Self-consistent Field Molecular Orbital Treatment of Benzenium Ion for a Simplified Model of Hyperconjugation

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Electronic spectra of a number of aromatic carbonium ions were studied theoretically by several investigators¹⁾. In their explorating work which was greatly suggestive, Muller, Pickett and Mulliken²⁾ treated the benzenium ion by the simple LCAO MO method including self-consistent technique taking into account the variations of resonance integrals with interatomic distances and of Coulomb integrals with charge distributions. These authors as well as Morita³,⁴⁾, who tried to explain spectral shifts of the protonated methyl benzenes by

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1) As to a general survey, see, T. Morita, *Progress Reports on Electronic Processes in Chemistry* (Published by the Japanese Research Group on the Electronic States), No. 1, 60 (1959) (in Japanese).

2) N. Muller, L. W. Pickett and R. S. Mulliken, *J. Chem. Phys.*, **21**, 1400 (1953); *J. Am. Chem. Soc.*, **76**, 4770 (1954).

3) T. Morita, *J. Chem. Phys.*, **25**, 1290 (1956).

4) T. Morita, This Bulletin, **31**, 322 (1958).

the methyl substituents, ignored the interelectronic interaction. In explaining electronic spectra, the self-consistent field molecular orbital (SCF MO) treatment seems to be most satisfactory. Works going along this are those of Mackor et al.[5,6] However, hyperconjugation of the H_2–C bond of protonated aromatics was shut out of their computations. When hyperconjugation of the H_2 quasi-atom is taken into account, aromatic carbonium ions have odd numbered centers and belong to the so-called "strongly hyperconjugated" system, or system of "isovalent hyperconjugation"[2,7,8]. Morita[9] also indicated that basic properties of isomeric xylenes were interpreted considerably well in terms of hyperconjugation of the H_2–C bond in their protonated compounds. Owing to reasons mentioned above, it seems to be of great significance to carry out the SCF MO calculations, taking the hyperconjugative effect into consideration. However, even in the benzenium ion, the simplest of the aromatic carbonium ions, the SCF MO calculation is rather cumbersome and simplification of the model for computation of hyperconjugation may be desired. This paper contains simplification of the model for hyperconjugation in the semiempirical SCF LCAO MO method and discussion of importance of hyperconjugation deduced from the calculated results for the hyperconjugation model compared with those for the bond localization model of the benzenium ion, a prototype of the aromatic carbonium ions.

A Model for Hyperconjugation in the Semi-empirical SCF MO Method

From the proton magnetic resonance absorption measurement of aromatic carbonium ions, MacLean, van der Waals and Mackor[10] showed that, when a bond was formed between a proton and a carbon atom in an aromatic hydrocarbon ring, valence state of the carbon atom attacked by a proton was altered from sp^2- to sp^3-hybridization. Accordingly, the configuration of the methylene group constructed at the position of proton attack should be tetrahedral. In a technique for the theory of hyperconjugation, however, it is customary, subject to Mulliken's original idea[11], to assume the sp^2-hybridized carbon atom and group orbitals of H_2, $\phi_1=2^{-1/2}(1+S)^{-1/2}(h_a+h_b)$ and $\phi_2=2^{-1/2}(1-S)^{-1/2}\times(h_a-h_b)$: ($h_a$, h_b: 1s orbital of hydrogen atoms a and b; S: overlap integral between H atoms). Of the two group orbitals ϕ_1 and ϕ_2, ϕ_1 forms σ-bond and ϕ_2 π-bond, the latter being in conjugation with the benzene ring. Aono[12], in his non-empirical SCF MO treatment of hyperconjugation in methylacetylene, replaced one of the H_3 group orbitals by the $2p\pi$ carbon orbital itself and assumed the distance between this orbital and the next carbon to be the same as the length of the C–H bond of the methyl group. We intend, however, in the following way, to treat the orbital ϕ_2 in question as the quasi-$2p\pi$ orbital and to give a reasonable value of the distance between this quasi-$2p\pi$ and the next lying carbon $2p\pi$ orbitals.

