The Electronic Structure of the t-Butyl Cation

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There is considerable experimental evidence to show that methyl or other alkyl substituents increase the stability of hydrocarbon molecules.[1-10] The stabilization may be attributed in general to the steric hindrance, inductive effect and hyperconjugation. Although in the case of neutral molecules there is a little doubt about the stabilization effect of hyperconjugation, the effect seems to be vivid and extensive in the case of carbonium ions.[9,10]

In the present paper, we have studied the electronic structure of the *t*-butyl cation, paying special attention to the hyperconjugation effect. One of ourmain purposes is to estimate as accurately as possible the hyperconjugation effect on the electronic structure of the carbonium ion. The fact that the *t*-butyl cation shows a strong absorption band at $290\sim295\,\mathrm{m}\mu$[11,12] in spite of the complete absence of any unsaturated bond may be unexpected from the π-electron theory developed so far and seems to be closely related to the hyperconjugation effect. Another important aim of the present study is to clarify the nature of this band.

The Configuration of the *t*-Butyl Cation

There is a little doubt about the configuration of the *t*-butyl cation.[9,11,12] In the present calculation, however, the ion is reasonably assumed to take a planar configuration, the central carbon atom being in a sp^2 hybrid valence state and a 2pπ AO perpendicular to the molecular plane being vacant. The configuration and the numbering of atoms are shown in Fig. 1.

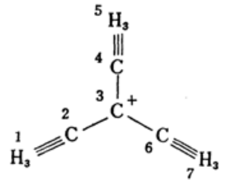
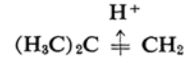


Fig. 1. The structure and numbering of *t*-butyl cation.
The distance between carbon atoms 2 and 3 is assumed to be 1.52Å (same as the distance between the carbon of methyl group and the ring carbon in toluene). The methyl group is assumed to have the same geometrical configuration as methane ($\angle$HCH$=109°28'$ and $R_{\mathrm{C-H}}=1.091$Å).

Another possibility is a configuration of the π-complex type:



$$(\mathrm{H_3C})_2\mathrm{C} \overset{\mathrm{H^+}}{\overset{\uparrow}{=}} \mathrm{CH_2}$$

This possibility, however, may be disregarded because $\mathrm{B(CH_3)_3}$, which is isoelectronic with the *t*-butyl cation, has a planar configuration.[12]

According to the usual treatment of hyperconjugation,[13] the following three pseudo AO's can be constructed from the 1s AO's of the hydrogen atoms:

$$\left.\begin{aligned} \chi_1&=N_1\cdot[\chi_a-1/2(\chi_b+\chi_c)] \\ \lambda_2&=N_2\cdot(\chi_b-\chi_c) \\ \lambda_3&=N_3\cdot(\chi_a+\chi_b+\chi_c) \end{aligned}\right\} \qquad (1)$$

where χ_1, λ_2 and λ_3 are three independent and orthonormal pseudo AO's, χ_a, χ_b and χ_c are the hydrogen 1s AO's, and N_i's are normalization constants. Of these, χ_1 can be regarded as a pπ-type pseudo AO antisymmetric with regard to the molecular plane; it can construct a π-type MO together with the 2pπ AO of the carbon atom in the methyl group.[14]

1a) V. A. Crawford, *Quart. Revs.*, **3**, 226 (1949).
1b) C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, **1953**, 2052.
1c) V. A. Crawford, ibid., **1953**, 2058, 2061.
2a) Y. I'Haya, *J. Chem. Phys.*, **23**, 1165 (1955).
2b) Y. I'Haya, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 314 (1956).
3a) T. Morita, *J. Chem. Phys.*, **27**, 1442 (1957).
3b) T. Morita, This Bulletin, **31**, 322 (1958).
3c) T. Morita, ibid., **32**, 893 (1959).
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5) Wei-Chuwan Lin, *J. Chinese Chem. Soc.*, **4**, 14 (1957).
6) R. S. Mulliken, *Tetrahedron*, **5**, 253 (1959).
7) R. S. Mulliken, ibid., **6**, 68 (1959).
8) R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).
9) N. Muller and R. S. Mulliken, ibid., **80**, 3489 (1958).
10) N. Muller, L. W. Pickett and R. S. Mulliken, ibid., **76**, 4770 (1954).
11) J. Rosenbaum and M. C. R. Symons, *Mol. Phys.*, **3**, 205 (1960).
12) J. Rosenbaum and M. C. R. Symons, *Proc. Chem. Soc.*, **1959**, 92.
13) C. A. Coulson, "Valence," Oxford Universtiy Press, Oxford (1961), p. 360.
14) The carbon atom is in a sp^3 hybrid valence state. However, taking a proper combination of the hybrid orbitals, we can tentatively obtain a pure 2pπ AO whose node is in the molecular plane.

TABLE I. THE VALENCE STATE ENERGIES AND IONIZATION POTENTIAL OF H_3 GROUP[a,b]

	I_{χ_1}	I_{λ_2}	I_{λ_3}	J_{12}	J_{23}	J_{31}	K_{12}	K_{23}	K_{31}
^4E	1	1	1	1	1	1	-1	-1	-1
^2E	1	1	1	1	1	1	1	$-1/2$	$-1/2$
$^2E'$	1	1	1	1	1	1	-1	$1/2$	$1/2$
E	1	1	1	1	1	1	$-1/2$	$-1/2$	$-1/2$
$^3E^+$	0	1	1	0	1	0	0	-1	0
$^1E^+$	0	1	1	0	1	0	0	1	0
E^+	0	1	1	0	1	0	0	$-1/2$	0
$-I_p(\chi_1)$	1	0	0	1	0	1	$-1/2$	0	$-1/2$

a) The numbers in a given row give the coefficients of the integrals, I's, J's and K's, in the formula representing the energy listed in the first column.

b)

$$I_\mu=\int\mu(1)H_h^c(1)\mu(1)\mathrm{d}v$$

where $\mu=\chi_1$, λ_2 or λ_3 and $H_h^c(1)=T(1)-\sum_{p=a,\,b,\,c}e^2/R_p(1)$

$T(1)$ and $R_p(1)$ being the kinetic energy operator and the distance between the electron (1) and the hydrogen core p respectively. Coulomb and exchange repulsion integrals are defined by

$$J_{\mu\mu'}=\int\mu(1)\mu(1)e^2/r_{12}\mu'(2)\mu'(2)\mathrm{d}v$$

and

$$K_{\mu\mu'}=\int\mu(1)\mu'(1)e^2/r_{12}\mu(2)\mu'(2)\mathrm{d}v$$

where μ and μ' are χ_1, λ_2 or λ_3.

