σ-Electronic Structure in Conjugated Systems

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In the last quarter of a century, the electronic structures of numerous unsaturated compounds have been calculated quantum-mechanically by either a non-empirical or a semi-empirical method; electronic spectra, chemical reactivities and other physical properties of these compounds have also been interpreted with sufficient accuracy in terms of their electronic behavior.

In those calculations, however, except for some simpler compounds such as carbon dioxide, formaldehyde, ethylene and benzene, σ electrons have not been treated explicitly but, rather, have been looked upon as constructing a framework of potential in which π electrons move.

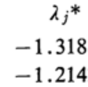
Some physico-chemical properties of unsaturated compounds, however, for example, the proton shift in the high resolution nuclear magnetic resonance spectroscopy, the frequency shift in the pure quadrupole resonance, the dipole moment, the polarographic reduction potential, the reactivity in the halogen substitution reaction, and inductive and hyperconjugative effects of substituents, can not be interpreted without an explicit consideration of the σ electrons in the system. Consequently, the appearance of a simple method of calculating the σ electronic structures of large unsaturated molecules has been loked for.

Recently Sandorfy[1] and the present authors[2] have computed the electronic states of saturated hydrocarbons and halides by a simple LCAO MO method where the molecular orbitals (MO's) are written as a linear combination of the atomic orbitals (LCAO) of the carbon, halogen and hydrogen atoms.

At this time, by extending the simple method stated above, the present authors have calculated the σ electronic structures in large

Table I. Calculated σ orbital energies and electron distributions

(a) Ethylene



Sym.	λ_j*	H_1	C_2	C_3
A	−1.31812	0.03874	0.05482	0.31288
AA**	−1.21430	0.22617	0.27383	0
S	−0.94858	0.14860	0.09424	0.01433
A	−0.66410	0.13385	0.03263	0.16703
S	+0.63769	0.07059	0.05606	0.24669
AA**	+0.65430	0.27383	0.22617	0
A	+1.16221	0.07741	0.16256	0.02007
S	+1.49089	0.03081	0.09970	0.23898

* λ_j is the coefficient in $\varepsilon_j=\alpha+\lambda_j\beta$, where ε_j is the jth molecular orbital energy.

** AA denotes the antisymmetric orbital with respect to C–C bonding axis. In this orbital, bonding electrons localize only C–H bond.

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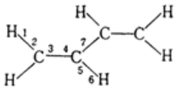
[1] C. Sandorfy, *Can. J. Chem.*, 33, 1337 (1955).

[2] K. Fukui, H. Kato and T. Yonezawa, This Bulletin, 34, 442, 1111 (1961).

Table I (Continued)

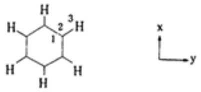
(b) Butadiene



j	Sym.	λ_j	H_1	C_2	C_3	C_4	C_5	H_6	C_7
18	A	−1.35539	0.0117	0.0177	0.1153	0.1290	0.0026	0.0017	0.1926
17	S	−1.30690	0.0192	0.0266	0.1455	0.1403	0.0710	0.0512	0.0003
16	A	−1.27763	0.0061	0.0080	0.0390	0.0339	0.1707	0.1299	0.0983
14,15	AA*	−1.21430	0.2262	0.2738	0	0	0	0	0
13	S	−1.05520	0.0347	0.0287	0.0321	0.0036	0.1497	0.1808	0.0068
12	A	−0.92480	0.0968	0.0576	0.0029	0.0175	0.0350	0.0589	0.0769
11	S	−0.74484	0.1058	0.0356	0.0608	0.1069	0.0103	0.0305	0.0087
10	A	−0.57576	0.0472	0.0075	0.1017	0.0623	0.0157	0.0982	0.1127
9	S	+0.62850	0.0314	0.0244	0.1132	0.1091	0.0035	0.0044	0.1582
8	A	+0.64104	0.0285	0.0228	0.0986	0.0999	0.0884	0.1104	0
7	S	+0.64650	0.0070	0.0057	0.0237	0.0246	0.1602	0.1976	0.0685
5,6	AA*	+0.65430	0.2738	0.2262	0	0	0	0	0
4	A	+1.03757	0.0342	0.0593	0.0013	0.0496	0.1577	0.0910	0.0134
3	S	+1.23235	0.0449	0.1043	0.0401	0	0.0396	0.0171	0.1048
2	A	+1.43497	0.0255	0.0771	0.1413	0.1078	0.0298	0.0099	0.0061
1	S	+1.57953	0.0069	0.0247	0.0845	0.1154	0.0657	0.0183	0.1528

* See Table I (a).

