The Electronic Structures of the Benzenium Ion and Its Methyl Derivatives

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It is well known that methylbenzenes are protonated in acidic media (HF, HF+BF_3, etc.) to give benzenium-type ions. They are considered to be a typical model of the intermediates of aromatic substitution reactions.[1)]

Mackor et al.[2)] studied the electronic absorption spectra of the methyl-substituted benzenium ions in HF+BF_3. According to them, the 2, 4, 6-trimethylbenzenium, 2, 3, 4, 6-tetramethylbenzenium and pentamethylbenzenium ions show two bands in the wavelength region longer than 200 mμ. One of them appears at 350—400 mμ, the other, at ~250 mμ.

Reid[3)] also studied the ultraviolet absorption spectra of the benzenium ion and its methyl derivatives under low temperatures (~70°C); he found that the benzenium ion itself shows a band at 410 mμ. Mackor et al.,[4)] however, reported that, at least at room temperature, they could not detect the formation of the benzenium ion in the benzene-HF-BF_3 system.

Kilpatrick and Hyman[5)] also observed the absorption spectra of benzene, mesitylene and hexamethylbenzene in various solvents. In the case of benzene, no new band appears in the visible and ultraviolet regions, even in strong acid (HF). On the other hand, in the case of mesitylene and hexamethylbenzene in strong acid, a new band appears in the 350—400 mμ region.

Recently Olah et al.[6)] succeeded in isolating the salts of the methyl-substituted benzenium ions with BF_4^- in the solid form. They were prepared at a low temperature and were gradually decomposed at room temperature even in a sealed capsule. They showed a rather high electric conductance in the solid state. This fact seems to support the existence of ionic species.

Mulliken et al.[7)] calculated the π-electron structure of the benzenium ion, including the hyperconjugation effect of the methylene group, by the ω-technique. They evaluated the stabilization energy (hyperconjugation energy) to be 14.5 kcal./mol. This work was restricted to the Hückel approximation, so it may not give reliable predictions to the excitation energies.

The SCFMO calculations were performed by Mackor et al.[2,8)] Although their calculation considered no hyperconjugation effect, they succeeded in predicting the excitation energies qualitatively.

Recently Morita[9)] studied the π-electronic structure of the benzenium ion by the SCFMO method including the hyperconjugation of the methylene group and obtained a reasonable agreement with the experimental results. There remain some ambiguities, however, in his determination of the parameters belonging to the methylene group.

In the present work, we have undertaken to improve the calculation of the π-electron structure of the benzenium ion by evaluating the molecular integrals belonging to the methylene group as rigorously as possible and by considering the effect of the electronic charge and of the configurational interaction with doubly excited electron configurations. Moreover, the effect of the substituted methyl groups has been studied in the following manner. The methyl-substituted ion is divided into its components, the benzenium ion and the methyl groups. Then the interaction among them is taken into account in terms of the configurational interaction among several electron configurations constructed by putting the electrons in the orbitals of the components.

The Benzenium Ion

The Simple SCFMO Calculation (Method I).—The geometrical structure of the benzenium

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[1)] V. Gold and F. L. Tye, *J. Chem. Soc.*, **1952**, 2172, 2181, 2184.

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

[3)] C. Ried, *J. Am. Chem. Soc.*, **76**, 3264 (1954).

[4)] a) C. MacLean, J. H. van der Waals and E. L. Mackor, ibid., **1**, 247 (1958); b) E. L. Mackor, A. Hofstra and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 66, 186 (1958).

[5)] M. Kilpatrick and H. H. Hyman, *J. Am. Chem. Soc.*, **80**, 77 (1958).

[6)] G. A. Olah and S. J. Kuhn, ibid., **80**, 6535 (1958).

[7)] N. Muller, L. W. Pickett and R. S. Mulliken, ibid., **76**, 4770 (1954); L. W. Pickett, N. Muller and R. S. Mulliken, *J. Chem. Phys.*, **21**, 1400 (1953).

[8)] J. P. Colpa, C. MacLean and E. L. Mackor, *Tetrahedron*, **19**, 65 (1963).

[9)] T. Morita, This Bulletin, **33**, 1486 (1960).

ion was confirmed by the NMR measurements[4a,10,11] as follows: H^+ attacks an appropriate carbon atom of the benzene ring, and two hydrogen atoms are both bonded to the atom symmetrically with respect to the ring plane. The hybridization of the carbon atom changes from sp^2 of the benzene to sp^3 of the benzenium ion* (Fig. 1).

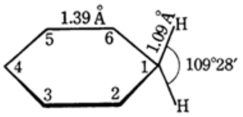

Fig. 1. The geometrical configuration of the benzenium ion.
(The conformation of the ring is assumed to be identical with benzene.)

First of all, let us consider the linear combination of the two hydrogen 1s orbitals, χ_1 and χ_2, of the methylene group:

$$\left.\begin{aligned}\chi_\sigma&=[2(1+S)]^{-1/2}(\chi_1+\chi_2)\\ \chi_\pi&=[2(1-S)]^{-1/2}(\chi_1-\chi_2)\end{aligned}\right\} \quad (1)$$

where S denotes the overlap integral between the two hydrogen 1s AO's. Of these, χ_σ corresponds to the σ-type orbital and χ_π corresponds to the π-type orbital. The sp^3 hybridized orbitals of the carbon, to which the two hydrogen atoms are attached, can be reduced into three nonequivalent sp^2 hybrid orbitals and the one $2p\pi$ AO by taking linear combinations of them. One of the nonequivalent sp^2 hybrid orbitals can make a bond with the χ_σ orbital, and the $2p\pi$ one can interact with the χ_π orbital and the conjugated system of the cyclopentadienyl ring. (See Appendix for the justification of this procedure.)

We have performed the SCF calculation taking the six $2p\pi$ AO's of the ring and the χ_π orbital into account. The calculation has been made by the method combining Pariser-Parr's method[12] with Roothaan's SCF method[13,14]. The orbital energy of the AO is replaced by the minus of the valence state ionization potential of the atom, and the one-center repulsion integrals (pp|pp) are replaced by the ionization potentials minus electron affinities.