The Ionization Potential of the H_3 Group

In the present calculation, the *t*-butyl cation was separated into four components; namely, the three methyl groups and the carbon ion with a positive charge. The interaction among them was accounted by the configurational interaction among several electron configurations constructed by putting the electrons into the orbitals of the components. In order to accomplish this kind of calculation, it is necessary to obtain accurate knowledge about the wave functions and energy values of the components. Therefore, we undertook first to evaluate the energy levels and wave functions of the H_3 group necessary for the calculation of the methyl group.

A neutral H_3 group in a methyl group has one electron in each of the pseudo AO's, χ_1, λ_2 and λ_3, so that following wave functions can be constructed as antisymmetrized wave functions:

quartet: $^4\psi=|\chi_1,\lambda_2,\lambda_3|$ 15) (2)

$$\text{doublet: } {}^2\psi=(2)^{-1/2}\{|\chi_1,\overline{\lambda_2},\lambda_3|+|\lambda_2,\overline{\chi_1},\lambda_3|\} \tag{3}$$

$$^2\psi'=(6)^{-1/2}\{|\chi_1,\overline{\lambda_2},\lambda_3|-|\lambda_2,\overline{\chi_1},\lambda_3|+2|\chi_1,\overline{\lambda_3},\lambda_2|\} \tag{4}$$

The energies for the states, ^4E, ^2E and $^2E'$, can be written in terms of integrals over the pseudo AO's, as is summarized in Table I. A valence state energy, E, of the neutral H_3 group can be calculated as an average of them over spin natural abundance;

$$E=(4\cdot{}^4E+2\cdot{}^2E+2\cdot{}^2E')/8 \tag{5}$$

Similarly, the H_3^+ ion, in which an electron in χ_1 is removed, has two electronic states, corresponding to the singlet and triplet states, whose energies are represented by $^1E^+$ and $^3E^+$ respectively. An average energy over spin natural abundance is:

$$E^+=(^1E^++3\cdot{}^3E^+)/4 \tag{6}$$

Therefore, the valence state ionization energy of an electron in χ_1 is:

$$I_p(\chi_1)=E^+-E \tag{7}$$

Now, taking Slater-type 1s AO's with the effective charge $Z=1$ for χ_a, χ_b and χ_c, the integrals in Table I can be reduced to integrals over AO's;

$$I_{\chi_1}=(\alpha_H-\beta_H)/(1-S_H) \tag{8}$$

$$\alpha_H=\int\chi_a(1)H_h^c(1)\chi_a(1)\mathrm{d}v^{16)}=W_H+2\langle b\mid aa\rangle \tag{9}$$

$$\beta_H=\int\chi_a(1)H_h^c(1)\chi_b(1)\mathrm{d}v=S_HW_H+\langle b\mid ab\rangle+\langle c\mid ab\rangle \tag{10}$$

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15) An abbreviated notation of the antisymmetrized wave function. For example,

$$|a,b,\bar{c}|=(3!)^{-1/2}\begin{vmatrix}a(1)\alpha(1), & b(1)\alpha(1), & c(1)\beta(1)\\ a(2)\alpha(2), & b(2)\alpha(2), & c(2)\beta(2)\\ a(3)\alpha(3), & b(3)\alpha(3), & c(3)\beta(3)\end{vmatrix}$$

16) See the footnote of Table I for the definition of $H_h^c(1)$.

TABLE II. ELECTRONIC REPULSION INTEGRALS IN TERMS OF THE INTEGRALS OVER ATOMIC ORBITALS a)

	eV.					
	$(aa\|aa)$ b) 17.0025	$(aa\|bb)$ b) 7.8892	$(aa\|22)$ c) 12.2564	$(bb\|22)$ c) 11.3329	$(22\|22)$ b) 16.9304	eV.
J_{12}	1/6	5/6	—	—	—	9.4081
J_{23}	1/3	2/3	—	—	—	10.9270
J_{31}	1/3	2/3	—	—	—	10.9270
K_{12}	1/6	$-1/6$	—	—	—	1.5189
K_{23}	x d)	$-x$	—	—	—	3.5165
K_{31}	x	$-x$	—	—	—	3.5165
$(22\|\lambda_2\lambda_2)$	—	—	—	1	—	11.3329
$(22\|\lambda_3\lambda_3)$	—	—	1/3	2/3	—	11.6407
$(12\|\lambda_2\lambda_2)$	$S/12$ e)	$5S/12$	—	$S/2$	—	6.6911
$(12\|\lambda_3\lambda_3)$	$S/6$	$S/3$	$S/6$	$S/3$	—	7.2803
$(11\|11)$	1/2	1/2	—	—	—	12.4459
$(11\|22)$	—	—	2/3	1/3	—	11.9486
$(11\|12)$	$S/4$	$S/4$	$S/3$	$S/6$	—	7.8697
$(12\|12)$	$S^2/8$	$S^2/8$	$S^2/3$	$S^2/6$	$S^2/4$	5.5442
$(12\|22)$	—	—	$S/3$	$S/6$	$S/2$	9.3164

a) The first column contains integrals including the pseudo AO's. J_{ij}'s and K_{ij}'s are defined in Table I. For the last nine integrals in the first column, notations 1 or 2 means χ_1 or χ_2 respectively.
For example,

$$(12|\lambda_2\lambda_2)=\int\chi_1(1)\chi_2(1)e^2/r_{12}\lambda_2(2)\lambda_2(2)\mathrm{d}v$$

