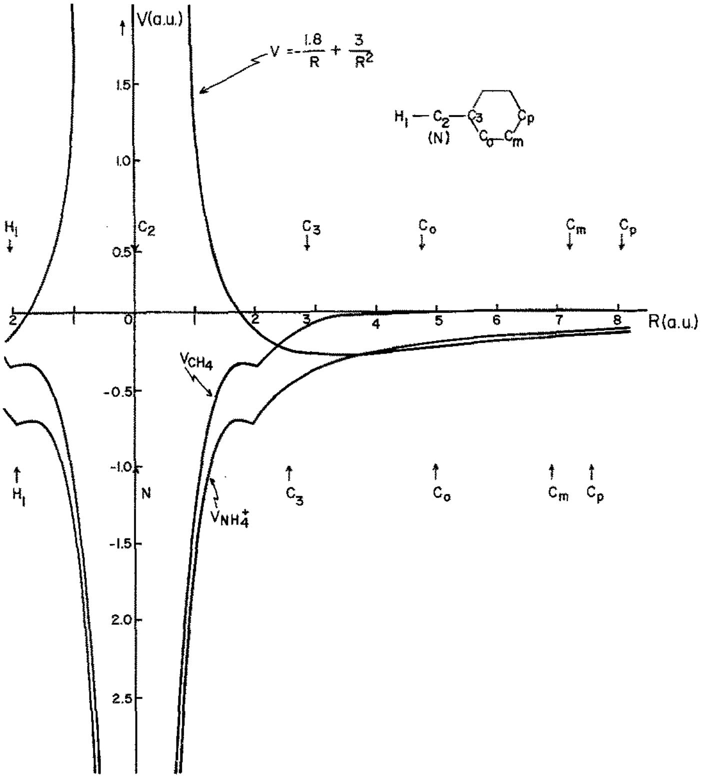

Fig. 3. The potential curves of methane and the ammonium ion compared with the potential curve for the NH_3^+ ion published by Bishop and Craig. The arrows indicated above the abscissa show the position of the atoms in toluene and those below the abscissa the position of the atoms in the anilinium ion

curve determined by Bishop and Craig [4]. In the present treatment it is important to note the perturbation potential is allowed to also influence the pseudo π-electron.

By the introduction of the potential difference:

$$V(R_i', R_i) = \frac{1}{\varepsilon}\left[V_{NH_4^+}(R_i' - R'_{NH_3^+}) - V_{CH_4}(R_i - R_{CH_3})\right], \tag{26}$$

the Hamiltonian for $Ph{-}NH_3^+$ becomes

$$\mathcal{H}' = \sum_{i=1} H_{core}(i) + \sum_{i>j} 1/r_{ij} + \sum_{i \neq 2} V(R_i', R_i). \tag{27}$$

For simplicity, the matrix elements are calculated approximately as

$$\alpha_p' = \langle \chi_p(i) | H_{core}(i) + V(R_i', R_i) | \chi_p(i) \rangle \doteqdot \alpha_p + V(R_p', R_p), \tag{28}$$

except for $p = 2$, where $\alpha_2' = \alpha_2$,

$$\beta_{pq}' \doteqdot \beta_{pq}, \tag{29}$$

where again primes indicate the anilinium ion and non-primed terms indicate, toluene. Two calculations (A and B) are carried out and are analogous to A and B of Sect. 2.

4. The C–C Type Hyperconjugation Model

To contrast with the C–H type hyperconjugation, it is interesting to perform a trial calculation on the C–C type (or N–C) type hyper-conjugation in t-butylbenzene (and N-trimethyl anilinium ion). To date there has been nothing published on this type of hyperconjugation. Let us designate the relevant linear combinations of ligand orbitals as $\chi_{\mathrm{Me}}^{\sigma}$, χ_{Me}^{π}, $\chi_{\mathrm{Me}}^{\bar{\pi}}$ and adopt for the ligand orbitals the tetrahedral hybrid orbitals T_i $(i=a, b, c)$:

$$T_i = \frac{1}{2}(s^* + \sqrt{3}p_{x_i}), \tag{30}$$

$$\begin{aligned} \chi_{\mathrm{Me}}^{\sigma} &= \frac{1}{\sqrt{3}}(T_a + T_b + T_c), \\ \chi_{\mathrm{Me}}^{\pi} &= \frac{1}{\sqrt{2}}(T_b - T_c), \\ \chi_{\mathrm{Me}}^{\bar{\pi}} &= \frac{1}{\sqrt{6}}(2T_a - T_b - T_c). \end{aligned} \tag{31}$$