To perform the above-mentioned calculation procedure, we must evaluate the ionization potential and the electron affinity of the pseudo χ_π orbital. Using the Slater 1s AO, the valence state energy of the pseudo atom H_2 is found to be:

$$E=I_\sigma+I_\pi+J_{\sigma\pi}-1/2\,K_{\sigma\pi} \quad (2)$$

where

$$\left.\begin{aligned}I_1&=\int\chi_1(1)\mathbf{H}^{\text{core}}(1)\chi_1(1)\,dv_1\\ J_{\sigma\pi}&=\int\chi_\sigma(1)\chi_\sigma(1)e^2/r_{12}\chi_\pi(2)\chi_\pi(2)\\ &\quad\times dv_1dv_2\\ K_{\sigma\pi}&=\int\chi_\sigma(1)\chi_\pi(1)e^2/r_{12}\chi_\sigma(2)\chi_\pi(2)\\ &\quad\times dv_1dv_2\end{aligned}\right\} \quad (3)$$

The valence state energy of the $H_2{}^+$ ion, in which an electron in χ_π is removed, is;

$$^+E=I_\sigma \quad (4)$$

Therefore, the valence state ionization potential is:

$$^+E-E=-I_\pi-J_{\sigma\pi}+\frac{1}{2}K_{\sigma\pi} \quad (5)$$

If we reduce these molecular integrals into integrals over the Slater-type 1s AO's with $Z=1$, we can evaluate them non-empirically.*

Similarly, the electron affinity can be evaluated from the relation:

$$E-E^-=-I_\pi-J_{\sigma\pi}-J_{\pi\pi}+\frac{1}{2}K_{\sigma\pi} \quad (6)$$

where E^- is the valence state energy of $H_2{}^-$ in which two electrons occupy χ_π:

$$E^-=I_\sigma+2I_\pi+J_{\pi\pi}+2J_{\sigma\pi}-K_{\sigma\pi} \quad (7)$$

Using the Slater AO's for hydrogen 1s:

$$\left.\begin{aligned}I_p(H_2)&={}^+E-E=9.4219\text{ eV.}\\ A_p(H_2)&=E-E^-=-0.7007\text{ eV.}\end{aligned}\right\} \quad (8)$$

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[10] C. MacLean and E. L. Mackor, *Mol. Phys.*, **4**, 241 (1961).

[11] C. MacLean and E. L. Mackor, *J. Chem. Phys.*, **34**, 2208 (1961).

* If sp^3 hybrid orbitals are formed completely, the carbon skeleton of the benzene ring may be deformed to a considerable extent. In fact, the hybridization may be in some intermediate state between sp^2 and sp^3. In the present work, however, the two hydrogen atoms are assumed to take the same geometrical configuration as in the case of methane, and the deformation of the ring skeleton is not considered explicitly.

[12] R. Pariser and R. G. Parr *J. Chem. Phys.*, ibid., **21**, 466, 767 (1953).

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

[14] a) A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 901 (1954); b) J. A. Pople, *Proc. Phys. Soc.*, **A68**, 81 (1955); c) H. Kon, This Bulletin, **28**, 275 (1955).

* Strictly speaking, the values of the same type of molecular integrals are different when they appear in E and in E^+:

$$E^+-E=-I_\pi-J_{\sigma\pi}+\frac{1}{2}K_{\sigma\pi}+(I_\sigma^+-I_\sigma)$$

the difference, $I_\sigma^+-I_\sigma$, being attributed to the difference in the electron distribution. (if we consider the Slater AO's, it is reduced to the difference in the effective charge.) Fortunately, $I_\sigma^+-I_\sigma$ may be canceled out with other types of errors (for example, the error coming from the atomic orbitals), so that we may still expect a good result when $I_\sigma^+-I_\sigma$ are disregarded. This is the reason why Koopmans' theorem holds generally with considerable exactness. (Cf. W. Moffitt, *Proc. Roy. Soc.*, **A202**, 534 (1950); R. G. Parr and R. S. Mulliken, *J. Chem. Phys.*, **18**, 1338 (1950).).

TABLE I. THE RESULT OF SCF CALCULATION FOR THE BENZENIUM ION (METHOD I)

ε*, eV.	MO wave function**						
	0	1	2	3	4	5	6
−23.0586	0.5132	0.7081	0.2946	0.1550	0.1172	0.1550	0.2946
−19.3204	−0.2687	−0.2593	0.1772	0.4827	0.5759	0.4827	0.1772
−17.7571	0	0	−0.5038	−0.4962	0	0.4962	0.5038
− 8.9572	−0.3706	−0.0805	0.5218	0.0164	−0.5578	0.0164	0.5218
− 6.2615	0	0	−0.4962	0.5038	0	−0.5038	0.4962
− 4.1381	−0.2716	0.1123	0.2384	−0.4802	0.5821	−0.4802	0.2384
− 0.5573	0.6733	−0.6421	0.2296	−0.1101	0.0684	−0.1101	0.2296

* Orbital energy.

** Coefficients of AO's in MO ϕ_i are shown in the i-th row. Numbering of carbon atoms are shown in Fig. 1. 0 means χ_π orbital constructed by the linear combination of the two hydrogen 1s orbital of the methylene group.

TABLE II. THE RESULT OF SCF CALCULATION FOR THE BENZENIUM ION (METHOD II)*

ε, eV.	MO wave function						
	0	1	2	3	4	5	6
−23.3453	0.5197	0.6733	0.3138	0.1719	0.1435	0.1719	0.3138
−19.9319	−0.2992	−0.2771	0.1559	0.4585	0.6039	0.4585	0.1559
−18.3641	0	0	−0.5263	−0.4722	0	0.4722	0.5263
− 9.8833	−0.3853	−0.0874	0.5207	0.0314	−0.5475	0.0314	0.5207
− 6.8657	0	0	−0.4722	0.5263	0	−0.5263	0.4722
− 4.7863	−0.2565	0.1116	0.2380	−0.4985	0.5581	−0.4985	0.2380
− 0.9909	0.6529	−0.6706	0.2224	−0.1040	0.0587	−0.1040	0.2224

* See Table I for the notation.