They are reduced into the integrals over AO's by means of Mulliken's approximation. The latters are shown in the first row, for example,

$$(aa|22)=\int\chi_a(1)\chi_a(1)e^2/r_{12}\chi_2(2)\chi_2(2)\mathrm{d}v$$

Calculated values for the integrals in the first column are shown in the last column (See also the footnote a of the Table I).

b) Values of $(aa|aa)$, $(aa|bb)$ and $(22|22)$ are taken from the table given by Roothaan.17)

c) See Appendix for the evaluation of $(aa|22)$ and $(bb|22)$.

d) $x=(2+S_H)^2/12(1+2S_H)(1-S_H)$.

e) $S=\int\chi_1(1)\chi_2(1)\mathrm{d}v$.

TABLE III. CORE ATTRACTION AND OTHER BASIC INTEGRALS a)

	eV.					
	$\langle 2\|aa\rangle$ -12.5410	$\langle a\|aa\rangle$ -27.2040	$\langle a\|bb\rangle$ -8.0385	$\langle a\|22\rangle$ -14.6474	$\langle b\|22\rangle$ -11.9043	eV.
$\langle 2\|11\rangle$	1	—	—	—	—	-12.5410
$\langle a\|12\rangle$	—	$S/3$ b)	$S/6$	$S/2$	—	-11.4404
$\langle b\|12\rangle$	—	$S/12$	$5S/12$	—	$S/2$	-7.4641

	eV.		eV.
$\langle a\|bc\rangle$	-2.2548	$\langle a\|ab\rangle$	-4.1015
$-W_H$ c)	13.595	$-W_2$ c)	11.28
S_H d)	0.2805	S_{12} d)	0.6452

a) Values for basic core integrals are shown in the second row of the first part of this table. See Appendix for the evaluation of these integrals. See also Table I, note a.

b) $S=S_{12}=\int\chi_1(1)\chi_2(1)\mathrm{d}v$.

c) W_H and W_2 are experimental ionization energies of hydrogen 1s and carbon 2p AO respectively.

d) Taken from the table given by Mulliken et al.18)

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17) C. C. J. Roothaan, "Special Issue of Technical Report of Laboratory of Molecular Structure and Spectroscopy," The University of Chicago (1955).

18) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

where W_H is the orbital energy of hydrogen 1s AO, S_H is the overlap integral between two hydrogen 1s AO's, and the integrals of the $\langle r \mid pq\rangle$ type are defined by:

$$\langle r \mid pq\rangle = -\int \chi_p(1)e^2/R_r(1)\chi_q(1)\mathrm{d}v \qquad (11)$$

Here $R_r(1)$ is the distance between the electron (1) and the r-th hydrogen core. The electronic repulsion integrals, $J_{\mu\mu'}$ and $K_{\mu\mu'}$ can be reduced to two integrals over atomic orbitals by using Mulliken's approximation,[19] as shown in Table II. Using theoretically calculated values for the integrals over atomic orbitals (Table III), the ionization potential, $I_p(\chi_1)$, is evaluated at 9.2880 eV.

The Ionization Potential of the Methyl Group

The next step in the calculation is to consider the interaction between the pseudo π AO, χ_1, and the 2pπ AO of the carbon atom of the methyl group—in other words, to treat the methyl group as an unsaturated diatomic molecule. The actual calculation was carried out by the aid of the SCF MO method.[20,21]

Denoting carbon 2pπ AO in a methyl group by χ_2, the molecular orbital in question has the form:

$$\varphi = c_1\chi_1 + c_2\chi_2 \qquad (12)$$

The familiar SCF matrix elements in this case are:

$$L_{pq} = I_{pq} + G_{pq} \qquad (13)$$

$$I_{pq} = \int \chi_p(1)H_m^c(1)\chi_q(1)\mathrm{d}v \qquad (14)$$

$$G_{pq} = \int \varphi(1)\varphi(1)e^2/r_{12}\chi_p(2)\chi_q(2)\mathrm{d}v \qquad (15)$$

Here,

$$H_m^c(1) = T(1) + A(1) - e^2/R_2(1)$$

$T(1)$ and $A(1)$ being a kinetic energy operator and a Coulomb potential from the H_3 core (including attractions from three hydrogen cores and repulsions from two electrons in λ_2 and λ_3) respectively.

$$\left.\begin{aligned} I_{11} &= W_1 + \langle 2 \mid 11\rangle \\ I_{22} &= W_2 + (22 \mid \lambda_2\lambda_2) + (22 \mid \lambda_3\lambda_3) \\ &\quad + \langle a \mid 22\rangle + 2\langle b \mid 22\rangle \\ I_{12} &= SW_2 + (12 \mid \lambda_2\lambda_2) + (12 \mid \lambda_3\lambda_3) \\ &\quad + \langle a \mid 12\rangle + 2\langle b \mid 12\rangle \end{aligned}\right\} \qquad (16)$$

Also,

$$\left.\begin{aligned} G_{11} &= c_1^2(11 \mid 11) + 2c_1c_2(12 \mid 11) + c_2^2(22 \mid 11) \\ G_{22} &= c_1^2(11 \mid 22) + 2c_1c_2(12 \mid 22) + c_2^2(22 \mid 22) \\ G_{12} &= c_1^2(11 \mid 12) + 2c_1c_2(12 \mid 12) + c_2^2(22 \mid 12) \end{aligned}\right\} \qquad (17)$$

Here W_1 corresponds to $I_p(\chi_1)$ computed above. W_2 is the 2p atomic orbital energy of carbon and can be taken to be -11.28 eV.[19] (the ionization potential of carbon). The other integrals are given in Tables II and III.