The hybrid orbitals T_i directed to the carbon atom will be considered to take part in the conjugation of the π-electrons as in the model of Section 2. The core potential of the tri-methyl group is written as

$$\begin{aligned} U_{(\mathrm{CH}_3)_3}^{+}(1) = &- \sum_{i=a,b,c} U_{\mathrm{Me}_i}^{+}(1) + J(\chi_{\mathrm{Me}}^{\bar{\pi}}\chi_{\mathrm{Me}}^{\bar{\pi}})(1) - \tfrac{1}{2}K(\chi_{\mathrm{Me}}^{\bar{\pi}}\chi_{\mathrm{Me}}^{\bar{\pi}})(1) \\ &+ J(\chi_{\mathrm{Me}}^{\sigma}\chi_{\mathrm{Me}}^{\sigma})(1) - \tfrac{1}{2}K(\chi_{\mathrm{Me}}^{\sigma}\chi_{\mathrm{Me}}^{\sigma})(1). \end{aligned} \tag{32}$$

If we consider a model for the methyl group in which all eight electrons except for the ligand electron will screen the force field of the nuclei of the carbon and hydrogens, we can write

$$U_{\mathrm{Me}_i}^{+}(1) = -1/r_i(1), \tag{33}$$

and use the approximation:

$$\{T(1) + U_{\mathrm{Me}}^{+}(1)\}\,|\chi_{\mathrm{Me}}^{\pi}\rangle = W_{\mathrm{CH}_4}^{\mathrm{exptl}}\,|\chi_{\mathrm{Me}}^{\pi}\rangle. \tag{34}$$

In calculation A we take the ionization potential of methane as the experimental value, 12.99 eV [31] and in Calculation B we calculate it analytically as a function of Z_{1s}^{Me} (see below). Thus, the scheme of calculation will become the same as in Sect. 2 except for the increase in the number of complicated integrals. In order to circumvent this difficulty, we will make the approximation in which the integer 1*s* AO is used instead of the tetrahedral hybrid, choosing an orbital exponent of the 1*s* AO to correlate with the charge distribution of the s^*p^3 hybrid. The best correlated value of the orbital exponent is determined to be 0.76 ± 0.01. Using this value, the orbital exponent of the methyl group is then allowed to vary by letting the charge density on the $(\mathrm{CH}_3)_3$-group obey the following relation

$$Z_{1s}^{\mathrm{Me}} = 0.76 - 0.3\,(P_{11} - 1). \tag{35}$$

As a result of this approximation, it may be recognized that the methyl group has actually been treated by regarding it as an electron of 1*s* type moving in the central non-Coulomb field of the nuclei shielded by the other electrons.

The bond angles used are taken to be: $\sphericalangle \text{CCC} = 120°$, $\cos^2\theta = 0.88895$, $\sin^2\theta = 0.11105$, $\cos^2\phi = 0.22216$, and $\sin^2\phi = 0.77784$. The bond distances in toluene [32] are $R_{\text{C-C}} = 1.392$ Å, $R_{\text{C-CH}_3} = 1.520$ Å and $R_{\text{C-H}} = 1.08$ Å. In t-butylbenzene, the geometry of toluene is adopted except that $R_{\text{C-CH}_3} = 1.540$ Å is used instead of $R_{\text{C-H}}$. The bond distances in the anilinium ion are [32]: $R_{\text{C-C}} = 1.395$ Å, $R_{\text{C-N}} = 1.350$ Å, and $R_{\text{N-H}} = 1.02$ Å. The bond distance $R_{\text{N-CH}_3}$ in N-trimethyl anilinium ion is assumed to be 1.465 Å instead of $R_{\text{N-H}}$, with the rest of the geometry the same as the anilinium ion.