(c) Benzene



j	Sym. xy	λ_j	C_1	C_2	H_3
24	AA	−1.38000	0.0833	0	0
22,23	SA, AS	−1.32743	0.1236	0.0509	0.0354
20,21	SS, AA	−1.28027	0.0613	0.1199	0.0908
19	SA	−1.27004	0.0232	0.0679	0.0524
18	SS	−1.09917	0.0018	0.0779	0.0851
16,17	SA, AS	−1.01199	0.0457	0.1033	0.1385
14,15	SS, AA	−0.71938	0.1029	0.0298	0.0978
13	SA	−0.50125	0.0547	0.0053	0.0520
12	AS	+0.62000	0.0833	0	0
10,11	SS, AA	+0.63752	0.0840	0.0732	0.0922
8,9	SA, AS	+0.64612	0.0409	0.1126	0.1390
7	SS	+0.64780	0.0162	0.0602	0.0740
6	SA	+0.95129	0.0055	0.0934	0.0623
4,5	SS, AA	+1.16119	0.0852	0.1104	0.0526
2,3	SA, AS	+1.49330	0.1232	0.0665	0.0205
1	SS	+1.63137	0.0653	0.0286	0.0075

substituted as well as non-substituted unsaturated compounds. In the present paper, as in the first of the series, the σ electronic structures of ethylene, butadiene, propylene, benzene, naphthalene and toluene will be discussed and some characteristics of the σ MO's in these compounds will be given.

Method of Calculation

The method of calculation is similar to the one that has been employed in previous papers where the electronic structures of saturated compounds have been discussed2).

The σ molecular orbitals in a conjugated hydrocarbon are represented by the linear combinations of atomic orbitals, the sp² hybridized orbitals of the carbon atoms and the 1s atomic orbitals of the hydrogen atoms. Thus, the jth σ MO is written as follows:

$$\psi_j=\sum_r^n C_{rj}\phi_{C,r}+\sum_l^m C_{lj}\phi_{H,l} \qquad (1)$$

in which C_{rj} denotes the coefficient of the

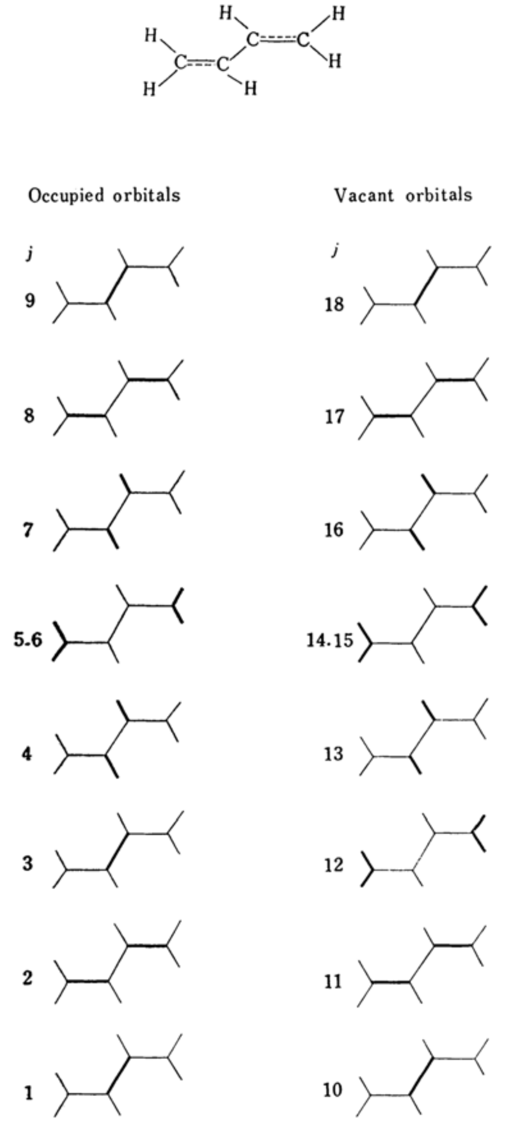


Fig. 1a. The σ electron distributions in butadiene. (Thick lines denote the most densely populated bonds.)