After the usual SCF procedure had been performed, the following secular equation was finally obtained:

$$\begin{vmatrix} 9.6837+\varepsilon, & 10.8957+0.6452\varepsilon \\ 10.8957+0.6452\varepsilon, & 11.6492+\varepsilon \end{vmatrix} = 0 \qquad (18)$$

The resultant orbital energies and molecular orbitals are:

$$\varepsilon_1 = -13.245\ \text{eV.} \quad \varphi_1 = 0.4362\chi_1 + 0.6619\chi_2 \qquad (19)$$

and,

$$\varepsilon_2 = +0.708\ \text{eV.} \quad \varphi_2 = 1.2347\chi_1 - 1.1299\chi_2 \qquad (20)$$

The ionization potential to remove an electron from the orbital φ_1 is the minus of the lower energy:

$$I_p(\text{methyl}) = 13.245\ \text{eV.}$$

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Now let us consider the interaction among the three methyl groups and the central carbon atom. The wave function for the ground configuration is

$$\Phi_G = |A, \overline{A}, B, \overline{B}, C, \overline{C}| \qquad (21)$$

where A, B and C are abbreviated notations of φ_A, φ_B and φ_C, the pseudo π molecular orbitals of the three methyl groups.[22] In the ground configuration, the $+1$ charge is localized on the central carbon atom.

In addition to the above ground configuration, we must take the three CT (charge-transfer) configurations into account:

$$\left.\begin{aligned} \Phi_1 &= (2)^{-1/2}\cdot\{|A, \overline{3}, B, \overline{B}, C, \overline{C}| \\ &\quad + |3, \overline{A}, B, \overline{B}, C, \overline{C}|\} \\ \Phi_2 &= (2)^{-1/2}\cdot\{|A, \overline{A}, B, \overline{3}, C, \overline{C}| \\ &\quad + |A, \overline{A}, 3, \overline{B}, C, \overline{C}|\} \\ \Phi_3 &= (2)^{-1/2}\cdot\{|A, \overline{A}, B, \overline{B}, C, \overline{3}| \\ &\quad + |A, \overline{A}, B, \overline{B}, 3, \overline{C}|\} \end{aligned}\right\} \qquad (22)$$

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[19] R. S. Mulliken, *J. chim. phys.*, **46**, 497 (1949).

[20] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

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

[22] φ is defined by Eq. 19. In this case, however, it is renormalized according to the zero-overlap approximation;

$$\varphi = 0.5505\chi_1 + 0.8348\chi_2$$

Similarly, φ_B and φ_C can be constructed using the AO's (and pseudo AO's) χ_4 and χ_5, and χ_6 and χ_7, respectively.

where number 3 is an abbreviated notation of χ_3, the $2p\pi$ AO of the central carbon atom. Locally excited configurations may be omitted because the excitation energies are considerably high.[23]

The following three new wave functions can be constructed by taking linear combinations of Φ_1, Φ_2 and Φ_3:

$$\left.\begin{aligned} \Phi_{\mathrm{I}} &= (3)^{-1/2}\cdot\{\Phi_1+\Phi_2+\Phi_3\} \\ \Phi_{\mathrm{II}} &= (2)^{-1/2}\cdot\{\Phi_2-\Phi_3\} \\ \Phi_{\mathrm{III}} &= (6)^{-1/2}\cdot\{2\cdot\Phi_1-(\Phi_2+\Phi_3)\} \end{aligned}\right\} \tag{23}$$

Among these, only Φ_{I} interacts with Φ_{G}, so that the ground state energy is obtained as the lower root of the secular equation:

$$\begin{vmatrix} -E, & H_{\mathrm{GI}} \\ H_{\mathrm{GI}}, & (H_{\mathrm{II}}-H_{\mathrm{GG}})-E \end{vmatrix}=0 \tag{24}$$

H_{GG} and H_{II} are defined by

$$H_{\mathrm{GG}}=\int \Phi_{\mathrm{G}} H \Phi_{\mathrm{G}} \mathrm{d}v \tag{25}$$

and

$$H_{\mathrm{II}}=\int \Phi_{\mathrm{I}} H \Phi_{\mathrm{I}} \mathrm{d}v \tag{26}$$

where H is the total electronic Hamiltonian of the system. Each element in Eq. 24 can be represented as follows:

$$H_{\mathrm{II}}-H_{\mathrm{GG}}=-I_p(3)+I_p(\text{methyl}) \tag{27}$$

$$H_{\mathrm{GI}}=2.044\cdot\beta \tag{28}$$

where $I_p(3)$ is the ionization potential of an electron in χ_3, $I_p(\text{methyl})$ is the ionization potential of the methyl group computed above, and β is the resonance integral between the carbon $2p\pi$ AO of a methyl group and χ_3.[24]

Φ_{II} and Φ_{III} both correspond to the lower excited state (doubly degenerate) and their energies (taking H_{GG} as the standard of energy) are:

$$\begin{aligned} E_{\mathrm{L}} &= H_{\mathrm{II\ II}}-H_{\mathrm{GG}} \\ &= H_{\mathrm{III\ III}}-H_{\mathrm{GG}} \\ &= -I_p(3)+I_p(\text{methyl})^{25)} \end{aligned}$$

Now taking $I_p(3)=11.28$ eV.[19] and $I_p(\text{methyl})=13.245$ eV.;

$$H_{\mathrm{II}}-H_{\mathrm{GG}}=E_{\mathrm{L}}=1.965\ \text{eV}. \tag{29}$$

If we assume $\beta=-1.52$ eV. which is reasonable as will be described later (in Discussion), the roots of Eq. 24 are calculated as follows:

$$E_{\mathrm{G}}=-2.28\ \text{eV}.$$

$$E_{\mathrm{U}}=4.24\ \text{eV}.$$

The first excitation energy is

$$E_{\mathrm{L}}-E_{\mathrm{G}}=4.25\ \text{eV}.$$

which is in good agreement with the empirical value ($290\sim295$ mμ $=4.27\sim4.20$ eV.) obtained by Symons et al.[11,12] (see Fig. 2).