On the basis of these results and of the valence state ionization potential (11.24 eV.) and electron affinity (0.62 eV.) of the carbon 2pπ AO, which have been derived from spectroscopic data,[15] two center repulsion integrals (pp|qq) over π-type AO's have been evaluated by using the Pariser-Parr method.[12]

The resonance integral, β_{CC}, between the adjacent carbon 2pπ AO's of the ring is taken to be −2.39 eV. which is the value determined by Pariser and Parr for benzene.[12] The resonance integral, $\beta_{C-\chi_\pi}$, between χ_π and the adjacent carbon 2pπ AO is determined from the equation:

$$\beta_{C-\chi_\pi}=(S_{C-\chi_\pi}/S_{C-C})\beta_{C-C}$$

where $S_{C-\chi_\pi}$ is the overlap integral between χ_π and the adjacent carbon 2pπ AO and S_{C-C} is the overlap integral between the adjacent carbon 2pπ AO's of benzene ($S_{C-C}=0.248$). Assuming the geometrical configuration shown in Fig. 1, $S_{C-\chi_\pi}$ has been evaluated as 0.613. Thus, $\beta_{C-\chi_\pi}$ is determined to be −5.90 eV.

The numerical calculation was performed using a FACOM 202 electronic computer at our Institute.* The result of the SCF calculation is shown in Table I. Of seven MO's, the lower three are occupied in the ground configuration.

The Effect of Changing the Effective Charge (Method II).—The above-mentioned calculation is based on the parameters which are determined from the ionization potentials and the electron affinities of neutral atoms.

In the present case, however, the molecule as a whole possesses a +1 charge in the conjugate system. For this reason, the appropriate Z values may differ to some extent from those of neutral atoms. In this connection, we have performed the 'SCE' calculation[16] in which the effective nuclear charge, Z, of an atom is changed proportionally to the change in the charge density of the atom; that is, for the carbon atom,

$$Z_p=3.25+0.35\,q_p \tag{9}$$

where q_p is the formal charge on atom p. For H_2 pseudo AO, χ_π, the relation is;

$$Z_H=1.00+0.39\,q_H \tag{10}$$

according to the Slater rule.

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[15] G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962).

* The computer programs for SCF and transition moment calculations were written by one of the present authors, while the program for secular equations was written by Mr. Hidechika Takahashi and revised by Mr. Suehiro Iwata.

[16] R. D. Brown and A. Penfold, *Trans. Faraday Soc.*, **53**, 397 (1957); R. D. Brown and M. L. Heffernan, ibid., **54**, 757 (1958).

TABLE III. MATRIX ELEMENTS FOR CONFIGURATION INTERACTION*

A. Method I

Symmetric:

	0	3→5**	2→4	2→6	1→4
0	0				
3→5	0	6.3861			
2→4	0	0.6199	5.4679		
2→6	0	−0.4250	0.1901	9.1331	
1→4	0	−0.2087	0.0227	0.2047	8.1417

Antisymmetric:

	3→4	3→6	2→5
3→4	3.6539		
3→6	−0.0562	7.8571	
2→5	−0.6841	−0.0136	7.3598

B. Method II

Symmetric:

	0	3→5	2→4	2→6	1→4
0	0				
3→5	0	6.4477			
2→4	0	0.7031	5.3051		
2→6	0	−0.3907	0.0987	9.1872	
1→4	0	−0.1556	0.0549	0.1972	7.5910

Antisymmetric:

	3→4	3→6	2→5
3→4	3.5366		
3→6	−0.0625	7.8501	
2→5	−0.6877	0.0301	7.3989

* All results are shown in eV.

** $i \rightarrow j$ denotes the configuration in which an electron in ϕ_i is excited to ϕ_j. The wave function is, for example,

$$\Psi_{3\rightarrow4}=\frac{1}{\sqrt{2}}\{|1\bar{1}2\bar{2}3\bar{4}|+|1\bar{1}2\bar{2}4\bar{3}|\}$$

TABLE IV. THE LOWER EXCITED STATES OF THE BENZENIUM ION

A. Method I

State	E, eV.	f*	Wave function
G	0		$1.000\,\Psi_0$
A_1	3.5309	0.202	$0.9843\,\Psi_{3\rightarrow4}+0.0133\,\Psi_{3\rightarrow6}+0.1759\,\Psi_{2\rightarrow5}$
S_1	5.1195	0.128	$-0.4659\,\Psi_{3\rightarrow5}+0.8797\,\Psi_{2\rightarrow4}-0.0893\,\Psi_{2\rightarrow6}-0.0327\,\Psi_{1\rightarrow4}$
S_2	6.6496	1.081	$0.8685\,\Psi_{3\rightarrow5}+0.4742\,\Psi_{2\rightarrow4}+0.1041\,\Psi_{2\rightarrow6}+0.1000\,\Psi_{1\rightarrow4}$

B. Method II

State	E, eV.	f	Wave function
G	0		$1.000\,\Psi_0$
A_1	3.4171	0.224	$0.9853\,\Psi_{3\rightarrow4}+0.0127\,\Psi_{3\rightarrow6}+0.1701\,\Psi_{2\rightarrow5}$
S_1	4.9504	0.163	$-0.4400\,\Psi_{3\rightarrow5}+0.8951\,\Psi_{2\rightarrow4}-0.0596\,\Psi_{2\rightarrow6}-0.0401\,\Psi_{1\rightarrow4}$
S_2	6.7341	1.079	$0.8816\,\Psi_{3\rightarrow5}+0.4457\,\Psi_{2\rightarrow4}+0.1140\,\Psi_{2\rightarrow6}+0.1053\,\Psi_{1\rightarrow4}$

* Oscillator strength

We then take the valence state ionization potential and the electron affinity[15] of the isoelectronic series of the carbon (B^-, C, N^+, O^{2+}) and hydrogen (H, He^+, Li^{2+}) atoms, and plot them against the Z values obtained by means of the Slater rule. Thus approximate quadratic equations are obtained between I_p or A_p and Z_p:

$$\left.\begin{array}{l} \left.\begin{array}{l} I_p=3.69\,Z_p^2-10.04\,Z_p+4.89 \\ A_p=3.75\,Z_p^2-16.50\,Z_p+14.64 \end{array}\right\}\text{(carbon)} \\ \left.\begin{array}{l} I_p=13.6064\,Z_p^2-4.2579\,Z_p \\ \quad +0.0734 \\ A_p=13.6051\,Z_p^2-12.7417\,Z_p \\ \quad -1.5641 \end{array}\right\}\text{(hydrogen)} \end{array}\right\} \quad (11)$$

These relations, together with Eqs. 9 and 10, allow us to determine the appropriate I_p's and A_p's as the functions of the charge densities. We calculate I_p and A_p by the use of the q_p, the formal charge of atom p, obtained by method I. The SCF procedure is then performed again by using the newly-evaluated I_p and A_p values. This procedure is repeated until the charge distribution becomes self-consistent.* The results are shown in Table II.