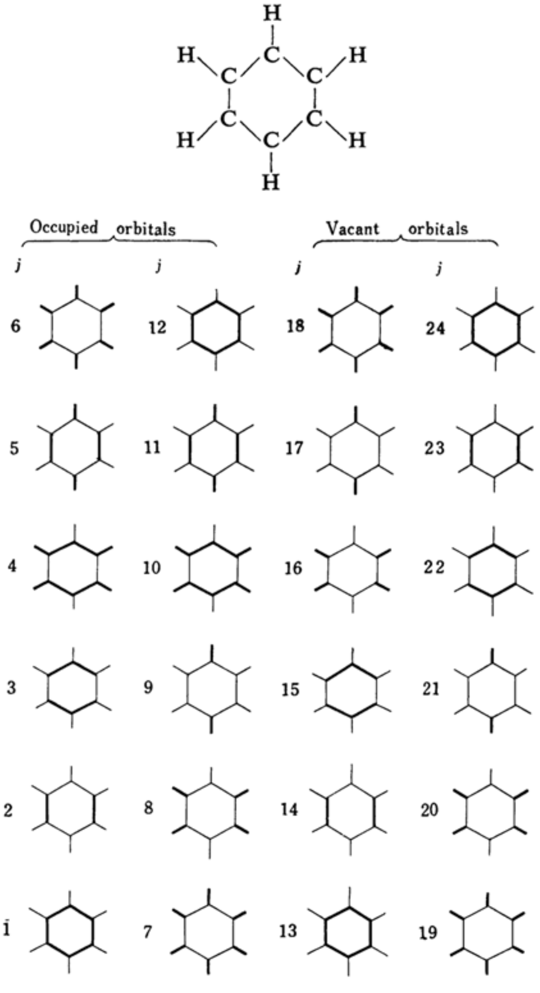


Fig. 1b. The σ electron distributions in benzene. (Thick lines denote the most densely populated bonds.)

rth sp^2 hybridized orbital of carbon in the jth MO, and C_{lj} denoted that of the 1s orbital of the lth hydrogen atom.

Referring to the simple LCAO MO approximation (the Hückel approximation) in the treatment of π electrons, the electronic interaction is not also explicitly considered in this σ problem. The overlap integrals between σ atomic orbitals are also neglected.

Furthermore, the σ electrons are assumed to be independent of the electronic distribution of π electrons. This neglect of so-called σ-π interaction is permissible in the present "simple" LCAO MO treatment.

The Coulomb and the resonance integrals are taken as follows:

$$\left.\begin{array}{l}
\text{The Coulomb integrals:} \\
\int \phi_{\mathrm{C},r}\mathrm{H}\phi_{\mathrm{C},r}\,\mathrm{d}\tau=\alpha \\
\int \phi_{\mathrm{H},l}\mathrm{H}\phi_{\mathrm{H},l}\,\mathrm{d}\tau=\alpha-0.2\beta \\
\text{The resonance integrals:} \\
\int \phi_{\mathrm{C},r}\mathrm{H}\phi_{\mathrm{C},r+1}\,\mathrm{d}\tau=\beta \\
\quad (r \text{ and } r+1 \text{ belonging to neighboring carbons}) \\
\int \phi_{\mathrm{C},r}\mathrm{H}\phi_{\mathrm{C},r+1}\,\mathrm{d}\tau=m\beta=0.38\beta \\
\quad (r \text{ and } r+1 \text{ belonging to the same carbon}) \\
\int \phi_{\mathrm{C},r}\mathrm{H}\phi_{\mathrm{H},r+1}\,\mathrm{d}\tau=\beta_{\mathrm{sp}^2-\mathrm{H}}=0.94\beta
\end{array}\right\} \quad (2)$$