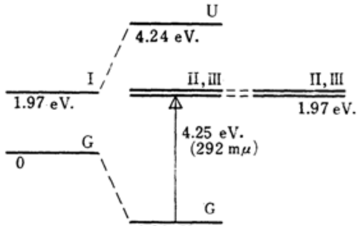

Fig. 2. The energy diagrams of the *t*-butyl cation.

The wave functions for the states are:

$$\left.\begin{aligned} \Psi_{\mathrm{G}} &= 0.8067\Phi_{\mathrm{G}}+0.5909\Phi_{\mathrm{I}} \\ \Psi_{\mathrm{L}_1} &= \Phi_{\mathrm{II}} \\ \Psi_{\mathrm{L}_2} &= \Phi_{\mathrm{III}} \\ \Psi_{\mathrm{U}} &= 0.5909\Phi_{\mathrm{I}}-0.8067\Phi_{\mathrm{G}} \end{aligned}\right. \quad \text{(doubly degenerate)} \tag{30}$$

The charge distributions for the ground and first excited states calculated from the above wave functions are shown in Fig. 3. The transition moments for the $\Psi_{\mathrm{G}}\rightarrow\Psi_{\mathrm{L}_1}$ and $\Psi_{\mathrm{G}}\rightarrow\Psi_{\mathrm{L}_2}$ transitions ($\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ respectively) were evaluated as:

$$|\boldsymbol{\mu}_1|=|\boldsymbol{\mu}_2|=0.681\ \text{Å}$$

by the usual formula

$$\boldsymbol{\mu}_{\mathrm{K}}=\int \Psi_{\mathrm{LK}} \sum_i \boldsymbol{r}_i \Psi_{\mathrm{G}} \mathrm{d}v$$

The oscillator strength for the first excitation was determined to be 0.346 from the equation:

$$f=(1.085\times10^{-5})\nu G|\boldsymbol{\mu}^2|$$

where ν is the wave number (in cm^{-1} units) for the transition and G is a degeneracy factor (in this case, $G=2$).[26]

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[23] The local excitation energy in the methyl group is given by

$$\varepsilon_2-\varepsilon_1-J_{\varphi_1\varphi_2}+2K_{\varphi_1\varphi_2}=5.228\ \text{eV}.$$

where ε_1 and ε_2 are the lower and upper roots of Eq. 18 and

$$J_{\varphi_1\varphi_2}=\int \varphi_1(1)\varphi_1(1)\mathrm{e}^2/r_{12}\varphi_2(2)\varphi_2(2)\mathrm{d}v$$

$$K_{\varphi_1\varphi_2}=\int \varphi_1(1)\varphi_2(1)\mathrm{e}^2/r_{12}\varphi_1(2)\varphi_2(2)\mathrm{d}v$$

The values of these integrals can be calculated using the basic integrals in Table II:

$$J_{\varphi_1\varphi_2}=13.2592\ \text{eV}.$$

$$K_{\varphi_1\varphi_2}=2.2670\ \text{eV}.$$

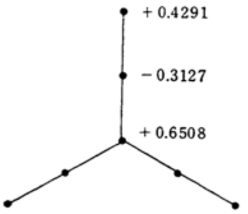
The effect of the locally excited configurations will be discussed below.

[24] See Appendix for the reduction of $H_{\mathrm{II}}-H_{\mathrm{GG}}$ and H_{GI}.

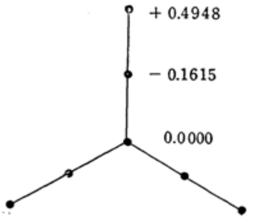
[25] Note $H_{\mathrm{II}}=H_{\mathrm{II\ II}}=H_{\mathrm{III\ III}}$ in this approximation.

[26] In the evaluation of charge distributions and transition moments, the assumption of zero-differential overlap[27] is invoked. This is in accordance with the fact that overlap integrals are disregarded formally in the above calculation of the interactions between the configurations, G, L_1, L_2 and U.

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



(a) The ground state.



(b) The first excited state.

Fig. 3. The charge distributions of the *t*-butyl cation.

Finally, the hyperconjugation energy, $-E_G$, of the *t*-butyl cation can be obtained as follows:

$$\begin{aligned} -E_G &= 2.28\ \text{eV.} \\ &= 53.9\ \text{kcal./mol.} \end{aligned}$$

Discussion

In the above calculation, the resonance integral, β, was determined to be -1.52 eV. If one plots the resonance integrals against the overlap integrals for this cation,[28] benzene, ethylene and butadiene,[29] all the points fit a straight line well. This seems to mean that the β value assumed for the *t*-butyl cation is reasonable.

From the absorption band of the *t*-butyl cation observed by Symons et al.,[11,12] the oscillator strength can be determined as follows:

$$\begin{aligned} f_{\text{obs.}} &= 4.32\times 10^{-9}\cdot \varepsilon_{\max}\cdot \varDelta H \\ &= 0.13 \end{aligned} \tag{31}$$

where $\varepsilon_{\max}$ and $\varDelta H$ are the peak molar extinction coefficient and the half-breadth in cm^{-1} units respectively. The theoretical f value (0.346) is about two or three times greater than the observed value. A discrepancy of this order of magnitude is usually found between observed and theoretical oscillator strength values. Moreover, the observed value is based on the assumption that the parent molecules (butyl alcohols, isobutene and *t*-butyl halides) can be completely converted into the cation in concentrated sulfuric acid. If they are not converted completely, or if the cation undergoes some futher reactions, the "apparent" extinction coefficient will be lower than the real one. In this connection, a further experimental check may be needed for a more quantitative comparison between the theoretical and observed oscillator strength values.