Configuration Interaction. — The above-mentioned two kinds of SCF calculations have

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* In the present calculation, the one-center integrals,

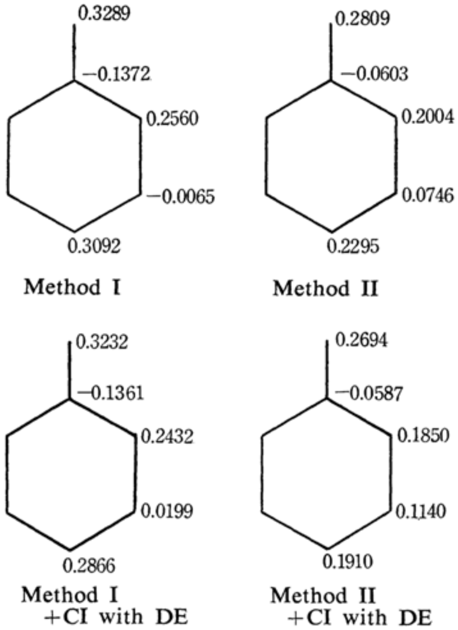
$$W_p=-I_p$$

and

$$(pp\mid pp)=I_p-A_p$$

are adjusted by the SCE procedure. However, the two-center integrals (β and $(pp\mid qq)$) are not adjusted because the change in these integrals caused by the change in the charge distribution is small.

been improved by considering the configuration interaction. Singly excited configurations, the excitation energies of which are below 10 eV., are taken into account. The selected configurations and matrix elements are shown in Table III. The resultant energies and wave functions for the ground and lower-excited states are shown in Table IV. The charge distributions of the ground state are shown in Fig. 2.



Method I | Method II

Method I +CI with DE | Method II +CI with DE

Fig. 2. The charge distribution in the ground state of the benzenium ion.
(The charge distributions calculated by SCF without CI and by SCF with CI among singly excited configurations are identical because the singly excited configurations do not mix with the ground configuration)

The Methyl-Substituted Benzenium Ions

In order to evaluate the hyperconjugation effect of the methyl group, the charge-transfer configuration, $A\rightarrow\phi_4$, where A denotes the occupied pseudo π MO of the methyl group A and ϕ_4 denotes the lowest vacant MO of the benzenium ion, was taken into account, in addition to the singly excited configurations mentioned above.

The ionization potential for removing an electron from the pseudo π MO of the methyl group had been evaluated in the case of the *t*-butyl cation: the pseudo π AO which can be constructed from the three 1s AO's of the H_3 group can form a pseudo π MO by means of interaction with the $2p\pi$ AO of the carbon atom of the methyl group. The calculations on this system were performed by the SCFMO method and gave the following results[17]:

$$\left.\begin{aligned} \varepsilon_1 &= -13.245\text{ eV.} \\ \phi_1 &= 0.5505\chi_H + 0.8348\chi_C \\ \varepsilon_2 &= +0.708\text{ eV.} \\ \phi_2 &= 0.8348\chi_H - 0.5505\chi_C \end{aligned}\right\} \quad (12)$$

where χ_C is the carbon $2p\pi$ AO and where the pseudo π AO χ_H is defined as:

$$\chi_H = \frac{1}{\sqrt{6(1-S)}}(2\chi_1 - \chi_2 - \chi_3) \quad (13)$$

χ_1, χ_2 and χ_3 being the 1s AO's of the three hydrogen atoms. The ionization potential for removing an electron from ϕ_1 is a minus of the orbital energy of ϕ_1:

$$I_p(\text{methyl}) = -\varepsilon_1 = 13.245\text{ eV.} \quad (14)$$

The electron affinity of the benzenium ion has never been measured; therefore, the minus of the calculated orbital energy of the lowest vacant MO was adopted. In the present calculation, however, we make use of the zero-differential overlap approximation, so there is probably some error. Hush and Pople[18] calculated the ionization potentials of alternant hydrocarbons and of odd alternant radicals with the approximation of neglecting the overlap integrals. They found that it is necessary to take the orbital energy of the carbon $2p\pi$ AO to be about −9.50 eV. in order to obtain a good agreement with the experimental data. The valence state ionization potential of carbon $2p\pi$ AO is 11.24 eV., so a correction of about 1.7 eV. is necessary. Therefore, in the present case, the electron affinity of the benzenium ion is corrected by about 1.7 eV. The calculated electron affinity by method I (neutral parameters) is 8.957 eV.; after the correction of 1.7 eV., it is reduced to 7.257 eV.

The diagonal element for the charge-transfer (hereafter abbreviated as 'CT') configuration is

$$E_{CT} = I_p(\text{methyl}) - A_p(\text{benzenium}) \quad (15)$$

where the small correction resulting from the electrostatic interaction between the methyl and benzenium groups has been disregarded. Putting the above-mentioned values into Eq. 15, the diagonal element is

$$E_{CT} = 13.245 - 7.257 = 5.988\text{ eV.} \quad (16)$$

(Taking the energy of the ground configuration as the standard)

The off-diagonal elements can also easily be obtained. When, for example, a methyl group

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[17] I. Hanazaki, H. Hosoya and S. Nagakura, This Bulletim, **36**, 1673 (1963).

[18] N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

is substituted at the 2 position,* the CT configuration, $CT_{A\to4}$, must be considered in addition to the configurations included in the case of the configuration interaction of the benzenium ion:

$$\begin{aligned}(\mathrm{G}|\mathbf{H}|\mathrm{CT}_{A\to4}) &= \int |1\bar{1}2\bar{2}3\bar{3}A\bar{A}| \\ &\times \mathbf{H}\frac{1}{\sqrt{2}}\{|1\bar{1}2\bar{2}3\bar{3}A\bar{4}| + |1\bar{1}2\bar{2}3\bar{3}4\bar{A}|\}\,d\tau \\ &= \sqrt{2}\,(A|\mathbf{H}^{\mathrm{core}}|4)^{**} \qquad (17)\end{aligned}$$

where the zero-differential overlap approximation is invoked. If we neglect resonance integrals between the non-adjacent atoms,

$$\begin{aligned}(A|\mathbf{H}^{\mathrm{core}}|4) &= \int (c_1\chi_H + c_2\chi_C)\mathbf{H}^{\mathrm{core}} \\ &\times (\sum_p c_{4p}\chi_p)\,d\tau \\ &= c_2c_{42}\beta \qquad (18)\end{aligned}$$

where c_2 denotes the coefficient of the carbon AO χ_C in the methyl group; c_{42} denotes the coefficient of the AO χ_2 in the MO ϕ_4 of the benzenium ion, and β is the resonance integral between ring carbon 2 and the carbon atom in the methyl group.