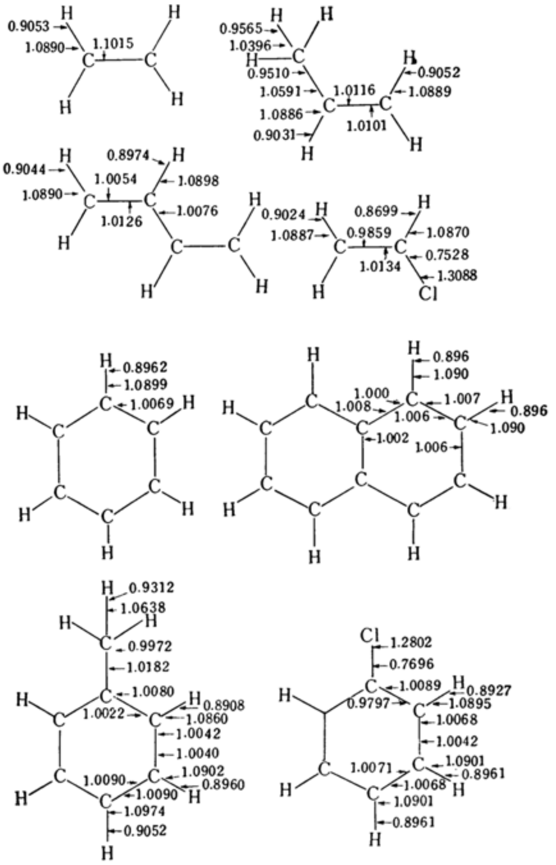


Fig. 2. The values of total σ electron densities of bonding orbitals ($q_r{}^O$) in some conjugated compounds.

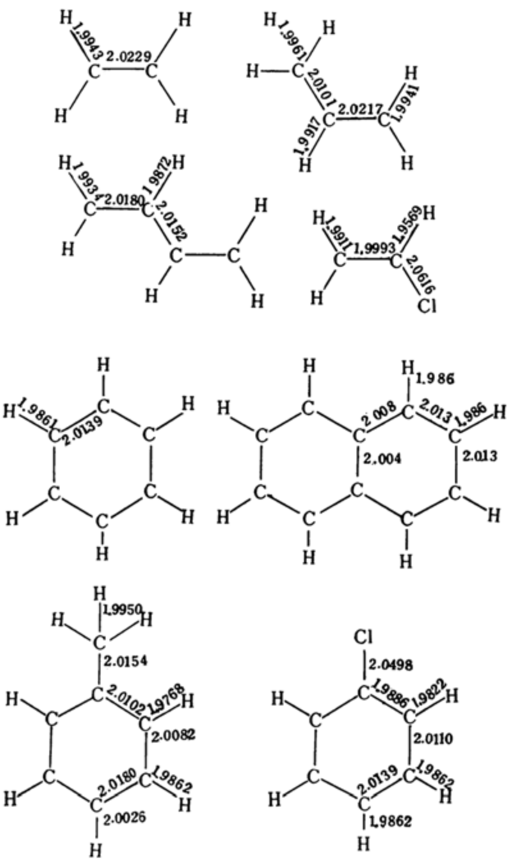


Fig. 3. The values of total σ electron densities of bonds ($q_r{}^B$) in some conjugated compounds.

in which H is the one electron hamiltonian of a σ electron. The value of m is determined by considering the degree of hybridization from the similar value of saturated hydrocarbons in previous papers[2,3]. The value of β_{sp^2-H} is estimated from the overlap integrals of a C–C and a C–H bond as calculated by Mulliken[4]. Further, α_H is determined so as to explain the C–H bond moment.

In treating propylene and toluene, the integrals containing the sp³ hybridized orbital of carbon are needed. They are estimated from the electron affinity and the ionization potential of valence states and also from overlap integrals, resulting in

$$\left.\begin{aligned}
&\int \phi_{sp^3,r} H \phi_{sp^3,r}\, d\tau = \alpha - 0.1\beta \\
&\int \phi_{sp^3,r} H \phi_{sp^2,r+1}\, d\tau = 0.92\beta \\
&\int \phi_{sp^3,r} H \phi_{sp^3,r+1}\, d\tau = m(sp^3)\beta = 0.29\beta \\
&\int \phi_{sp^3,r} H \phi_{H,r+1}\, d\tau = \beta_{sp^3-H} = 0.93\beta
\end{aligned}\right\} \quad (3)$$

in which α and β are the integrals of the sp² orbitals defined in Eq. 2.