In the SCF MO calculations, the quantities associated with the ϕ_2 orbital, which embody its characteristics well, are its energy and the effective nuclear charge of H_2^+ core. The former determines the valence state ionization potential of the H_2 group and the latter contributes to the estimation of interelectronic Coulomb repulsion integrals. In consequence, the matter reduces to the estimation of these quantities. The energy of the ϕ_2 orbital is calculated from

$$W(\phi_2)=\int\phi_2{}^*H\phi_2d\tau \qquad (1)$$

using the Hartree-Fock type Hamiltonian,

$$H=T+U,\ U=-\frac{1}{r_a}-\frac{1}{r_b}+(\phi_1\phi_1\mid-\frac{1}{2}(\phi_1\mid\phi_1 \qquad (2)$$

where, $1/r_i$ is the operator showing the potential energy from the i'th hydrogen nucleus; $(\phi_1\phi_1\mid$ and $(\phi_1\mid\phi_1$ are respectively electronic Coulomb and exchange potential energy operators. $I(H_2)=-W(\phi_2)$ indicates the valence state ionization potential of the H_2 group. For the isoelectronic series of C, N^+ and O^{++}, the empirical relation between valence state ionization potentials (I_μ) and effective nuclear charges (Z_μ) determined using the Slater rule for $2p\pi$ orbitals is formulated by the use of energy values of appropriate valence state[13] and of the atomic spectroscopic data[14]. Knowledge of $I(H_2)$, hence, enables us to obtain the effective nuclear charge $Z(\phi_2)$ associated with the ϕ_2 orbital. The $Z(\phi_2)$ value is also determined by the alternative method. Subject to Paoloni[15] an empirical relation exists between the nuclear effective charges obtained by the use of Slater rule and one center electronic Coulomb repulsion integrals, for the first row atoms, as follows:

$$(\mu\mu\mid\mu\mu)=3.29_4\,Z_\mu \qquad (3)$$

The calculated value of one center Coulomb repulsion integral on the ϕ_2 orbital, $(\phi_2\phi_2\mid\phi_2\phi_2)$, allows us to estimate the value of the effective nuclear charge associated with the ϕ_2 orbital by the use of Eq. 3.

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[5] A. A. V. Stuart and E. L. Mackor, *J. Chem. Phys.*, **27**, 826 (1957).

[6] G. Dallinga, E. L. Mackor and A. A. V. Stuart, *Mol. Phys.*, **1**, 123 (1958).

[7] N. Muller and R. S. Mulliken, *J. Am. Chem. Soc.*, **80**, 3489 (1958).

[8] R. S. Mulliken, *Tetrahedron*, **5**, 253 (1959).

[9] T. Morita, This Bulletin, **32**, 893 (1959).

[10] C. MacLean, J. H. van der Waals and E. L. Mackor, *Mol. Phys.*, **1**, 247 (1958).

[11] R. S. Mulliken, C. A. Riecke and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941); see also, C. A. Coulson, "Valence", Oxford University Press, London (1952), p. 310.

[12] S. Aono, *Busseiron Kenkyu*, No. 94, p. 24 (1956).

[13] H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953); see also, R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934).

[14] Landolt-Börnstein, "Zahlenwerte und Funktionen", I Band, 1 Teil Springer, Berlin (1950); C. E. Moore, "Atomic Energy Levels", Vol. I, N. B. S., Circular 467 (1949).

[15] L. Paoloni, *Nuovo Cimento*, **4**, 410 (1956).

The distance between the quasi-$2p\pi$ and the next lying carbon $2p\pi$ orbitals may be estimated in the following way. The interelectronic Coulomb integral between ϕ_2 and the next lying carbon $2p\pi$ orbitals is evaluated legitimately by the equation[16] (cf. Fig. 1),

$$(\phi_2\phi_2 \mid 2p\pi\mathrm{C}\,2p\pi\mathrm{C}) = [(\mathrm{aa} \mid \mathrm{CC}) - (\mathrm{ab} \mid \mathrm{CC})]/(1-S) \tag{4}$$

The empirical formula indicating the same quantity may be formulated by the Pariser-Parr's method[17] using the value of the effective nuclear charge $Z(\phi_2)$ obtained by either $I_\mu \sim Z_\mu$ relation or Eq. 3, this being a functional relation of the distance $r(\mathrm{H_2}\text{-}\mathrm{C})$ between ϕ_2 and carbon $2p\pi$ orbitals. By putting the value obtained by Eq. 4 into this empirical formula, the distance $r(\mathrm{H_2}\text{-}\mathrm{C})$ in question may be evaluated.

Core integral $\beta_{\mathrm{H_2\text{-}C}}$ between $\mathrm{H_2}$ and C can be obtained by the assumption of the proportionality relation,

$$\beta_{\mathrm{H_2\text{-}C}}/\beta = S_{\mathrm{H_2\text{-}C}}/S \tag{5}$$

where, β is the core integral in benzene molecule; S the overlap integral between two carbon $2p\pi$ orbitals separated by 1.39Å; $S_{\mathrm{H_2\text{-}C}}$ the overlap integral between carbon $2p\pi$ and next lying $\mathrm{H_2}$ quasi-$2p\pi$ orbitals.

As above mentioned, the role of the methylene in the SCF MO method may be understood in the simplified manner.