5. Results and Discussion

The results of Calculations 2-A and 2-B summarized in Tables 1 and 2 are in good agreement with experiment. For toluene, the values of the π dipole moment and the intensity ratio given by Calculation B are better than those given by Calculation A but the value for the $^1A'$ transition energy is worse. But overall there is only a slight difference between the spectroscopic data obtained by 2-A and 2-B for both toluene and the anilinium ion. We therefore note that the transition energies and the oscillator strengths do not strongly depend upon the ionization potential of the pseudo hydrogen atom used in Eq. (14).

In Tables 1 and 2 results of other calculations [33–35, 42] are included for comparison. Denis and Pullman [33] have introduced in their hyperconjugation model of toluene (based on a "scaled" PPP-SCF method) the inductive effect of the methyl group through a reduction of the effective nuclear charge of the π–AO on the substituted carbon atom. This treatment is similar to varying the parameters in the simple LCAO method. In the present work, the effective nuclear charges required are taken as variable parameters by using Eqs. (18) and (20). It may be seen that in this sense the inductive effect is implicitly introduced but that the short range inductive effect is not stressed as in the work of Denis and Pullman. After the SCF calculations in 2-A (and 2-B), we obtained the effective orbital exponents of 1*s* AO: $Z_{1s} = 1.185$ (and $= 1.253$). These values can be compared with the value of $Z_{1s} = 0.756$ which has been obtained by Denis and Pullman. As these workers also chose one of their parameters, β_{CH_3} by trial and error to reproduce as many properties of toluene as possible, their method is more empirical than ours and not strictly comparable.

Attention is drawn to the results of the modified CNDO method used by Del Bene and Jaffé [34] and the results of the non-empirical extended Hückel method by Newton and co-workers [42] in which neither the hyperconjugation nor the inductive effect is explicitly considered. It is worthwhile to note that Newton and co-workers concluded that hyperconjugation is not required to account for the dipole moments of the alkylsubstituted unsaturated molecules, in the sense that this concept is invoked only in the framework of the π-electron approximation. Their conclusion however does not deny the validity of the concept of hyperconjugation. The parameters of their model (extended Hückel theory) were taken from SCF results for closely related simple molecules. Un-

Table 1. *Calculated results for toluene*

Method	Sym.	Excitation energy (eV)		f^{a}		$\mu^{\pi}(D)$
		Calc.	Obs.	Calc.	Obs.	
2-A	$^1A''$	4.945	4.75	0.028	(225)	0.252
	$^1A''$	6.967		1.103		(exptl
	$^1A'$	5.997	6.00	0.088	(7500)	0.37)
	$^1A'$	6.927		1.149		
2-B	$^1A''$	4.904	4.75	0.030	(225)	0.340
	$^1A''$	6.890		1.050		
	$^1A'$	5.863	6.00	0.171	(7500)	
	$^1A'$	6.826		1.000		
Denis and Pullman [33]	$^1A''$	4.7	4.75	0.002	(225)	
(PPP-SCF)	$^1A''$	6.5		1.03		
	$^1A'$	5.9	6.00	6.00	(7500)	
	$^1A'$	6.4		1.34		
Del Bene and Jaffé [34]	$^1A''$	4.6	4.75	0.002		(0.757)
	$^1A''$	6.8		0.567		from [42]
(Modified CNDO)	$^1A'$	5.1	6.00	0.003		
	$^1A'$	6.8		0.605		
I'Haya [35] Simple LCAO	$^1A''$	4.650	4.647	0.0016	0.0015	0.372

[a] Extinction coefficients are given in parentheses.