Next, the electronic structure of the 2,4,6-trimethylbenzenium ion was calculated. The wave functions of the CT configurations in this case are as follows:

$$\left.\begin{aligned}\Psi_{CT_1} &= \frac{1}{\sqrt{2}}[\Psi_{CT_A} + \Psi_{CT_E}]^{***} \\ \Psi_{CT_2} &= \Psi_{CT_C} \\ \Psi_{CT_3} &= \frac{1}{\sqrt{2}}[\Psi_{CT_A} - \Psi_{CT_E}]\end{aligned}\right\} \qquad (19)$$

the first two wave functions being symmetric and the last antisymmetric. The matrix elements between the ground and locally excited configurations and those within the locally excited configurations are the same as in the case of the non-substituted benzenium ion. The matrix elements including the CT configurations are as follows:

$$\begin{aligned}\langle \mathrm{G}|\mathbf{H}|\mathrm{CT}_1\rangle &= \frac{1}{\sqrt{2}}\{\langle \mathrm{G}|\mathbf{H}|\mathrm{CT}_A\rangle \\ &+ \langle \mathrm{G}|\mathbf{H}|\mathrm{CT}_E\rangle\} = 2\langle\phi_4|\mathbf{H}|A\rangle \\ \langle \mathrm{G}|\mathbf{H}|\mathrm{CT}_2\rangle &= \langle \mathrm{G}|\mathbf{H}|\mathrm{CT}_C\rangle \\ &= \sqrt{2}\langle\phi_4|\mathbf{H}|C\rangle\end{aligned}$$

TABLE V. THE LOWER EXCITED STATES OF THE METHYL-SUBSTITUTED BENZENIUM IONS (METHOD I)

2,4,6-Trimethylbenzenium ion (Δ=0.4299 eV.*)

	Calcd.			Obs.	
	eV.	(*f*)**	CT%***	eV.	(ε)
G	0		6.3		
A_1	3.673	(0.268)	9.5	3.493	(11100)
S_1	5.147	(0.321)	25.2	4.844	(8800)
S_2	6.480	(0.247)	56.1		
A_2	6.698	(0.067)	89.1		

2,3,4,6-Tetramethylbenzenium ion (Δ=0.4300 eV.)

	Calcd.			Obs.	
	eV.	(*f*)	CT%	eV.	(ε)
G	0		6.3		
1	3.543	(0.247)	12.9	3.397	(7500)
2	4.992	(0.301)	28.6	4.751	(5350)
3	6.417	(0.126)	95.8		
4	6.514		55.4		

Pentamethylbenzenium ion (Δ=0.4301 eV.)

	Calcd.			Obs.	
	eV.	(*f*)	CT%	eV.	(ε)
G	0		6.3		
A_1	3.438	(0.234)	17.6	3.289	(9800)
S_1	4.813	(0.273)	33.3	4.559	(4300)
S_2	6.411	(0.143)	95.5		
A_2	6.430	(0.012)	100		

* Ground state depression by the methyl substitution.

** Oscillator strength.

*** Percentage of the charge-transfer configurations in the wave function of the state.

TABLE VI. THE LOWER EXCITED STATES OF SOME METHYL-SUBSTITUTED BENZENIUM IONS*

	E, eV.**		Δ, eV.***
o-Toluenium	3.536	5.238	0.146
m-Toluenium	3.373	4.903	0.000
p-Toluenium	3.696	4.976	0.165
2,5-Dimethylbenzenium	3.400	4.994	0.146
2,4-Dimethylbenzenium	3.689	5.070	0.302
3,5-Dimethylbenzenium	3.251	4.658	0.000
2,3-Dimethylbenzenium	3.387	5.045	0.146
3,4-Dimethylbenzenium	3.536	4.817	0.165
2,3,4,5-Tetramethylbenzenium	3.434	4.721	0.302
2,3,5,6-Tetramethylbenzenium	3.290	4.899	0.282

* Calculated by method I.

** The energies of the lower two excited states are shown (the ground state energy is taken to be zero in each case).

*** The ground state energy depression caused by the methyl substitution.

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* See the footnote of Table I for the numbering. Hereafter, the methyl groups substituted at the 2, 3, 4, 5 and 6 positions are denoted as A, B, C, D and E respectively.

** Here A denotes the π-type MO (ϕ_1 of Eq. 12) of the methyl group A.

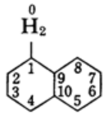
* CT_A and CT_E denote the CT configurations $CT_{A\to E}$ and $CT_{E\to4}$ respectively.

TABLE VII. THE RESULT OF THE SCF CALCULATION

MO Wave

ε, eV.	0	1	2	3	4
−22.3064	0.4834	0.6691	0.2871	0.1661	0.1433
−19.7560	−0.2832	−0.3020	−0.0669	0.1437	0.3425
−18.3811	−0.1025	−0.1019	0.3675	0.5770	0.4239
−16.4698	0.0004	0.0015	−0.3345	−0.3018	0.0985
−16.1632	−0.2015	−0.1308	0.1219	0.2257	0.0553
− 8.4763	−0.2949	−0.0667	0.5461	0.0042	−0.5924
− 5.5295	0.0315	0.0046	−0.4691	0.4624	−0.0429
− 5.0915	−0.2019	0.0354	0.1198	−0.1257	0.4302
− 3.7692	−0.1548	0.0602	0.2678	−0.4815	0.5231
− 1.9361	−0.2310	0.1422	−0.0203	−0.0735	0.1928
4.2848	−0.6549	−0.6357	0.2159	−0.0994	0.0659