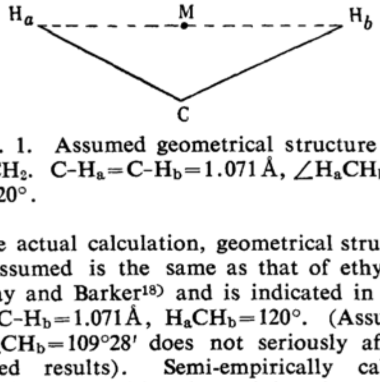

Fig. 1. Assumed geometrical structure of $\mathrm{CH_2}$. $\mathrm{C\text{-}H_a}=\mathrm{C\text{-}H_b}=1.071$ Å, $\angle\mathrm{H_aCH_b}=120°$.

In the actual calculation, geometrical structure of $\mathrm{C\text{-}H_2}$ assumed is the same as that of ethylene by Gallaway and Barker[18] and is indicated in Fig. 1; $\mathrm{C\text{-}H_a}=\mathrm{C\text{-}H_b}=1.071$Å, $\mathrm{H_aCH_b}=120°$. (Assumption of $\angle\mathrm{H_aCH_b}=109°28'$ does not seriously affect the calculated results). Semi-empirically calculated values of the quantities determining the model for hyperconjugation are shown in Table I. Although the procedure of this paper goes along the approximation including zero differential overlap by Pariser-Parr[19], or Pople[20], it is desirable to obtain $W(\phi_2)$ with moderate exactness. Indeed, the value calculated with neglect of differential overlap is -11.834 eV., and unsuitable for our purpose, if we remember the valence state ionization potential of the $2p\pi$ carbon is 11.54 eV. The value calculated with inclusion of differential overlap is -11.176 eV. and this value also may not be said to be appropriate. The moderate value, -10.256 eV., is obtained omitting the interelectronic Coulomb integral, (ab | ab)[21].

Using the value, 2.83, of the effective nuclear charge $Z(\phi_2)$, estimated from Eq. 3, the empirical formula of the interelectronic Coulomb integral $(\mathrm{H_2H_2} \mid \mathrm{CC})$ is obtained as follows,

$$(\mathrm{H_2H_2} \mid \mathrm{CC}) = 10.203 - 2.4607r + 0.1933r^2 \quad (r \leqq 2.8\mathrm{A}) \tag{6}$$

Substituting the value of $(\phi_2\phi_2 \mid 2p\pi\mathrm{C}\ 2p\pi\mathrm{C})$ in the $\mathrm{C\text{-}H_2}$ group calculated from Eq. 4 into Eq. 6, the distance $r(\mathrm{C\text{-}H_2})$ between quasi-$2p\pi$ and carbon $2p\pi$ orbitals in the $\mathrm{C\text{-}H_2}$ group is estimated as 1.383 and 1.031 Å for the cases with and without differential overlap. (For the case with differential overlap, $r(\mathrm{H_2}\text{-}\mathrm{C})$ is estimated to be 1.031 Å from somewhat different equation from Eq. 6 based on somewhat different value of $Z(\phi_2)$). It will be noticed here that when differential overlap is neglected Eq. 4 reduces to

$$(\phi_2\phi_2 \mid 2p\pi\mathrm{C}\ 2p\pi\mathrm{C}) = (\mathrm{aa} \mid \mathrm{CC}) \tag{7}$$

It is clear that this approximation 7 is too crude. It is desirable, therefore, to adopt for $r(\mathrm{H_2}\text{-}\mathrm{C})$ the middle value between 1.031 and 1.383 Å.

We have performed calculations by the use of some assumed values of $r(\mathrm{H_2}\text{-}\mathrm{C})$ between 1.031 and 1.383 Å, and, for $r(\mathrm{H_2}\text{-}\mathrm{C})=1.10$ Å, obtained satisfactory results in agreement with experimental observations. Hence, we describe below on the assumption of $r(\mathrm{H_2}\text{-}\mathrm{C})=1.10$Å. Table I indicates the semi-empirically fixed values of quantities determining the model of hyperconjugation for $\mathrm{C\text{-}H_2}$ group (values on the last row of Table I are referred to in the next paragraph).

Somewhat larger value of the C-H distance than that usually accepted in aliphatic hydrocarbons is seen in some papers[22] published after our calculations have finished. Reasonable assumption of $r(\mathrm{H\text{-}C})=1.11$Å based on these papers leads to $r(\mathrm{H_2}\text{-}\mathrm{C})=1.10$Å by the similar calculations with

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16) T. Morita, *J. Chem. Phys.*, **27**, 1442 (1957).

17) R. Pariser and R. G. Parr, ibid., **21**, 767 (1953).

18) W. S. Gallaway and E. F. Barker, ibid., **10**, 88 (1942).

19) R. Pariser and R. G. Parr, ibid., **21**, 466 (1953).

20) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953); *J. Phys. Chem.*, **61**, 6 (1957).

21) In the semi-empirical calculation of $W(\phi_2)$, it is assumed that $\int \frac{h_a h_a}{r_b} d\tau = (\mathrm{aa} \mid \mathrm{bb})$ and $\int \frac{h_a h_b}{r_b} d\tau = (\mathrm{ab} \mid \mathrm{bb}) = S\,(\mathrm{MM} \mid \mathrm{bb})$, where M is the midpoint of $\mathrm{H_a}$-$\mathrm{H_b}$ (Fig. 1). We also obtained $W(\phi_2)=-9.602$ eV. by the non-empirical calculation. Of these four values $W(\phi_2)=-10.256$ eV. is the most appropriate. In our calculations was omitted the correction to be considered in evaluating one center Coulomb repulsion integral $(1s1s \mid 1s1s)$. See, R. D. Brown, *Mol. Phys.*, **1**, 304 (1958).

22) a) K. Kuchitsu, This Bulletin, **32**, 748 (1959); R. A. Bonham, L. S. Bartell and D. A. Kohl, *J. Am. Chem. Soc.*, **81**, 4765 (1959). These authors revealed by the sectormicrophotometer method of electron diffraction that the C-H distances in *n*-butane, *n*-pentane, *n*-hexane and *n*-heptane are 1.100±0.003, 1.118±0.0004, 1.118±0.006 and 1.121±0.007Å, respectively.

b) B. K. Vainshtein, *Kristallografiya*, **3**, 452 (1958); *Chem. Abstr.*, **52**, 19299 (1958). Vainshtein showed that the C-H distance in solid paraffins is 1.123±0.015Å.

c) For ethylene also, recent measurements show somewhat larger value of the C-H distance; see, L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **27**, 1414 (1957); H. C. Allen, Jr. and E. K. Plyler, *J. Am. Chem. Soc.*, **80**, 2673 (1958).

d) It ought to be noticed here that the problem of the C-H bond distance has been recently discussed in a wider scope. See, H. J. Bernstein, *J. Phys. Chem.*, **63**, 565 (1959); L. E. Sutton, *Tetrahedron*, **5**, 118 (1959); M. J. S. Dewar and H. N. Schmeising, ibid., **5**, 166 (1959); R. S. Mulliken, ibid., **6**, 68 (1959).

TABLE I. SEMI-EMPIRICALLY FIXED VALUES OF QUANTITIES DETERMINING THE MODEL OF HYPERCONJUGATION FOR $C\text{-}H_2$ GROUP

$W(\psi_2)$ eV.	$(\psi_2\psi_2 \mid \psi_2\psi_2)$ eV.	$Z(\psi_2)$	$(\psi_2\psi_2 \mid 2p\pi C 2p\pi C)$ eV.	$r(H_2\text{-}C)$ Å
−10.256	9.326	2.83	7.73	1.10
−10.373	9.214	2.80	7.73	1.10

zero differential overlap to those mentioned above. Values of quantities relating to hyperconjugation of $C\text{-}H_2$ group are listed on the last row of Table I, and these are almost identical with those mentioned in the preceding paragraph, hence leading to seriously unaffected results.

At any rate we assume for the orbital of H_2 group, which take part in hyperconjugation with the residual part of the molecule, the $2p\pi$ orbital, associated with the effective nuclear charge, 2.83, and standing at a distance, 1.10 Å, from the carbon $2p\pi$ orbital in the methylene group.

The SCF LCAO MO CI calculation for benzenium ion whose co-ordinate system and numbering are as indicated in Fig. 2, is carried out by means of Poples scheme[23] which is based on the theory of Roothaan[24] and combined with Pariser-Parr's approximation[17,19]. The technical procedure for computation is described elsewhere[23,25,26]. What should be stated here is that the core integral $H_{\mu\mu}$ is assumed as follows,

$$H_{\mu\mu} = U_{\mu\mu} - \sum_{\alpha(\neq\mu)}' (\mu \mid V_\alpha \mid \mu) = U_{\mu\mu} - \sum_{\alpha(\neq\mu)}' Z_\alpha (\mu\mu \mid \alpha\alpha) \tag{8}$$

where, Z_α is assumed to be unity.