Table 2. *Calculated results for the anilinium ion*

Method	Sym.	Excitation energy (eV)		f		$\mu^{\pi}(D)$
		Calc.	Obs.	Calc.	Obs.	
2-A	$^1A''$	4.952	4.88	0.036	(160)	0.642
	$^1A''$	6.985		1.102		
	$^1A'$	6.007	6.11	0.055	(7500)	
	$^1A'$	6.966		1.144		
2-B	$^1A''$	4.948	4.88	0.037	(160)	0.408
	$^1A''$	6.987		1.103		
	$^1A'$	6.009	6.11	0.055	(7500)	
	$^1A'$	6.964		1.142		
3-A[a]	$^1A''$	4.929	4.88	0.070	(160)	1.949
	$^1A''$	6.916		0.990		
	$^1A'$	5.698	6.11	0.196	(7500)	
	$^1A'$	6.896		0.969		
3-B[a]	$^1A''$	4.810	4.88	0.049	(160)	0.856
	$^1A''$	6.483		0.689		
	$^1A'$	5.007	6.11	0.344	(7500)	
	$^1A'$	6.356		0.076		
Del Bene and Jaffé [34]	$^1A''$	4.6	4.88	0.005	(160)	
(Modified CNDO)	$^1A''$	6.8		0.515		
	$^1A'$	5.0	6.11	0.009	(7500)	
	$^1A'$	6.8		0.556		

[a] $\varepsilon = 2.39$.

Table 3. *The excitation energies, the oscillator strengths and dipole moments of the anilinium ion for changes of dielectric constant in calculations* 3-A *and* -B

	Sym.	3-A			3-B		
		ΔE (eV)	f	$\mu^{\pi}(D)$	ΔE (eV)	f	$\mu^{\pi}(D)$
$\varepsilon = 1.0$	$^1A''$	4.913	0.166	4.584	4.498	0.023	2.310
	$^1A''$	6.931	0.788		5.565	0.417	
	$^1A'$	5.264	0.283		3.434	0.331	
	$^1A'$	6.553	0.133		5.748	0.032	
$\varepsilon = 2.0$	$^1A''$	4.927	0.080	2.301	4.781	0.050	1.074
	$^1A''$	6.909	0.965		6.342	0.602	
	$^1A'$	6.632	0.214		4.764	0.344	
	$^1A'$	6.882	0.887		6.248	0.023	
$\varepsilon = 2.39$	$^1A''$	4.929	0.070	1.949	4.810	0.049	0.856
	$^1A''$	6.916	0.990		6.483	0.689	
	$^1A'$	5.698	0.196		5.007	0.344	
	$^1A'$	6.896	0.969		6.356	0.076	
$\varepsilon = 2.50$	$^1A''$	4.929	0.067	1.871	4.816	0.049	0.807
	$^1A''$	6.918	0.996		6.512	0.710	
	$^1A'$	5.713	0.192		5.060	0.343	
	$^1A'$	6.898	0.984		6.382	0.094	

fortunately, the only result we can compare is μ^{π} for toluene: we obtain 0.252 D (Calculation A) and 0.340 D (Calculation B) they obtain 0.757 D and the experimental value is 0.37 D. Though our values are closer to the experimental, this is not enough evidence to demonstrate unambiguously that our method is better.

The method introduced by Del Bene and Jaffé [34] is formally exactly analogous to the CNDO/2 formulation of Pople and co-workers [8, 9, 10] but with some modification to the parametrization. The integral $(\mu\mu|\mu\mu)$ is approximated as $I_{\mu} - A_{\mu}$ (as in the PPP method) and the $H_{\mu\nu}$ terms are evaluated as $H_{\mu\nu} = \frac{1}{2}K(\beta_{\mathrm{M}}^0 + \beta_{\mathrm{N}}^0)\, S_{\mu\nu}$ where β_{M}^0 are purely empirical atomic parameters and not related to Pople's values, $K = 1$ when $S_{\mu\nu}$ measures σ-type overlap and $K = 0.585$, a purely empirical value, when $S_{\mu\nu}$ measures π-type overlap. A comparison of their results with ours, shows considerable differences in particular for the excitation energy to the lowest $^1A'$ state. We have agreement, essentially, with the experimental result whereas for both toluene and the anilinium ion they are roughly 1 eV too low. We would conclude therefore that their method will have to be refined further before it can be used to predict excitation energies with certainty.