The calculated hyperconjugation energy (53.9 kcal./mol.) may be said to be unexpectedly large. However, this large stabilization energy due to hyperconjugation is thought to be reasonable from the experimental point of view. Franklin et al.[30] obtained the value 84 kcal./mol. for the stabilization energy of the *t*-butyl cation. Although there is a little question whether or not the observed stabilization energy corresponds to the *t*-butyl cation with the planar structure,[9] the calculated and observed results on the stabilization energy seem to show that the hyperconjugation effect is extraordinarily large in this cation.

As was mentioned in the introductory part of the present paper, the appearance of the absorption band in the 290 mμ region is difficult to be accounted for in molecules without any unsaturated bond. However, it has been established by the present calculations that the absorption can be understood in terms of the electron releasing ability (hyperconjugation effect) of the methyl groups. The excited state of the 290 mμ band is composed of the charge-transfer configurations caused by the electron transfer from the methyl groups towards the central carbon cation. Therefore, the transition corresponding to the 290 mμ band is accompanied by an electron transfer in the same direction. This may easily be seen from the electron distributions in the ground and first excited states shown in Fig. 3. In this interpretation, the band may be regarded as the intramolecular charge-transfer absorption,[31,32] the methyl groups and the carbon cation being the electron donor and the acceptor respectively.

Finally, let us check the effect of locally excited configurations within the methyl groups which were excluded in the above-mentioned calculations. The wave functions for these configurations are:

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[28] $S_{23}=0.211$ for the overlap integral between a methyl group and the central carbon atom.

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

[30] L. L. Franklin and H. E. Lumpkin, ibid., **20**, 745 (1952).

[31] S. Nagakura and J. Tanaka, ibid., **22**, 236 (1954); S. Nagakura, ibid., **23**, 1441 (1954); *Mol. Phys.*, **3**, 105 (1960).

[32] J. N. Murrell, *Quart. Revs.*, **15**, 191 (1960).

$$\left.\begin{aligned}
\Phi_1^{\mathrm{L}} &= (2)^{-1/2}\{|A, \overline{A'}, B, \overline{B}, C, \overline{C}| \\
&\quad + |A', \overline{A}, B, \overline{B}, C, \overline{C}|\} \\
\Phi_2^{\mathrm{L}} &= (2)^{-1/2}\{|A, \overline{A}, B, \overline{B'}, C, \overline{C}| \\
&\quad + |A, \overline{A}, B', \overline{B}, C, \overline{C}|\} \\
\Phi_3^{\mathrm{L}} &= (2)^{-1/2}\{|A, \overline{A}, B, \overline{B}, C, \overline{C'}| \\
&\quad + |A, \overline{A}, B, \overline{B}, C', \overline{C}|\}
\end{aligned}\right\} \qquad (32)$$

where A', B' and C' denote $\varphi_{A'}$, $\varphi_{B'}$ and $\varphi_{C'}$ respectively, the upper MO's in each methyl group. If we take three linear combinations:

$$\left.\begin{aligned}
&\Phi_{\mathrm{I}}^{\mathrm{L}} = (3)^{-1/2}(\Phi_1^{\mathrm{L}} + \Phi_2^{\mathrm{L}} + \Phi_3^{\mathrm{L}}) \\
&\Phi_{\mathrm{II}}^{\mathrm{L}} = (2)^{-1/2}(\Phi_2^{\mathrm{L}} - \Phi_3^{\mathrm{L}}) \\
&\text{and} \\
&\Phi_{\mathrm{III}}^{\mathrm{L}} = (3/2)^{-1/2}\{\Phi_1^{\mathrm{L}} - (1/2)(\Phi_2^{\mathrm{L}} + \Phi_3^{\mathrm{L}})\}
\end{aligned}\right\} \qquad (33)$$

$\Phi_{\mathrm{I}}^{\mathrm{L}}$ interacts with Φ_{I} and Φ_{G}; $\Phi_{\mathrm{II}}^{\mathrm{L}}$, with Φ_{II}, and $\Phi_{\mathrm{III}}^{\mathrm{L}}$, with Φ_{III}.

The secular equations are:

$$\begin{vmatrix} -E & 2.04\beta & 1.83 \\ & 1.97-E & -0.551\beta \\ & & 6.23-E \end{vmatrix}^{33)} = 0 \qquad (34)$$

and

$$\begin{vmatrix} -E & -0.551\beta \\ & 3.72-E \end{vmatrix} \qquad (35)$$

Assuming the same value of β (-1.52 eV.) as before, the results are:

Ground state: $E_{\mathrm{G}} = -2.71$ eV. (taking H_{GG} as the standard of energy)

$$\Psi_{\mathrm{G}} = 0.795\Phi_{\mathrm{G}} + 0.566\Phi_{\mathrm{I}} - 0.216\Phi_{\mathrm{I}}^{\mathrm{L}} \qquad (36)$$

First excited state: $E_{\mathrm{L}} = 1.79$ eV.

$$\Psi_{\mathrm{L}_1} = 0.977\Phi_{\mathrm{II}} - 0.210\Phi_{\mathrm{II}}^{\mathrm{L}} \qquad (37)$$

$$\Psi_{\mathrm{L}_2} = 0.977\Phi_{\mathrm{III}} - 0.210\Phi_{\mathrm{III}}^{\mathrm{L}} \qquad (38)$$

The first excitation energy is, then, 4.50 eV., and the corresponding oscillator strength is calculated to be 0.365. From these results, we can see that the inclusion of the locally excited configurations does not bring about any significant change in the transition energy or in the oscillator strength.