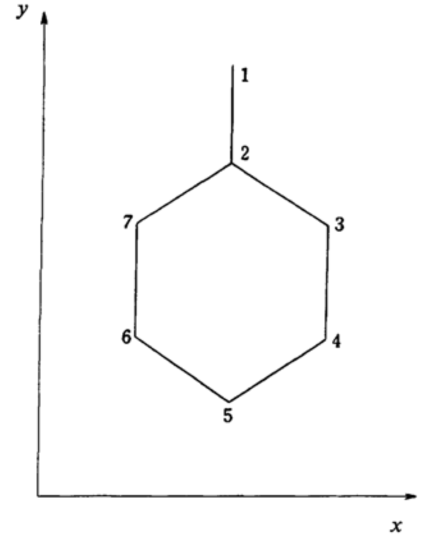

Fig. 2. Co-ordinate system and numbering of benzenium ion for computation.
$\overline{12} = 1.10\,\text{Å},\ \overline{23} = \overline{34} = \cdots\cdots = \overline{72} = 1.39\,\text{Å}$

The approximation of Eq. 8, which Sidman[27] also assumed, leads to that of Pariser and Parr[17,19].

The value of the core integral β is taken to be −2.39 eV. except for β_{H_2-C} which is estimated to be −4.111 eV. from Eq. 5. Values of valence state ionization potentials are taken from the tables of Skinner and Pritchard[13]. Values of electronic Coulomb repulsion integrals are evaluated using Pariser-Parr's approximations[17].

Results and Discussion

(a) Self-consistent Field Molecular Orbitals. —SCF MO's calculated and expressed by the linear combination of atomic orbitals, χ_μ, for the models of hyperconjugation and bond localization are shown in Tables II (A) (hyperconjugation) and II (B) (bond localization), which include also the energies, ε, of MO's. The highest occupied molecular orbital is ϕ_3 in each case and $-\varepsilon_3$ correspond to the ionization potential.

TABLE II. CALCULATED SELF-CONSISTENT FIELD MOLECULAR ORBITALS AND ENERGIES

(A) For the hyperconjugation model

$$\varepsilon_1 = -21.379\text{ eV.}\quad \phi_1(1b_2) = 0.500\chi_1 + 0.715\chi_2 + 0.294(\chi_3+\chi_7) + 0.151(\chi_4+\chi_6) + 0.143\chi_5$$

$$\varepsilon_2 = -18.381\text{ eV.}\quad \phi_2(2b_2) = 0.248\chi_1 + 0.239\chi_2 - 0.103(\chi_3+\chi_7) - 0.462(\chi_4+\chi_6) - 0.658\chi_5$$

$$\varepsilon_3 = -16.592\text{ eV.}\quad \phi_3(1a_2) = 0.464(\chi_4-\chi_6) + 0.534(\chi_3-\chi_7)$$

$$\varepsilon_4 = -8.249\text{ eV.}\quad \phi_4(3b_2) = 0.561\chi_1 - 0.043\chi_2 - 0.503(\chi_3+\chi_7) - 0.045(\chi_4+\chi_6) + 0.416\chi_5$$

$$\varepsilon_5 = -5.607\text{ eV.}\quad \phi_5(2a_2) = 0.534(\chi_4-\chi_6) - 0.464(\chi_3-\chi_7)$$

$$\varepsilon_6 = -4.083\text{ eV.}\quad \phi_6(4b_2) = 0.461\chi_1 - 0.396\chi_2 + 0.012(\chi_3+\chi_7) + 0.408(\chi_4+\chi_6) - 0.545\chi_5$$

$$\varepsilon_7 = -2.122\text{ eV.}\quad \phi_7(5b_2) = 0.400\chi_1 - 0.523\chi_2 + 0.548(\chi_3+\chi_7) - 0.437(\chi_4+\chi_6) - 0.274\chi_5$$

(B) For the bond localization model

$$\varepsilon_1 = -19.757\text{ eV.}\quad \phi_1(1b_2) = 0.644\chi_1 + 0.765\chi_2$$

$$\varepsilon_2 = -19.198\text{ eV.}\quad \phi_2(2b_2) = 0.214(\chi_3+\chi_7) + 0.484(\chi_4+\chi_6) + 0.664\chi_5$$

$$\varepsilon_3 = -17.056\text{ eV.}\quad \phi_3(1a_2) = 0.457(\chi_4-\chi_6) + 0.540(\chi_3-\chi_7)$$

$$\varepsilon_4 = -8.277\text{ eV.}\quad \phi_4(3b_2) = 0.602(\chi_3+\chi_7) + 0.085(\chi_4+\chi_6) - 0.512\chi_5$$

$$\varepsilon_5 = -6.023\text{ eV.}\quad \phi_5(2a_2) = 0.540(\chi_4-\chi_6) - 0.457(\chi_3-\chi_7)$$

$$\varepsilon_6 = -3.684\text{ eV.}\quad \phi_6(4b_2) = 0.765\chi_1 - 0.644\chi_2$$

$$\varepsilon_7 = -3.678\text{ eV.}\quad \phi_7(5b_2) = 0.304(\chi_3+\chi_7) - 0.509(\chi_4+\chi_6) + 0.545\chi_5$$

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[23] J. A. Pople, *Proc. Phys. Soc.* (*London*), A **68**, 81 (1955).