The results of Calculation 3-A and 3-B are given in Table 3. It is seen that the $^1A'$ transitions of the anilinium ion (polarized in the long axis) and their oscillator strengths are very sensitive to the variation of the dielectric constant, especially in case B. Fig. 3 indicates that this may be due to the fact that the potential felt by a π-electron in the neighbourhood of the atom in position 2 is greatly changed by making the dielectric constant larger than unity, so that the charge density on the H's is changed and hence the effective nuclear charge of the 1*s* AO is considerably changed. It is interesting to note that introduction of the inductive effect in the hyperconjugation model seems to lead to erroneous results in case B of Sect. 3, although both A and B give equally good results when the inductive effect is not involved (i.e. Calculation 2).

It should be noted that in Calculations 3-A and 3-B the potentials of the CH_3- and the NH_3^+-groups used for the perturbation are approximated by the potentials of the CH_4 and the NH_4^+. From Eq. (21), the error in the potentials due to the extra protons of the CH_4 and the NH_4^+ obviously cancels out for the $1/R_{HA}$ terms in Eqs. (22, 23), but it remains in the electron repulsion terms. The effects due to this error will decrease rapidly as distance from position 2 increases because the perturbation potential itself will decrease rapidly. A comparison of Calculations 2-A and 3-A ($\varepsilon = 2.39$) for the anilinium ion in Table 2 shows that the value of the dipole moment is larger in Calculation 3-A and that the calculated intensity ratio of the lowest lying $^1A''$ and $^1A'$ transitions comes closer to the experimental ratio for these transitions in Calculation 3-A. So far as information for the intensity ratio is concerned such a joint inductive-hyperconjugative model appears to be warranted. Though the method of Sect. 3 has been shown to work reasonably well, it is difficult to know what value to choose for ε (the dielectric constant); perhaps when μ^π has been experimentally determined, ε could be chosen so that the calculated μ^π is in agreement with it.

Table 4. *Calculated results for t-butylbenzene*

Method	Sym.	Excitation energy (eV)		f^a		$\mu^\pi(D)$
		Calc.	Obs.	Calc.	Obs.	
4-A	$^1A''$	4.916	4.82	0.002	(170)	0.501 (exptl. 0.7 *D*)
	$^1A''$	6.837		1.061		
	$^1A'$	5.874	5.97	0.176	(7800)	
	$^1A'$	6.788		1.029		
4-B	$^1A''$	4.685	4.82	0.004	(170)	2.304
	$^1A''$	6.206		0.445		
	$^1A'$	5.045	5.97	0.383	(7800)	
	$^1A'$	6.511		0.360		
I'Haya [35] Simple LCAO	$^1A''$	4.680	4.670	0.00082	0.005	0.746 (0.588) from [42]

[a] Extinction coefficients are given in parentheses.

Table 5. *Calculated results for* N-*trimethyl anilinium ion*

Method	Sym.	Excitation energy (eV)		f		$\mu^\pi(D)$
		Calc.	Obs.	Calc.	Obs.	
4-A	$^1A''$	4.949	4.9	0.004	0.0031	0.772
	$^1A''$	6.943		1.156		
	$^1A'$	6.063		0.038		
	$^1A'$	6.938		1.200		
4-B	$^1A''$	4.945	4.9	0.002	0.0031	1.351
	$^1A''$	6.942		1.163		
	$^1A'$	6.077		0.032		
	$^1A'$	6.939		1.200		

