Theoret. chim. Acta (Berl.) 13, 220—229 (1969)

The Role of the Doubly Excited Configurations in the π-Electronic Structure of the Croconate Anion

KAZUYOSHI SAKAMOTO and Y. J. I'HAYA

Department of Chemistry, Tokyo Kyoiku University, Otsuka, Tokyo, Japan, and Department of Materials Science, The University of Electro-Communications, Chofu-shi, Tokyo, Japan

Received November 4, 1968

The electronic structure of the croconate anion is investigated by the semi-empirical VESCF method with CI including up to the doubly excited configurations. The effect of the doubly excited configuration is quite large in the lowest singlet state which turns out to be a ground state, while the calculation including only singly excited configurations produces a triplet ground state. The calculated first transition energy (${}^1A'_1 \rightarrow {}^1E'_1$) is in fair agreement with the observed value. The interpretation of the transition moment in case that the doubly excited configurations are included is also discussed.

Die Elektronenstruktur des Croconat-Anions wurde mit der halbempirischen VESCF-Methode mit Konfigurationswechselwirkung, die bis zu zweifach angeregte Konfigurationen einschloß, untersucht. Der Einfluß der zweifach angeregten Konfigurationen ist im niedrigsten Singulettzustand, der sich als Grundzustand herausstellt, sehr stark. Schließt die Rechnung hingegen nur einfach angeregte Konfigurationen ein, so erhält man einen Tripletgrundzustand. Die berechnete erste Übergangsenergie (${}^1A'_1 \rightarrow {}^1E'_1$) stimmt gut mit dem beobachteten Wert überein. Ebenso wird die Interpretation des Übergangsmomentes für den Fall, daß auch zweifach angeregte Konfigurationen berücksichtigt werden, diskutiert.

La structure électronique de l'anion croconique est étudieé par la méthode VESCF semi-empirique avec IC, configurations diexcitées comprises. L'effet des configurations diexcitées est très important sur l'état singulet le plus bas qui est un état fondamental, alors que si l'on ne tient compte que des configurations monoexcitées on obtient un état fondamental triplet. La première énergie de transition calculée (${}^1A'_1 \rightarrow {}^1E'_1$) est en bon accord avec la valeur observée. Le moment de transition est interprété dans les cas où l'on tient compte des configurations diexcitées.

1. Introduction

The croconate anion, $(C_5O_5)^{-2}$, has received considerable attention from both a theoretical and experimental point of view. An ultraviolet absorption [1], normal coordinate analysis of the infrared and Raman spectral data [2], and a X-ray analysis [3] of the croconate anion all indicate that it is a new class of aromatic substances, an oxocarbon anion $(C_nO_n)^{-m}$, and has a planar structure of D_{5h} symmetry.

Molecular orbital calculations for this anion were first carried out by West and Powell [4] and Baenzinger and Hegenbarth [5] with simple Hückel approximations. Quite recently, Cignitti [6] applied the Pariser-Parr-Pople method to the calculation of the lower excited electronic states of the anion. His results show that the first singlet excited state comes up closer to the experimental value when 1) a sp^2 hybridized valence state is assumed for each oxygen, 2) no penetration integrals are included, 3) Pariser-Parr type interpolation formula for the two-centre electronic repulsion integrals are adopted. An important feature, however, is that the ground state of the anion is randomly predicted to be a singlet or a triplet depending on the set of parameters chosen and approximations adopted. Experimental evidence, on the other hand, shows that the croconate anion is diamagnetic at 25° C [7], so that its ground state is considered to be a singlet.

We have confirmed that the inclusion of all the singly excited configurations yields a triplet ground state. This was a reason why Cignitti did not carry out a usual configuration interaction treatment. In order to explain the magnetic experiment mentioned above, we intend to examine whether doubly excited configurations play a role to lower the energy of the lowest singlet state rather than that of the corresponding triplet state. The contribution of the doubly excited configurations is considered to be rather predominant in a hetero atom system compared with the ordinary aromatic hydrocarbon like benzene, naphthalene and so on. The major purpose of the present paper is to make this matter clear.