[24] C. C. J. Roothaan, *Revs. Mod. Phys.*, **23**, 69 (1951).

[25] N. Mataga and K. Nishimoto, *Z. physik. Chem.*, *N. F.*, **13**, 140 (1957).

[26] As to the expressions for the interconfigurational matrix elements, see, Ref. 23 and also, R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956). As to the expression for the oscillator strength, see, R. Pariser, loc. cit.

[27] J. W. Sidman, ibid., **27**, 429 (1957).

(b) Electronic Spectra.—In the calculations with configurational interactions (CI), the singlet configurations considered of excited states for $^1B_1$ symmetry are $V_{3\to4}$, $V_{3\to6}$ and $V_{2\to5}$; those for $^1A_1$ symmetry are $V_{2\to4}$, $V_{3\to5}$ and $V_{1\to4}$. Table III shows, for the hyperconjugation model, the wave functions of excited states with the values of matrix elements.

Electronic spectra theoretically calculated are denoted in Tables IV, V and Fig. 3. The calculated energy of the first transition is, for example, in the case with no configuration interactions, considerably larger for the bond localization model than for the hyperconjugation (Table IV). This suggests that the hyperconjugative effect would possibly be much larger in such a system of isovalent hyperconjugation as benzenium ion than is in the ordinary hyperconjugated molecules.

It is seen in Fig. 3, that the order of excited configurations differs considerably between bond localization and hyperconjugation models. As the experimental absorption data for protonated compounds of benzene and methylbenzenes are referred those of Reid[28], of Kilpatrick and Hyman[29], as well as of Dallinga, Mackor and Stuart[6]. Among these, the data of Kilpatrick-Hyman and Dallinga-Mackor-Stuart coincide with each other for methylbenzenes. Methyl shifts of the spectra by these investigators are reasonably bathochromic, while are hypsochromic by Reid's measurements. We take up, therefore, the data by Dallinga, Mackor and Stuart, 3700, 2600 and 2000 Å absorptions for benzenium ion, although the experimental extinction curve has not been given explicitly. Theoretical data agree satisfactorily with those experimentally observed (Table V). The oscillator strengths calculated also coincide, in the tendency, with the experimental extinction coefficients by Dallinga, Mackor and Stuart[6] for the protonated compounds of some methylbenzenes. Among these, for example, the mesitylene carbonium ion has the following values of the molar extinction coefficients, 11100, 8800, >13000, respectively, for the first, second and third bands. Further the calculated oscillator strengths by Dallinga, Mackor and Stuart are cited in Table V. These also agree well with our values.

TABLE III. WAVE FUNCTIONS OF EXCITED STATES WITH THE VALUES OF THE MATRIX ELEMENTS

$^1B_1$-Symmetry

$\Phi(1\,^1B_1)=0.985\,V_{3\to4}-0.017\,V_{3\to6}-0.174\,V_{2\to5}$

$\Phi(2\,^1B_1)=0.082\,V_{3\to4}+0.924\,V_{3\to6}+0.373\,V_{2\to5}$

$\Phi(3\,^1B_1)=0.155\,V_{3\to4}-0.381\,V_{3\to6}+0.911\,V_{2\to5}$

$\{V_{3\to4}\mid V_{3\to6}\}=-0.00988$ eV.

$\{V_{3\to4}\mid V_{2\to5}\}=0.73213$ eV.

$\{V_{3\to6}\mid V_{2\to5}\}=-0.39409$ eV.

$\{V_{3\to4}\mid V_{3\to4}\}=-204.03227$ eV.

$\{V_{3\to6}\mid V_{3\to6}\}=-200.64365$ eV.

$\{V_{2\to5}\mid V_{2\to5}\}=-199.98658$ eV.

$^1A_1$-Symmetry

$\Phi(1\,^1A_1)=0.884\,V_{2\to4}+0.445\,V_{3\to5}+0.143\,V_{1\to4}$

$\Phi(2\,^1A_1)=0.370\,V_{2\to4}-0.854\,V_{3\to5}+0.366\,V_{1\to4}$

$\Phi(3\,^1A_1)=0.285\,V_{2\to4}-0.271\,V_{3\to5}-0.919\,V_{1\to4}$

$\{V_{2\to4}\mid V_{3\to5}\}=-0.45738$ eV.

$\{V_{2\to4}\mid V_{1\to4}\}=-0.52381$ eV.

$\{V_{3\to5}\mid V_{1\to4}\}=0.34067$ eV.

$\{V_{2\to4}\mid V_{2\to4}\}=-202.22097$ eV.

$\{V_{3\to5}\mid V_{3\to5}\}=-201.73760$ eV.