Electronic Structure of the σ-Skeleton in a Conjugated System

The calculated values of the energy level and the charge distribution of each orbital are listed in Table I for ethylene, butadiene and benzene. The characteristics of the σ-electronic structure of the polyene are found to be similar to those of the normal aliphatic hydrocarbons discussed in a previous paper[2].

On investigating Table I and Figs. 1—4, the following conclusions may be derived.

a) The bonding electrons belonging to each orbital tend to localize in certain particular bonds. For instance, the charge distribution of each orbital for butadiene, benzene, and so on, shows the above-mentioned characteristics, as is

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3) H. Yoshizumi, *Trans. Faraday Soc.*, 53, 125 (1957).

4) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, 17, 1248 (1949); R. S. Mulliken, *J. Am. Chem. Soc.*, 72, 4493 (1950).

clearly seen in Fig. 1. Namely, the electron densities in the highest occupied orbital as well as in the lowest vacant orbital are largest in the carbon-carbon σ bond. Such general trend is also seen in benzene, naphthalene and chlorobenzene, where electrons belonging to the highest occupied orbital localize completely in carbon-carbon σ bonds.

b) The energy gap between the highest occupied orbital and the lowest vacant one is much greater than that of the π-orbitals. This point is discussed in detail in the following section.

c) Generally speaking, the charge distribution is not uniform. The values of the total electron density of the carbon hybridized orbital or hydrogen 1s orbital ($q_r{}^{\mathrm{O}}$), the electron density of each bond ($q_r{}^{\mathrm{B}}$), and the net charge of each atom (Q_r) for some compounds are indicated in Figs. 2, 3 and 4. The quantities of $q_r{}^{\mathrm{O}}$, $q_r{}^{\mathrm{B}}$ and Q_r are given in the following formulas:

$$\left.\begin{aligned} q_r{}^{\mathrm{O}} &= 2\sum_i^{\mathrm{occ}} C_{ir}{}^2 \\ q_r{}^{\mathrm{B}} &= q_s{}^{\mathrm{O}} + q_{s+1}{}^{\mathrm{O}} \\ Q_r &= (\text{valence number of the } r\text{th atom}) \\ &\quad -\sum{}' q_s{}^{\mathrm{O}} \end{aligned}\right\} \quad (4)$$

in which $\sum'$ denotes the summation carried out over all valence orbitals belonging to the rth atom.

It is worthy of notice that the magnitudes of the total electron densities of hydrogen atoms of benzene and naphthalene are smaller than those of ethylene and butadiene. The following interesting conclusion may accordingly be derived. In σ electron systems the benzene ring exerts an electron-attracting effect. Further, the hydrogen atoms belonging to the methyl group of propylene and toluene have larger electron densities than those of the hydrogen atoms attached to the sp^2 hybridized carbon orbital.

d) The order of magnitude of I-effect for many substituents can be indicated by referring to the values of Q_r listed in Fig. 4 for toluene, chlorobenzene* and so on. The more electronegative the substituent is, the larger the electron density of the substituent. The effect of the substituent, however, becomes smaller in the distant atom from the substituent, and the magnitude of the change in electron density effected by a substituent is approximately proportional to m^{2n}, where n is the number of atoms along the carbon chain from the substituent to the atom in question**. In this case the remarkable effect of the bond alteration is not revealed.