* Atoms are numbered in the following way;



$$\left.\begin{aligned}
&\langle 2\to 4|\mathbf{H}|\mathrm{CT}_1\rangle\\
&\quad=\frac{1}{\sqrt{2}}\{\langle 2\to 4|\mathbf{H}|\mathrm{CT}_\mathrm{A}\rangle\\
&\qquad+\langle 2\to 4|\mathbf{H}|\mathrm{CT}_\mathrm{E}\rangle\}\\
&\quad=-\sqrt{2}\langle\phi_2|\mathbf{H}|\mathrm{A}\rangle\\
&\langle 2\to 4|\mathbf{H}|\mathrm{CT}_2\rangle=-\sqrt{2}\langle\phi_2|\mathbf{H}|\mathrm{C}\rangle\\
&\langle 1\to 4|\mathbf{H}|\mathrm{CT}_1\rangle=-\sqrt{2}\langle\phi_1|\mathbf{H}|\mathrm{A}\rangle\\
&\langle 1\to 4|\mathbf{H}|\mathrm{CT}_2\rangle=-\sqrt{2}\langle\phi_1|\mathbf{H}|\mathrm{C}\rangle\\
&\langle 3\to 4|\mathbf{H}|\mathrm{CT}_3\rangle\\
&\quad=\sqrt{2}\langle 3\to 4|\mathbf{H}|\mathrm{CT}_\mathrm{A}\rangle\\
&\quad=-\sqrt{2}\langle\phi_3|\mathbf{H}|\mathrm{A}\rangle
\end{aligned}\right\}\quad(20)$$

All other elements including the CT configurations vanish.

The pentamethyl- and 2, 3, 4, 6-tetramethylbenzenium ions are treated in a similar manner. The results are shown in Table V, together with the experimental data. Some other methyl-substituted benzenium ions are also calculated in the same manner. The results are shown in Table VI.

The Effect of Doubly Excited Configurations

In the last part of this work, we shall examine the effect of doubly excited configurations. Let us take the naphthalenium ion as an example.* There are two possibilities of protonation when naphthalene is dissolved in a HF+BF$_3$ solution; protonation at the α- or at the β-position.[2] The SCF calculation was carried out for the two ions by method I to give π-electron energies of −427.2 eV. and −422.8 eV. for the α- and β-ions respectively. Therefore, the α-ion probably predominates in the HF-BF$_3$ solution.**

TABLE VIII. THE RESULTS OF CONFIGURATION INTERACTION FOR α-NAPHTHALENIUM ION

Calcd.				Obs.	
I[a]		II[b]			
eV.	(f)	eV.	(f)	eV.	(ε)
3.172	(0.053)	2.887	(0.043)	3.024	(shoulder)
3.459	(0.211)	3.277	(0.323)	3.179	(10900)
5.175	(0.139)	4.811	(0.059)	4.430	(14800 ?)
5.406	(0.048)	5.228	(0.024)	4.880	(13000 ?)

a) Singly excited configurations alone.
b) Singly and doubly excited configurations included.

The result of the SCF calculation (method I) for the α-naphthalenium ion is given in Table VII. The results improved by considering the configuration interaction with and without doubly excited configurations are shown in Table VIII.

The 2, 4, 6-trimethyl-, 2, 3, 4, 6-tetramethyl- and pentamethylbenzenium ions are also calculated by means of the configuration interaction, including the doubly excited configurations (Table IX).

Discussion

It can be seen from the results summarized in Tables V, VIII and IX that the calculated

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* The methyl-substituted benzenium ions are not adequate for examining the effect of the doubly excited configurations because of some arbitrariness in the choice of parameters belonging to the CT configurations. The absorption spectrum of the benzenium ion itself has not been observed, so it is necessary to examine the effect in the case of the non-substituted naphthalenium ion.

** The energy of the σ-electron system is approximately the same for both ions, so it is reasonable to compare the total stabilities in terms of the π-electron energies.

FOR α-NAPHTHALENIUM ION (METHOD I)

function*

5	6	7	8	9	10
0.0821	0.0440	0.0614	0.1358	0.3384	0.2067
0.3848	0.2946	0.2432	0.2404	0.2531	0.5198
−0.0643	−0.2139	−0.3172	−0.3400	−0.2410	0.0852
−0.0968	−0.4815	−0.4750	−0.1225	0.3439	0.4236
−0.5271	−0.3397	0.1729	0.5442	0.3453	−0.1869
0.2939	−0.0245	−0.2908	0.0037	0.2925	0.0481
0.1437	0.2825	−0.3712	−0.0271	0.3933	−0.4118
−0.5185	0.4257	0.1587	−0.5492	0.3797	0.0698
0.0801	0.2268	−0.3852	0.2382	0.0361	−0.3618
0.4093	−0.4510	0.4261	−0.3526	0.2683	−0.3669
0.0626	−0.0417	0.0587	−0.1165	0.2610	−0.1241

TABLE IX. THE LOWER EXCITED STATES OF THE METHYL-SUBSTITUTED BENZENIUM IONS BY THE CONFIGURATION INTERACTION INCLUDING THE DOUBLY EXCITED CONFIGURATION[a)]

2, 4, 6-Trimethylbenzenium ion	
E, eV.	f[b)]
3.603	0.231
4.580	0.095
6.317	0.595
2, 3, 4, 6-Tetramethylbenzenium ion	
E, eV.	f
3.481	0.218
4.494	0.102
6.265	0.556
Pentamethylbenzenium ion	
E, eV.	f
3.384	0.205
4.380	0.106
6.209	0.465

a) The ground state energy is taken to be zero in each case.

b) Oscillator strength.

transition energies for the methyl-substituted benzenium ions and for the α-naphthalenium ion are in good agreement with the experimental results. Although the calculated absorption intensities can not be expected to be satisfactorily coincident with the observed values in this type of calculation, the results obtained by considering the configuration interaction including the doubly excited configurations seem to be rather good (The ε values for the 280 mμ and 254 mμ bands of the α-naphthalenium ion do not represent true intensities, since these two bands are superposed with the very intense band with a peak probably below 200 mμ; the true intensities are far less than that of the second transition).

The shift of the 350 mμ and 250 mμ bands upon the methyl substitution is well explained by the present calculation. It has been observed that the substitution of a methyl group for one of the ring hydrogen atoms of the 2, 4, 6-trimethylbenzenium ion causes these two bands to shift toward a longer wavelength by 0.1 eV. The corresponding calculated values are 0.13 (0.12) and 0.16 (0.09) eV. respectively (the results with doubly excited configurations are shown in parentheses). When a methyl group is substituted for the ring hydrogen atom of the 2, 3, 4, 6-tetramethylbenzenium ion, the first and second bands shift toward longer wavelengths by 0.1 and 0.2 eV. respectively. The corresponding calculated values are 0.11 (0.10) and 0.18 (0.11) eV. respectively.