$\{V_{1\to4}\mid V_{1\to4}\}=-200.36226$ eV.

TABLE IV. TRANSITION ENERGIES CALCULATED WITHOUT CONFIGURATION INTERACTIONS

Bond localization model (eV.)	Hyperconjugation model (eV).
0 (ground state)	0 (ground state)
4.116 ($V_{3\to4}$)	3.529 ($V_{3\to4}$)
5.358 ($V_{1\to4}$)	5.341 ($V_{3\to5}$)
5.621 ($V_{2\to4}$)	5.824 ($V_{2\to4}$)
5.864 ($V_{3\to5}$)	6.918 ($V_{3\to6}$)
7.344 ($V_{2\to5}$)	7.199 ($V_{1\to4}$)
7.959 ($V_{3\to6}$)	7.575 ($V_{2\to5}$)

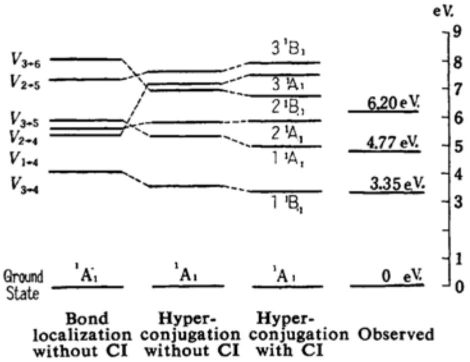

Fig. 3. Observed and calculated π-electron configurational energy levels.

It is striking that the hyperconjugation shift of the first absorption band is, as is seen in Table IV, toward red, while it is, in the Hückel MO calculations, toward blue. Indeed, our Hückel MO calculations using $\alpha_1=\alpha-0.4\beta$ show for the first transition energy the values 1.0709 $(-\beta)$ and 1.0000 $(-\beta)$, of which the former refers to the hyperconjugation and the latter to the bond localization model[30]. By means of the semi-empirical ASMO method also the similar tendency is seen. In performing the semi-empirical ASMO calculations our

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[28] C. Reid, *J. Am. Chem. Soc.*, **76**, 3264 (1954).

[29] M. Kilpatrick and H. H. Hyman, ibid., **80**, 77 (1958).

[30] The Hückel MO method for toluenium and mesitylenium ions also shows the hypsochromic shift for the hyperconjugative effect. See, Refs. 3 and 4.

TABLE V. CALCULATED ELECTRONIC SPECTRA FOR HYPERCONJUGATION MODEL COMPARED WITH EXPERIMENTS

Symmetry	Polarization	Transition energies for hyperconjugation with CI (eV.)	Transition energies observed (eV.)	Oscillator strengths calculated	
1 $^1B_1$	x	3.400	3.35	0.219[a]	(0.21)[b]
1 $^1A_1$	y	5.025	4.77	0.012[a]	(0.06)[b]
2 $^1A_1$	y	5.876	6.20	0.630[a]	(0.99)[b]
2 $^1B_1$	x	6.758		0.117[a]	
3 $^1A_1$	y	7.462		0.017[a]	
3 $^1B_1$	x	7.864		0.354[a]	

a) These values are calculated by the use of the wave functions in Table III.

b) Values in parentheses are those calculated by Dailinga, Mackor and Stuart; see, Ref. 6.

TABLE VI. ENERGIES OF THE FIRST TRANSITION CALCULATED BY THE HÜCKEL AND PARISER-PARR METHODS

	Hückel method	Pariser-Parr's method	Modified Hückel method	Modified Pariser-Parr's method
Hyperconjugation	1.0709 $(-\beta)$	3.798 eV.	1.0709 $(-\beta)$	3.798 eV.
Bond localization	1.0000 $(-\beta)$	3.575 eV.	1.0833 $(-\beta)$	3.864 eV.

procedure is almost the same as that for toluene by Morita[16]. The value of the core integral β_{H_2-C} used is -4.435 eV., which is somewhat different from that in the semi-empirical SCF MO method extended in the early part of this paper. Values of the atomic integrals also differ from those used in the SCF MO method. This does not prevent us, however, from judging the calculated results. The calculated energies for the first transition are 3.798 eV. for the hyperconjugation model and 3.575 eV. for the bond localization.

This discrepancy between the results of the SCF MO and ASMO methods might be taken off by introducing the laborious technique of configurational interaction. This seems to be in vain, however, if we take into account the same extent of configurations as in the SCF MO calculations. If any simple modification is tried, however, for the naive and the anti-symmetrized molecular orbital calculations, the identical tendency in all cases will be accomplished.