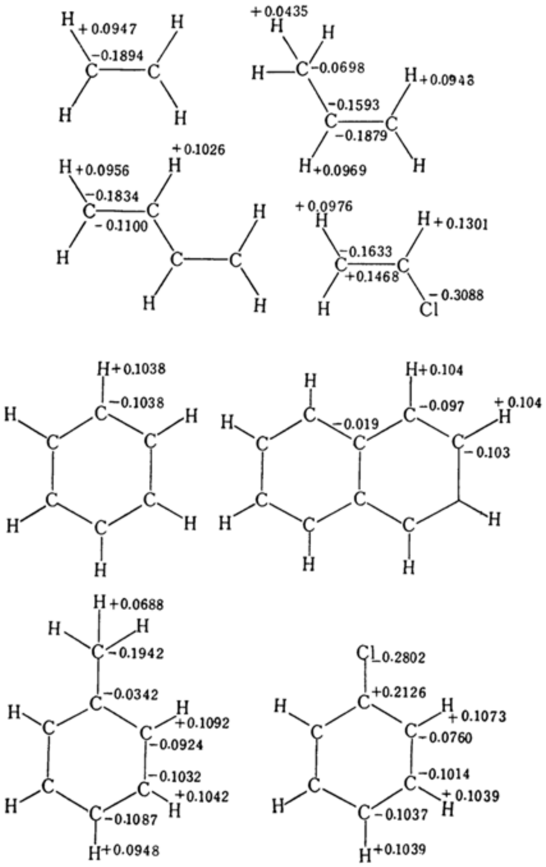

Fig. 4. The values of net charges of atoms (Q_r) in some conjugated compounds.

Comparative Discussion on σ- and π-Electronic Structures

Energy of σ-MO's

It has been believed that the energies of σ- and π-molecular orbitals increase in the following order:

$$\sigma\text{-occupied} < \pi\text{-occupied} < \pi\text{-unoccupied} < \sigma\text{-unoccupied orbitals}$$

Hence, it is required that the energy gap between the lowest vacant and the highest occupied σ-orbitals be large enough to include all the π-orbitals within it. The calculated energies of these σ-orbitals in some compounds

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[*] The values of the Coulomb and the resonance integrals of a chlorine atom are put tentatively at $\alpha_{\mathrm{Cl}}=\alpha+0.3\beta$ and $\beta_{\mathrm{C-Cl}}=0.6\beta$ respectively.

[**] In the case of a simple LCAO MO treatment of the π electron systems, the I-effect upon the Coulomb integral is taken as $(1/3)^n$ by Dewar[5]. This approximation seems to be reasonable on the basis of the result obtained in the present paper.

5) M. J. S. Dewar, *J. Chem. Soc.*, **1949**, 463.

TABLE II. THE CALCULATED VALUES OF ENERGIES OF HIGHEST OCCUPIED (ho) AND LOWEST VACANT (lv) ORBITALS OF σ, AND OF ENERGIES OF LOWEST OCCUPIED (lo) AND HIGHEST VACANT (hv) ORBITALS OF π ELECTRONS OF SOME CONJUGATED COMPOUNDS

	σ (in unit of β_{sp^2})		π (in unit of β_p)	
	λ_{ho}	λ_{lv}	λ_{lo}	λ_{hv}
Ethylene	0.6377	−0.6641	1.000	−1.000
Butadiene	0.6258	−0.5758	1.618	−1.618
Propylene	0.5853	−0.6031	1.414	−1.414*
Benzene	0.6200	−0.5013	2.000	−2.000
Naphthalene	0.6200	−0.4428	2.300	−2.300
Toluene	0.6057	−0.4805	2.000	−2.000*

* These values were obtained by neglecting hyperconjugation of methyl group.

which are summarized in Table II show that the energy gap amounts to 1.1∼1.4 in units of $-\beta_{sp^2}$ or 11∼14 eV., which is sufficiently large to include all the π-MO's of ordinary conjugated compounds since in these the energies of the π-MO's lie in the range of $\alpha_p+2.5\beta_p$ to $\alpha_p-2.5\beta_p$*.

In some exceptional cases, for instance in chlorobenzene, however, the lowest vacant σ-orbital, whose energy is $\alpha_{sp^2}-0.2\beta_{sp^2}$ lies in proximity to the nonbonding π-MO of zero energy. Thus the lowest vacant σ-MO may be situated below the lowest vacant π-orbital in these compounds. This fact may have an important bearing on the chemical reaction and the polarographic reduction. The details of these facts will be published in the future.