As has been pointed out earlier, the SCE treatment does not have any significant effect on the excitation energy or on the transition intensity of the benzenium ion* (see Table IV).

The results of the NMR absorption measurement, however, show that the charge distribution (0.22, 0.16 and 0.25 for the ortho-, meta- and para-positions respectively[8)]) is more even than that calculated by the usual SCF procedure. In this connection, the charge distribution calculated by method II seems to be more adequate than that calculated by method I (see Fig. 2). However, too much importance should not be attached to this comparison, because there is some ambiguity in determining the charge distributions from the NMR data.

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* The same is true for the methyl-substituted benzenium ions, although the calculated results are not shown in the present paper.

TABLE X. THE LOWER EXCITED STATES OF THE BENZENIUM ION BY SEVERAL METHODS[*1,*2]

Without CI	With CI(SE)[*3]	With CI(DE)[*4]
	Method I	
3.65 (0.271)	3.53 (0.202)	3.54 (0.172)
5.47 (0.601)	5.12 (0.128)	4.36 (0.026)
6.39 (0.537)	6.65 (1.081)	6.76
	Method II	
Without CI	With CI(SE)	With CI(DE)
3.54 (0.298)	3.42 (0.224)	3.37 (0.181)
5.31 (0.620)	4.95 (0.163)	4.07 (0.038)
6.45 (0.536)	6.73 (1.079)	6.34 (0.549)

[*1] Energies are shown in eV. (the ground state is taken to be zero.)

[*2] Oscillator strengths are shown in parenthesis in each case.

[*3] Configuration interaction with the singly excited configurations alone.

[*4] Configuration interaction with the singly and doubly excited configurations.

The inclusion of the doubly excited configurations changes the energies and the wave functions to some extent. The effect is negligible on the first excitation energies and on the intensities of the benzenium, methyl-substituted benzenium and α-naphthalenium ions. However, the effect seems to be significant on the second excited states of the benzenium and methyl-substituted benzenium ions (see Table X for a comparison in the case of the benzenium ion), while there is no significant effect on the four excited states of the α-naphthalenium ion. When we compare the calculated intensity ratio of the methyl-substituted benzenium ions with the experimental results, the calculation with the doubly excited configurations seems to be better.

The results of the semi-empirical calculation of this type always depend on the choice of the parameter β (the resonance integral). The value selected in the present work, -2.39 eV., was originally evaluated to fit to the lowest excitation energy of benzene in the configuration-interaction calculation with singly excited configurations alone.[12)] Anno et al.[19)] examined the effect of the doubly excited configurations in the case of benzene and found the β value of -2.72 eV. to be adequate. If we also take $\beta=-2.72$ eV. in our calculation of the configuration interaction including the doubly excited configurations, the lower excitation energies may become closer to the values evaluated by the configuration-interaction calculation without the doubly excited configuration.

As is shown in Table VI, the methyl substitution at ortho- and para-positions stabilizes the ground state of the benzenium ion by $\delta_o=0.146$ eV. (3.45 kcal./mol.) and $\delta_p=0.165$ eV. (3.89 kcal./mol.) respectively, while the meta-substitution causes little stabilization. An approximate additivity is satisfied for the stabilization due to the methyl-substitution. Thus the following equation can be obtained assuming that the stabilization energy due to the methyl substitution at the meta-position is zero:

$$\Delta=n_o\delta_o+n_p\delta_p$$

where Δ is the total stabilization energy of the methyl-substituted ion, and where n_o and n_p are the numbers of the methyl groups substituted at the ortho- and para-positions respectively. For example, the stabilization in the 2, 4-dimethylbenzenium ion is evaluated at 0.302 eV., while the sum of the stabilization energies of the ortho- and para-methylbenzenium ions is $0.146+0.165=0.311$ eV.

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Appendix

The Valence State Energy of the Carbon Atom.—The carbon atom to which H^+ is attached may be considered to be nearly in the sp^3 hybrid valence state. In the present calculations, a pure $2p\pi$ AO was extracted by taking a linear combination of the sp^3 hybrid AO's, and the valence state ionization potential of the 2p AO of the non-hybridized carbon was used for the orbital energy of the extracted $2p\pi$ AO. In order to examine the validity of this choice, we shall consider here the valence state of the carbon atom in the methane molecule.

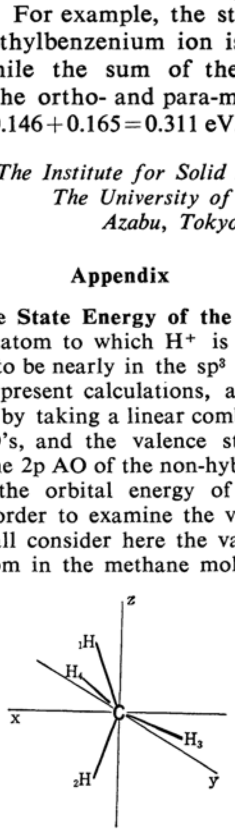

Fig. 3. Location and numbering of the four hydrogen atoms in the methane molecule.

If two hydrogen atoms, H_1 and H_2, are located in the xz plane and H_3 and H_4, in the xy plane (Fig. 3), the electronic states can generaly be represented by the following four bonding MO's:

$$\left.\begin{aligned}\phi_1&=\frac{1}{\sqrt{1+\lambda_1^2}}\left[s+\frac{\lambda_1}{2}(h_1+h_2+h_3+h_4)\right]\\ \phi_2&=\frac{1}{\sqrt{1+\lambda_2^2}}\left[x+\frac{\lambda_2}{2}(h_1+h_2-h_3-h_4)\right]\\ \phi_3&=\frac{1}{\sqrt{1+\lambda_3^2}}\left[y+\frac{\lambda_3}{\sqrt{2}}(h_3-h_4)\right]\\ \phi_4&=\frac{1}{\sqrt{1+\lambda_4^2}}\left[z+\frac{\lambda_4}{\sqrt{2}}(h_1-h_2)\right]\end{aligned}\right\}\quad(21)$$

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19) T. Anno and A. Sado, *J. Chem. Phys.*, **39**, 2293 (1963).