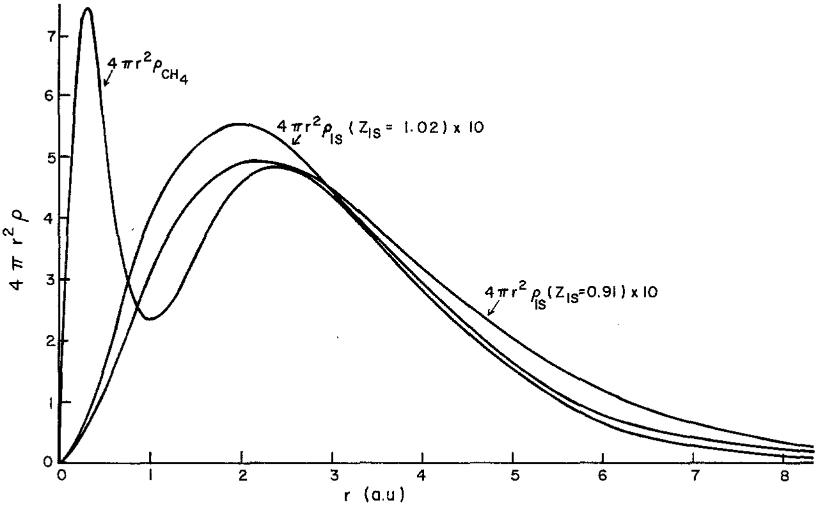

Fig. 4. Comparison of the radial charge distribution of CH_4 (calculated from Ref. [29]) with that of a 1*s* AO with orbital exponents obtained in Calculation 4 – *A*

In the treatment of Sect. 4 (see Tables 4 and 5), the results of t-butylbenzene obtained in Calculation A are in good agreement with experiment, but the results from Calculation B for the ^1A, transition energy and the dipole moment are rather poor. This is due to the greater π-electron transfer from the $(CH_3)_3$-group into the ring. In other words, the effective nuclear charge of the 1*s* AO takes a value which deviates considerably from that chosen so as to correlate with the s^*p^3 hybrid radial charge distribution discussed in Sect. 4. Agreement with experiment is best for the results of Calculation 4-A, where the radial charge distribution of the 1*s* AO with $\zeta = 0.912$ (cf. $\zeta = 1.019$ in 4-B) is well correlated with that of CH_4 whose broad peak is constituted mainly by the non-integer 2*s*, 2*p*, AO's (see Fig. 4).

It is experimentally observed that the first $^1A'$ transition of t-butylbenzene greatly reduces its intensity and shows a blue shift relative to the same transition in toluene. For the anilinium ion and the N-trimethyl anilinium ion, slight differences between the first $^1A'$ transition energies and their intensities have been reported [40]. Our results for toluene and t-butylbenzene (Calculation A and B) reproduce qualitively the experimental ratio of intensities but fail to show the blue shift. Comparison of Tables 2 and 5 does not demonstrate the experimental relation between the anilinium ion and the N-trimethyl anilinium ion. However since the value of the observed shift falls within the margin of error inherent in the π-electron theory, it may be impossible to obtain it from a calculation of this type. Besides, although the inductive effect of the methyl group may be negligible in toluene, this may not be the case for the t-butyl group because of the additional methyl groups. It may accordingly be considered that the neglect of inductive effects introduces an error comparable to that of approximating the s^*p^3 radial charge distribution by a 1*s* radial charge distribution.

This model of treating a methyl group in methyl substituted aromatics as a pseudo-atom is necessarily at this stage exploratory and we don't as yet, have

Table 6. *Comparison of Π-electron charge densities and frontier electron densities with the experimental results* [14]

Compound	Method	Π-electron density			Frontier electron density			Orientation (%)			Ratio of partial rate factors
		P_{00}	P_{mm}	P_{pp}	$f_0^{(E)a}$	$f_m^{(E)}$	$f_p^{(E)}$	O–	M–	P–	F_m/F_p
Toluene	2-A	1.001	0.939	0.979	0.552	0.454	0.000	56.5	3.5	40	2.5/58
	2-B	0.999	0.936	0.993	0.550	0.450	0.000				
t-Butylbenzene	4-A	1.022	0.958	0.978	0.140	0.152	0.592	12.0	8.5	79.5	4.0/75
	4-B	1.029	0.961	1.004	0.164	0.038	0.294				
Anilinium Ion	2-A	1.010	0.927	0.963	0.566	0.434	0.000	6	34	60	162/195
	2-B	1.011	0.925	0.968	0.566	0.434	0.000				
	3-A	1.001	0.909	0.922	0.588	0.412	0.000				
	3-B	1.002	0.904	0.944	0.084	0.090	0.362				
N-trimethyl-	4-A	1.027	0.952	0.978	0.548	0.412	0.000		100		4.2/1.0
Anilinium Ion	4-B	1.031	0.953	0.989	0.132	0.190	0.690				

[a] $f_0^{(E)}$ stands for the electrophilic frontier electron density at the ortho-position.

results of other methods (except for simple LCAO [35]) for comparison. But, the results we have presented here for t-butyl benzene and N-trimethyl anilinium ion would certainly seem to warrant further investigation particularly as the method is a good deal easier to apply than any comparable alternatives.