σ-Electron Density

In the alternant hydrocarbon, the total π-electron density at the carbon atom is always equal to unity, whereas the σ-electron density at the carbon atom (Eq. 4), in the σ-skeleton of conjugated molecules is not necessarily uniform, as has been pointed out by the present authors2).

It may be reasonable, therefore, to consider that this σ-electron distribution modifies the Coulomb integral of the π-electron system and causes an alteration of the π-electron density. In this connection a comprehensive SCF treatment, including both σ-electrons and π electrons, should be carried out.

One should bear in mind that the position of attack in the reaction is never determined by the magnitude of the σ-electron density, even when the π-electron distribution is uniform. Thus, in butadiene, the σ-electron densities, at positions 1 and 4, are larger than those at positions 2 and 3, as is shown in Fig. 4. This distribution appears to indicate that positions 1 and 4 are more susceptible to electro philic attack than positions 2 and 3, in agreement with experience. However, this distribution is incompatible with the fact that nucleophilic attack also takes place at positions 1 and 4. According to the self-consistency consideration, this σ-electron distribution may bring about a decrease in π-electron densities at positions 1 and 4 and an increase of those at 2 and 3. This result leads us again to a contradiction to the experimental facts in electrophilic substitutions. Also, in naphthalene, the σ-electron density increases in the order

$$9\text{-} < 1\text{-} < 2\text{-position}$$

which is reverse to the order of reactivity in electrophilic substitutions. In toluene, the calculated σ-electron density increases in the order

$$\text{ortho} < \text{meta} < \text{para}$$

which is not consistent with the *o, p*-directing property of this compound. All of these facts show that the σ-electron density has no direct concern with the chemical reaction and that the electron which plays an important role is not the σ-electron but the π-electron.

The σ-electron distribution stated above may be provide us with an indirect support of the validity of the π approximation in discussing the reactivity of conjugated molecules.

With respect to propylene and toluene, the σ-electron distribution of some σ occupied orbitals is shown in Table III. The molecular orbitals localized in the methyl group are closely similar to a normal π-type orbital and are orthogonal to each other. The mode of this distribution suggests that hyperconjugation may take place in these compounds, as has been pointed out by Mulliken6) and Coulson7).

Other Problems

Many other facts are successfully explained by the present results. Some of these will be described here. Full details of each topic will be published in the future.

Proton Shift

The calculated density of σ-electrons at the hydrogen atom will provide us with information about the local diamagnetic shielding of the proton in nuclear magnetic resonance spectra.

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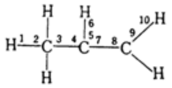
* See, for example, B. Pullman and A. Pullman, "Les Théories Electroniques de la Chimie Organique", Masson & Cie, Paris (1952).

6) R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).

7) C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, **1953**, 2052; C. A. Coulson, *Quart. Rev.*, **1**, 144 (1947).

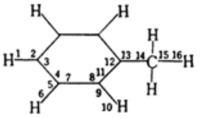
TABLE III (a). SOME σ OCCUPIED ORBITALS OF PROPYLENE



λ_j	H_1	C_2	C_3	C_4	C_5	H_6	C_7	C_8	C_9	H_{10}
+0.58534*	0.03218	0.02295	0.27069	0.28179	0.04471	0.06406	0.05312	0.06568	0.01121	0.01606
+0.63984**	0.36721	0.29946	0	0	0	0	0	0	0	0
+0.64174	0.00042	0.00034	0.00307	0.00388	0.20291	0.25305	0.17756	0.17467	0.04062	0.05066
+0.65430	0	0	0	0	0	0	0	0	0.22617	0.27383
+1.09543	0.02628	0.05100	0.00165	0.07096	0.20094	0.10580	0.04894	0.00086	0.11104	0.05846

* Highest occupied orbital ** Localized orbital in CH_3 group

TABLE III (b–1). SOME σ OCCUPIED ORBITALS OF TOLUENE

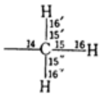


λ_j	H_1	C_2	C_3	C_4	C_5	H_6	C_7	C_8
+0.60570*	0.0047	0.0034	0.0014	0.0010	0.0046	0.0062	0.0140	0.0119
+0.61264**	0	0	0	0	0	0	0	0
+0.62000	0	0	0.0833	0.0833	0	0	0.0833	0.0833
+0.63752	0	0	0.0619	0.0641	0.0549	0.0692	0	0
+0.64070	0.1278	0.1022	0.0298	0.0277	0.0078	0.0097	0.0685	0.0700