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Appendix

Electronic Repulsion Integrals.—The integrals $(aa \mid 22)$ and $(bb \mid 22)$ are evaluated as follows: let us denote the direction of the axis of 2p AO, χ_2, as the z-axis, the carbon core C_2 as an origin, and the angle between the z-axis and the direction of hydrogen atom a as θ (see Fig. 1). Similarly, φ is the angle between $-z$ and the direction of hydrogen atom b. 2p AO, χ_2, then, can be represented by:[18]

$$\begin{aligned}
\chi_2 &= \cos\theta \cdot \chi_{\sigma a} + \sin\theta \cdot \chi_{\pi a} \\
&= -\cos\varphi \cdot \chi_{\sigma b} + \sin\varphi \cdot \chi_{\pi b} \qquad (1\mathrm{A})
\end{aligned}$$

where $\chi_{\sigma a}$ is the 2p AO of carbon atom 2 directed toward hydrogen atom a, and $\chi_{\pi a}$ is that perpendicular to it. $\chi_{\sigma a}$ and $\chi_{\pi b}$ are defined similarly for b. The integrals $(aa \mid 22)$ and $(bb \mid 22)$ are, then:[34]

$$\begin{aligned}
(aa \mid 22) &= \cos^2\theta \cdot (aa \mid \sigma\sigma) + \sin^2\theta \cdot (aa \mid \pi\pi) \\
&= 0.8889(aa \mid \sigma\sigma) + 0.1112(aa \mid \pi\pi) \qquad (2\mathrm{A})
\end{aligned}$$

and

$$\begin{aligned}
(bb \mid 22) &= \cos^2\varphi \cdot (bb \mid \sigma\sigma) + \sin^2\varphi \cdot (bb \mid \pi\pi) \\
&= 0.2221(bb \mid \sigma\sigma) + 0.7778(bb \mid \pi\pi) \qquad (3\mathrm{A})
\end{aligned}$$

$\cos\theta$, $\sin\theta$, $\cos\varphi$ and $\sin\varphi$ being determined from the assumed bond distance and bond angles. The integrals, $(aa \mid \sigma\sigma)$ etc., are taken from the table given by Roothaan,[17] for the Slater-type 2p AO of the carbon, with $Z=3.18$, and for the 1s AO of the hydrogen, with $Z=1.00$.

Core Attraction Integrals.—The core attraction integrals $\langle a \mid bb\rangle$ and $\langle a \mid ab\rangle$ were calculated non-empirically:

$$\begin{aligned}
\langle a \mid bb\rangle &= -\int \chi_b(1) e^2/R_a(1) \chi_b(1) \mathrm{d}v \\
&= -(2/R) \cdot [1-(1+R)e^{-2R}] \qquad (4\mathrm{A})
\end{aligned}$$

and

$$\begin{aligned}
\langle a \mid ab\rangle &= -\int \chi_a(1) e^2/R_a(1) \chi_b(1) \mathrm{d}v \\
&= -2(R+1)e^{-R} \qquad (5\mathrm{A})
\end{aligned}$$

where R is the distance (in atomic units) between hydrogen cores a and b ($R=3.367$) and χ_a and χ_b are AO's with $Z=1.00$. The three-center integral $\langle a \mid bc\rangle$ is reduced to the form:

$$\begin{aligned}
\langle a \mid bc\rangle &= (S_{\mathrm{H}}/2)(\langle a \mid bb\rangle + \langle a \mid cc\rangle) \\
&= S_{\mathrm{H}}\langle a \mid bb\rangle \qquad (6\mathrm{A})
\end{aligned}$$

using Mulliken's approximation. $\langle 2 \mid aa\rangle$ is obtained from Eq. 4A, putting $R=2.062$, the distance

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33) In the evaluation of the off-diagonal element (H_{GL}) between the ground and locally excited configurations, only the inductive effect by the central carbon ion was taken into account; i.e., the off-diagonal element belonging to the field of the methyl group, $H_{\mathrm{GL}}^{\mathrm{Me}}$, was disregarded. This is true when the MO's φ_A and $\varphi_{A'}$ are self-consistent with respect to the methyl group. As has been mentioned above (see footnote 22), however, φ_A and $\varphi_{A'}$ were renormalized in accordance with the zero-overlap approximation, so that we can not put the $H_{\mathrm{GL}}^{\mathrm{Me}}$ value at zero with the same values of α's and β as in the SCF calculation mentioned above (the overlap integral was not disregarded there). However, if we put $\beta = -2.35$ eV., the $H_{\mathrm{GL}}^{\mathrm{Me}}$ value vanishes. This value of β seems to be reasonable in the case of the zero-overlap approximation.

34) Note, $(aa \mid \sigma\pi) = (bb \mid \sigma\pi) = 0$.

between carbon core 2 and hydrogen core a.[35)]

$\langle a \mid 22\rangle$ is reduced to the form:

$$\langle a \mid 22\rangle=\cos^2\theta\cdot\langle a \mid \sigma\sigma\rangle+\sin^2\theta\cdot\langle a \mid \pi\pi\rangle \tag{7A}$$

using Eq. 1A. $\langle a \mid \sigma\sigma\rangle$ is evaluated non-empirically, giving the formula:

$$\langle a \mid \sigma\sigma\rangle=-(Z/2)\rho^{-3}\cdot[2(\rho^2+12)-(\rho^5/4 +3\cdot\rho^4/2+11\cdot\rho^3/2+14\cdot\rho^2+24\cdot\rho+24)e^{-\rho}] \tag{8A}$$

where $\rho=(Z/2)R$, with $Z=3.18$ and $R=2.062$ a. u. The integrals $\langle a \mid \pi\pi\rangle$ and $\langle b \mid 22\rangle$ are calculated by the aid of the "uniformly charged sphere" approximation,[27)] in which $\chi_2(1)\chi_2(1)e$ is replaced by a pair of tangent uniformly-charged spheres of the diameter:

$$D=4.597/Z \text{ Å} \tag{9A}$$

where Z is the effective charge of the carbon 2p AO χ_2 $(Z=3.18)$.[36)]