The modification is done as follows. In the bond localization model, as is seen in Fig. 4, the π-electron system is cut off into two parts, one being the system 1-2 (A), the other the system 3-4-5-6-7 (B). In the part B, terminal carbons (3 and 7) seem to be electropositive compared to the inner carbons[31]. Consequently, we should give negative value of δ for the Coulomb integral α_3 or $\alpha_7=\alpha+\delta\beta$. We have no thorough materials which suggest the exact way determining the value of δ in this case. It may not be said, however, that the leectropositiveness of the carbon atom 3 or 7 is not satisfactory when it is equated to that of the H_2 group. Hence, we assume, for a moment, $\alpha_3=\alpha_7=\alpha-0.4\beta$. The corresponding modification in the ASMO method is to equalize I_3 (the valence state ionization potential of the carbon atom 3 or 7) to $I(H_2)$ (the valence state ionization potential of the H_2 group, namely $I(H_2)=-W(\psi_2)=-\int\psi_2^*H\psi_2d\tau$) in the formula expressing the core integral α_3 or α_7 (Pariser-Parr's notation)

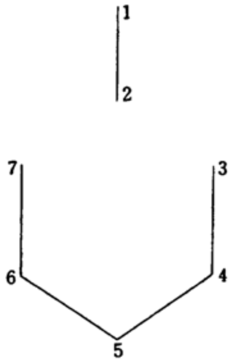

Fig. 4. The effective π-electron system of the benzenium ion for its bond localization model.

$$\alpha_3=\alpha_7=-I_3-\sum_{\nu\neq 3}{}'\,(33\mid\nu\nu) \tag{9}$$

(Although the electronic Coulomb repulsion integrals, $(33\mid\nu\nu)$, have to take different values corresponding to the change in I_3, this correction may be omitted for the present purpose.) These modifications in the naive and antisymmetrized molecular orbital methods lead to the

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[31] R. G. Parr and R. S. Mulliken, *J. Chem. Phys.*, **18**, 1338 (1950).

same tendency as in the SCF MO method with regard to the absorption spectra. Calculated results are indicated in Table VI.

(c) Charge Densities and Bond Orders.—Fig. 5 shows π-electron densities and π-bond orders calculated for the hyperconjugation and bond localization models.

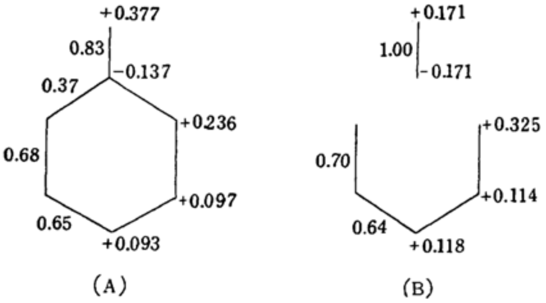

Fig. 5. Calculated formal charges (unit of $+e$) and π-bond orders of benzenium ion.
A: hyperconjugation, B: bond localization

The proton magnetic resonance spectra of pentamethylbenzene in $CF_3COOH+H_2O\cdot BF_3$ and in $HF+BF_3$ show for the methyl groups the following shifts compared to the benzene proton signal; 196, 199, 204 and 180, 187, 198 (in c/sec.) in each case[10]. The manner in which the assignment of the signals is undertaken is different, according as which model, hyperconjugation or bond localization, is adopted. Namely, the hyperconjugation model predict the signals 196, 199, 204 or 180, 187, 198 (in c/sec.) attributing, in order, to the methyl groups at the positions 3, 4, 5; in contrast, for the bond localization model, these signals should be assigned to the methyl groups at the positions 3, 5, 4 in order. This discrepancy will probably be due to the crudeness of approximations. It will be probably necessary, in the configurational interaction calculations, to take into account further more configurations including the ground state configuration, V_0, which is shut out of our computations.

(d) Hyperconjugation Energy.—The hyperconjugation energy is obtained by subtracting the energy of hyperconjugation model from that of bond localization one, taking further the compressional energy correction into consideration. The compression energy is evaluated on the assumption of harmonical distortion of a bond. Calculated energy of hyperconjugation is 19.7 kcal./mol., which is much larger than in the case of the ordinary hyperconjugation.

Summary

Semi-empirical SCF LCAO MO calculations of benzenium ion was undertaken for the model of localization as well as hyperconjugation of the H_2-C bond constructed at the position of proton attack. A simplified model of hyperconjugation in the semi-empirical SCF MO method was extended. Calculated results for the hyperconjugation model agreed satisfactorily with the experimental electronic spectra.

Superiority of the SCF MO method to the Hückel MO or ASMO method was indicated in connection with the ordinarily accepted spectral shift through hyperconjugation. Further, some modifications were tried, for the bond localization model, which would have to be taken in the Hückel MO as well as ASMO calculations.

The proton magnetic resonance signals due to methyl substituents in the carbonium ions of methylbenzenes were discussed from charge densities of benzenium ion.

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