and the corresponding antibonding MO's. (Here s, x, y and z denote the 2s, 2px, 2py and 2pz AO's of carbon respectively, and h_i denotes the 1s AO of hydrogen H_i.) If the ideal sp^3 hybridization is achieved, the relation:

$$\lambda_1=\lambda_2=\lambda_3=\lambda_4=1$$

must hold. In this case the ground state energy is;

$$E=2\sum_{i=1}^{4}I_i+\sum_{i=1}^{4}J_{ii}+4\sum_{i<j}J_{ij}-2\sum_{i<j}K_{ij} \tag{22}$$

The orbital energy of the MO ϕ_4 is:

$$\begin{aligned}\varepsilon_4&=I_4+\sum_{j=1}^{4}(2J_{4j}-K_{4j})\\&=\frac{1}{2}\alpha_z+\frac{1}{4}J_{zz}+\frac{1}{2}(J_{yz}+J_{xz}+J_{sz})\\&\quad-\frac{1}{4}(K_{yz}+J_{xz}+J_{sz})\\&\quad+\{\text{Integrals belonging to the hydrogen 1s AO's}\}\\&\quad+\{\text{Integrals representing the interaction between the carbon and hydrogens}\}\end{aligned} \tag{23}$$

If we define:

$$W_z=\alpha_z+(J_{yz}+J_{xz}+J_{sz})-\frac{1}{2}(K_{yz}+K_{xz}+K_{sz}) \tag{24}$$

then

$$\varepsilon_4=\frac{1}{2}W_z+\frac{1}{4}J_{zz}+\cdots\cdots \tag{25}$$

In the conventional π-electron treatment, W_z is taken to be the minus of the valence state ionization potential of the carbon 2p AO.

The valence state ionization potential is determined from the atomic spectroscopy data as follows. For example, we consider first the ionization potential for removing an electron from the 2p AO in the non-hybridized carbon (in $(2s)(2p)^3$ configuration). The valence state energies of C and C^+ are;

$$E=\alpha_s+3\alpha_p+3(J_{sp}+J_{pp'})-\frac{3}{2}(K_{sp}+K_{pp'})$$

$$E^+=\alpha_s^++2\alpha_p^++2J_{sp}^++J_{pp'}^+-K_{sp}^+-\frac{1}{2}K_{pp'}^+$$

and the ionization potential in question is:

$$\begin{aligned}-I_p(\mathrm{sxyz}\rightarrow\mathrm{sxy})&=\alpha_p+J_{sp}+2J_{pp'}\\&\quad-\frac{1}{2}K_{sp}-K_{pp'}+\varDelta\end{aligned}$$

where $\varDelta$ is the sum of the differences in the corresponding integrals in C and C^+ caused by the change in the distribution of the electron cloud (the change in the effective charge, Z, if we consider the Slater atomic orbitals).

We will consider next the ionization of the electron in the 2pπ AO in sp-hybridized carbon:

$$\begin{aligned}E&=\alpha_{d_1}+\alpha_{d_2}+\alpha_y+\alpha_z+J_{d_1y}+J_{d_1z}+J_{d_2y}+J_{d_2z}\\&\quad+J_{d_1d_2}+J_{yz}-\frac{1}{2}(K_{d_1y}+K_{d_1z}+K_{d_2y}+K_{d_2z}\\&\quad+K_{d_1d_2}+K_{yz})\\&=\alpha_s+3\alpha_p+\frac{1}{8}(J_{ss}+J_{pp})+\frac{11}{4}J_{sp}+3J_{pp'}\\&\quad-2K_{sp}-\frac{3}{2}K_{pp'}\end{aligned}$$

$$\begin{aligned}E^+&=\alpha_{d_1}^++\alpha_{d_2}^++\alpha_y^++J_{d_1y}^++J_{d_2y}^++J_{d_1d_2}^+\\&\quad-\frac{1}{2}(K_{d_1y}^++K_{d_2y}^++K_{d_1d_2}^+)\\&=\alpha_s^++2\alpha_p^++\frac{1}{8}(J_{ss}^++J_{pp}^+)+\frac{7}{4}J_{sp}^++J_{pp'}^+\\&\quad-\frac{3}{2}K_{sp}^+-\frac{1}{2}K_{pp'}^+\end{aligned}$$

$$\begin{aligned}\therefore\quad -I_p(\mathrm{d_1d_2yz}\rightarrow\mathrm{d_1d_2y})&=E-E^+\\&=\alpha_p+J_{sp}+2J_{pp'}-\frac{1}{2}K_{sp}-K_{pp'}+\varDelta\end{aligned}$$

Here d_1 and d_2 are the digonal orbitals:

$$d_1=\frac{1}{\sqrt{2}}(s+x)$$

$$d_2=\frac{1}{\sqrt{2}}(s-x)$$

Therefore, if we neglect $\varDelta$, $-I_p(\mathrm{d_1d_2yz}\rightarrow\mathrm{d_1d_2y})$, $-I_p(\mathrm{sxyz}\rightarrow\mathrm{sxy})$ and W_z should be equal. The same equality can be proved for $-I_p(\mathrm{t_1t_2t_3z}\rightarrow\mathrm{t_1t_2t_3})$.

There is a little difference between the ionization potentials of the various hybridization states tabulated in the references:[15]

	I_p, eV.
sxyz → sxy	11.31
d_1d_2yz → d_1d_2y	11.24
$t_1t_2t_3z$ → $t_1t_2t_3$	11.22

It is possible to calculate the total π-electron state of the CH_4 molecule starting from several sets of orbitals; that is, non-hybridized (s, p_x, p_y and p_z), digonally-hybridized (d_1, d_2, y and z), trigonally-hybridized (t_1, t_2, t_3 and z) or tetragonally-hybridized (T_1, T_2, T_3 and T_4) AO's. There are some differences in the orbital energies (the ionization potentials) of these orbitals depending on whether we choose one set of orbitals or another. For example, the ionization potential of the $2p_z$ orbital differs to some extent (see the data tabulated above) according to the choice of the set of σ-orbitals. This difference, however, may be canceled by the difference in σ-π interaction caused by the difference in the type of σ-orbitals; if we adopt an approximation or a set of parameters in common, the calculations based on different hybridization states give the exactly same result.

In the present case, however, we adopt the π-electron approximation, so the above-mentioned cancellation does not appear exactly. Fortunately, the difference, caused by the choice of the σ-orbitals (caused by the difference in $\varDelta$) is very small, and no significant effect may be expected even if we chose any value of the ionization potentials tabulated above.