λ_j	C_9	H_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	H_{16}
+0.60570*	0.0094	0.0128	0.0548	0.0484	0.2355	0.2512	0.0270	0.0319
+0.61264**	0	0	0	0	0	0	0.3083	0.3584
+0.62000	0	0	0.0833	0.0833	0	0	0	0
+0.63752	0.0549	0.0692	0.0641	0.0619	0	0	0	0
+0.64070	0.0735	0.0919	0.0008	0.0004	0.0036	0.0035	0.0004	0.0005

* Highest occupied orbital ** Localized orbital in CH_3 group

TABLE III (b–2). ORBITALS LOCALIZED IN CH_3 GROUP



λ_j	C_{15}	H_{16}	$C_{15'}$	$H_{16'}$	$C_{15''}$	$H_{16''}$
0.61264	0.3083	0.3584	0.0771	0.0896	0.0771	0.0896
0.61264	0	0	0.2312	0.2688	0.2312	0.2688

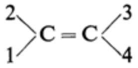
In the case of benzene and naphthalene (Fig. 2), the σ-electron densities at each hydrogen atom do not vary much according to the position attached. Therefore, it is considered that the difference in the chemical shift between α- and β-hydrogen atoms in naphthalene is ascribable to the unequal contribution of the induced π-ring current.

The σ-electron densities and values of chemical shifts in propylene and toluene are indicated in Table IV. In both cases, σ-electron densities at methyl hydrogen atoms are greater than those at other hydrogen atoms. These results coincide with the experimental fact that the resonance fields for methyl protons is higher than those for other protons.

In conclusion, a more quantitative explanation of the proton chemical shift is possible by the present procedure. The results will be published in the future.

TABLE IV. CHEMICAL SHIFTS AND σ ELECTRON DENSITIES OF HYDROGEN ATOMS IN SOME COMPOUNDS

(a)



		Shift1)*	Density
Ethylene	H_2	−0.9	0.905
	H_3	−0.9	0.905
	H_4	−0.9	0.905
Propylene	H_2	−0.8	0.903
	H_3	−0.2	0.905
	H_4	−0.1	0.905
	CH_3	+3.3	0.957
(b)			
Benzene	Ring proton	−2.52	0.896
Toluene	Ring proton	−2.35	0.905∼0.891
	CH_3 Proton	+2.45	0.931

1) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance", McGraw-Hill, London (1959).

* In p.p.m. referred to water.

Dipole Moment

The dipole moment of conjugated molecules has hitherto been calculated as the sum of π moment obtained theoretically and the σ moment estimated empirically. The present treatment enables us to calculate the σ moment theoretically. According to our results, the σ dipole moments of toluene and propylene become 0.57 D and 0.05 D respectively*. Though it needs further investigation to decide whether these values are reasonable or not, the calculated result clearly indicates that conjugated compounds containing both sp^2 and sp^3 hybridized carbon atoms may have a σ moment of an appreciable magnitude. At least the usual procedure for explaining the dipole moment of these compounds only by hyperconjugation must be re-examined.

Summary

The σ-electronic structures and σ-electron densities of σ skeletons in some conjugated compounds are calculated by a simple LCAO MO method developed by the present authors.

The inductive and hyperconjugative effects, dipole moment, proton shift, and so on, are briefly discussed. Agreements of the results with experiments seem to be almost entirely satisfactory.

A part of the calculation has been carried out with the KDC-I digital computer of Kyoto University.

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* The values of the Coulomb integral of the H atom in the CH_3 group in toluene and propylene are tentatively put $\alpha_H=\alpha-0.25\beta$ and $\alpha-0.2\beta$ respectively. Thus, the difference of σ-electron densities at these atoms is partially dependent on the difference of the values of parameters. In calculating the values of σ dipole moments in these compounds, the center of gravity of sp^3 and sp^2 hybridzed orbital is located at the positions of 0.44 Å and 0.41 Å apart from the carbon nucleus respectively.