The Evaluation of Matrix Elements.—The matrix elements necessary for the calculation of the configuration interaction between the ground and charge-transfer configurations of the *t*-butyl cation were evaluated under the approximation of zero-differential overlap:[27)]

$$\begin{aligned}H_{\mathrm{GG}}&=\int|A,\overline{A},B,\overline{B},C,\overline{C}|H|A,\overline{A},B,\overline{B},C,\overline{C}|\mathrm{d}v\\&=2(I_{\mathrm{A}}+I_{\mathrm{B}}+I_{\mathrm{C}})+J_{\mathrm{AA}}+J_{\mathrm{BB}}+J_{\mathrm{CC}}\\&\quad+4(J_{\mathrm{AB}}+J_{\mathrm{BC}}+J_{\mathrm{CA}})\end{aligned} \tag{10A}$$

where

$$I_i=\int\varphi_i H^c\varphi_i\mathrm{d}v \tag{11A}$$

$$J_{ij}=\int\varphi_i\varphi_i e^2/r_{12}\varphi_j\varphi_j\mathrm{d}v \tag{12A}$$

and

$$H^c=T-\sum_{i=1}^{7}(e^2/R_i) \tag{13A}$$

T and R_i being the kinetic energy operator and the distance of an electron from the i-th core. Similarly,

$$\begin{aligned}H_{\mathrm{II}}&=I_{\mathrm{A}}+I_3+2(I_{\mathrm{B}}+I_{\mathrm{C}})+J_{\mathrm{BB}}+J_{\mathrm{CC}}\\&\quad+2(J_{\mathrm{AB}}+2J_{\mathrm{BC}}+J_{\mathrm{CA}})+J_{\mathrm{A3}}+2(J_{\mathrm{B3}}+J_{\mathrm{C3}})\end{aligned} \tag{14A}$$

Accordingly,

$$\begin{aligned}H_{\mathrm{II}}-H_{\mathrm{GG}}&=I_3-I_{\mathrm{A}}-J_{\mathrm{AA}}-2(J_{\mathrm{AB}}+J_{\mathrm{CA}})\\&\quad+J_{\mathrm{A3}}+2(J_{\mathrm{B3}}+J_{\mathrm{C3}})\end{aligned} \tag{15A}$$

On the other hand,

$$\begin{aligned}I_{\mathrm{A}}&=\int\varphi_{\mathrm{A}}(T-e^2/R_1-e^2/R_2)\varphi_{\mathrm{A}}\mathrm{d}v+\sum_{i=3}^{7}\langle i \mid AA\rangle\\&=I_{\mathrm{A}}^{\mathrm{A}}-2(J_{\mathrm{AB}}+J_{\mathrm{CA}})-J_{\mathrm{A3}}\end{aligned} \tag{16A}$$

where the approximate relations

$$\begin{aligned}&\langle 3 \mid AA\rangle\fallingdotseq-J_{\mathrm{A3}},\ \langle 4 \mid AA\rangle+\langle 5 \mid AA\rangle\fallingdotseq-2J_{\mathrm{AB}}\\&\text{and } \langle 6 \mid AA\rangle+\langle 7 \mid AA\rangle\fallingdotseq-2J_{\mathrm{CA}}\end{aligned} \tag{17A}$$

are used. $I_{\mathrm{A}}^{\mathrm{A}}$ is a core integral in the absence of an attraction from the other two methyl groups and from carbon core 3, so that we have a relation:

$$-I_{\mathrm{p}}(\text{methyl})=I_{\mathrm{A}}^{\mathrm{A}}+J_{\mathrm{AA}} \tag{18A}$$

Similarly, we have:

$$I_3=I_3^3-2(J_{\mathrm{A3}}+J_{\mathrm{B3}}+J_{\mathrm{C3}}) \tag{19A}$$

and

$$-I_{\mathrm{p}}(3)=I_3^3 \tag{20A}$$

Putting Eqs. 16A, 18A, 19A and 20A into Eq. 15A, we have

$$H_{\mathrm{II}}-H_{\mathrm{GG}}=I_{\mathrm{p}}(\text{methyl})-I_{\mathrm{p}}(3) \tag{21A}$$

The off-diagonal element H_{GI} is reduced as follows:

$$H_{\mathrm{GI}}=(3)^{-1/2}(H_{\mathrm{G1}}+H_{\mathrm{G2}}+H_{\mathrm{G3}})=(3)^{1/2}H_{\mathrm{G1}} \tag{22A}$$

$$\begin{aligned}H_{\mathrm{G1}}&=(2)^{1/2}\int\varphi_{\mathrm{A}}H^c\chi_3\mathrm{d}v\\&=(2)^{1/2}\int(0.5525\chi_1+0.8348\chi_2)H^c\chi_3\mathrm{d}v\\&\fallingdotseq(0.8348)(2)^{1/2}\int\chi_2H^c\chi_3\mathrm{d}v\end{aligned} \tag{23A}$$

Denoting $\int\chi_2H^c\chi_3\mathrm{d}v=\beta$ and putting Eq. 23A into Eq. 22A,

$$H_{\mathrm{GI}}=2.044\beta.$$

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35) Under the assumption of disregarding a Coulomb penetration integral, the core attraction integral $<2 \mid aa>$, as is well known, can be approximated as equal to the two-center Coulomb integral $-(22 \mid aa)$. This value, -12.256 eV., is rather close to the value, -12.541 eV., obtained by the above-mentioned method.

36) If the "uniformly charged sphere" model is applied directly to $<a \mid 22>$, hydrogen core a is "inside" of one of the spheres. Therefore, rigorous computation was carried out for $<a \mid \sigma\sigma>$.