In Table 6, the charge distributions of these molecules are found to predict ortho and para orientation for electrophilic reagents. The frontier electron densities [36, 37] fail to describe the ortho and para orientation in toluene. Experimentally, the anilinium ion is more reactive in the meta than in the ortho position, and the N-trimethyl anilinium ion shows only meta orientation [13, 14]. The frontier electron densities indicate these trends only in Calculation 3-B and 4-B. The results of Del Bene and Jaffé [34] also fail to explain the reactivity. The failure of charge densities and frontier electron densities to predict the observed reactivities (see Table 6) should not provide the final criterion to judge the present calculation, since there is good agreement between calculated and experimental spectroscopic data. It seems that reactivities should be predicted by considering the influence of the attacking electrophile as done by Bishop and co-workers [4, 38] and Chandra and Coulson [39] rather than solely by the static influence of substituents.

Appendix

The basic integrals required in these calculations which were not mentioned in detail in the text are listed below.

1. One Center Integrals

$$(1s_a 1s_a | 1s_a 1s_a) = \int 1s_a(1)\, 1s_a(1)\, (1/r_{12})\, 1s_a(2)\, 1s_a(2)\, \mathrm{d}v_1\, \mathrm{d}v_2\,, \qquad \text{(calculated analytically)}$$

$$(pp|pp)_\pi = (2p_\pi 2p_\pi | 2p_\pi 2p_\pi) = (I.P)_p - (E.A)_p \quad \text{(Pariser and Parr)},$$

$$(pp|pp)_\sigma = (2p_\sigma 2p_\sigma | 2p_\sigma 2p_\sigma) = \tfrac{636}{501}(pp|pp)_\pi\,,$$

which can be derived from the following assumption:

$$\frac{(pp|pp)^e_\sigma}{(pp|pp)^e_\pi} = \frac{(pp|pp)^t_\sigma}{(pp|pp)^t_\pi} = \frac{F_0(2p2p) + 19F_2(2p2p)}{F_0(2p2p) + \ 4F_2(2p2p)}.$$

The superscripts e and t indicate "experimental" and analytical values, respectively and F's are the Franck-Condon parameters.

$(1s_a|\frac{1}{2}\Delta|1s_a) = \int 1s_a(1)\,(-\frac{1}{2}\Delta)\,1s_a(1)\,\mathrm{d}v_1$

(calculated either "experimentally" from Eqs. (14) and (34), or analytically).

For the integrals necessary for the calculation of the potentials in Eqs. (21) and (22) see Ref. [41].

2. Two Center Integrals

$$(1s_a 1s_a|1s_b 1s_b) \quad \text{(analytically)},$$

$$(pp|qq) = \frac{1}{r_{pq} + 2/\{(pp|pp)_\pi + (qq|qq)_\pi\}} \quad \text{(Nishimoto and Mataga)},$$

$$(1s1s|2p_\pi 2p_\pi) = l r_{pq}^2 + m r_{pq} + \tfrac{1}{2}\{(1s1s|1s1s)^t + (pp|pp)_\pi\} \quad \text{(Pariser and Parr)},$$

$$(1s1s|2p_\sigma 2p_\sigma) = l' r_{pq}^2 + m' r_{pq} + \tfrac{1}{2}\{(1s1s|1s1s)^t + (pp|pp)_\sigma\} \quad \text{(Pariser and Parr)},$$

$$S_{pq} = \int \chi_p(1)\,\chi_q(1)\,\mathrm{d}v_1 \quad \text{(analytically)},$$

$$(a|bb) = -\int 1s_b(1)\,(1/r_a(1))\,1s_b(1)\,\mathrm{d}v_1 \quad \text{(analytically)},$$

$$(a|ab) = -\int 1s_a(1)\,(1/r_a(1))\,1s_b(1)\,\mathrm{d}v_1 \quad \text{(analytically)},$$

$$(1s_b|-\tfrac{1}{2}\Delta|1s_a) \quad \text{("experimentally" or analytically)}.$$

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