2. Method of Calculation

The croconate anion (Fig. 1) is treated as a 10 centre 12 electron problem within the framework of the π-electron theory. We assume that the carbon ring is a perfect pentagon with the C–C distance 1.46 Å and all the C–O bonds are equivalent, 1.26 Å.

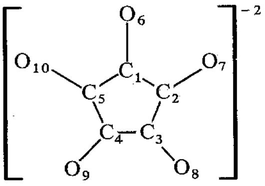

Fig. 1. Geometry of the croconate anion

The calculation of the molecular orbital (MO) functions and energies is carried out by the VESCF (Variable Electronegativity Self-Consistent Field) method [8, 9] with the assumption of the zero differential overlap, starting from appropriate Hückel molecular orbitals. Core resonance integrals β_{pq} are evaluated from the following formula [10] at each iteration in the SCF routine:

$$\beta_{pq} = -\tfrac{1}{2} S_{pq}(I_p + I_q),$$

where S_{pq} is the overlap integral between $2p\pi$ atomic orbitals on atoms p and q. I_p and I_q are the valence state ionization potentials of atom p and atom q, respectively, and are assumed to vary with the effective nuclear charge of the core [8, 9]. The one-centre electronic repulsion integrals γ_{pp} are taken as the difference between I_p and the valence state electron affinity A_p [11]. The dependence of I_p and A_p upon the effective nuclear charge Z_p is assumed to be the same as in Ref. [9]. The penetration integrals are assumed to be constant through the whole SCF routine and are given the following values [6]: $(C_1 : O_6O_6) = 1.66$ eV, $(C_1 : C_2C_2) = 0.83$ eV, $(O_6 : C_1C_1) = 0.98$ eV, and all others are neglected.

Several types of the SCF calculations are made: a) only nearest-neighbour resonance integrals are considered (β_{near}); b) non-nearest neighbour β's are also included (β_{all}) [12]; c) the Mataga-Nishimoto equation is used for the two-centre electronic repulsion integrals γ_{pq}(M–N) [13]; d) a Pariser-Parr type quadratic equation is used for γ_{pq}(P–P) [11].

The configuration interaction (CI) calculation is divided into two classes, one including only singly excited configurations (S.CI) and the other doubly excited configurations as well (D.CI). The doubly excited configurations considered are of the type Ψ_{ii}^{kk}, Ψ_{ii}^{kl}, Ψ_{ij}^{kk} and Ψ_{ij}^{kl}. In the calculation of D.CI, some of the singly excited configurations which are considered to make minor contributions are omitted, due to the insufficient capacity of our computer. The calculation of the oscillator strength for the singlet state is made in both the cases of S.CI and D.CI. Its procedure is given in Appendix A.

3. Results and Discussion

In the SCF routine, the integrals are modified by new Z_p's through the following formula at each stage of iteration [8, 9]:

$$Z_p = N_p - 1.35 - 0.35(\sigma_p + q_p)$$

where N_p is the atomic number of atom p, σ_p the number of $2s$ and $2p$ electrons contributed to the core by atom p, and q_p the π-electron density at atom p. The set of such modified integrals in turn produces the new molecular orbitals in the next stage of iteration. The molecular orbitals were defined to be self-consistent when there was no change at seven decimal places in both energies and atomic orbital (AO) coefficients. The SCF orbital energies were obtained after twenty iterations on the average.

All secular equations were solved by the Jacobi method. The symmetries of the degenerate energy levels can not be determined immediately from the MO coefficients, while the non-degenerate MO's are easily assigned to have the a_2'' symmetry. How to determine the symmetries for the degenerate MO's is described in Appendix B. The orders of these SCF energy levels and symmetry relations remain unchanged under the approximations (β_{all}, M–N) and (β_{all}, P–P) and even under other approximations. The electron densities and bond orders calculated from the SCF–MO's under the combinations of approximations a), b), c) and d), are given in Table 1.

Table 1. *Electron densities and bond orders*

Approximations	Electron density[a]		Bond order[a]	
	q_C	q_O	p_{CC}	p_{CO}
M–N β_{near}	1.0039	1.3963	0.3975	0.7251
M–N β_{all}	0.9838	1.4162	0.3854	0.7302
P–P β_{near}	0.9495	1.4505	0.3900	0.7204
P–P β_{all}	0.9289	1.4711	0.3806	0.7211

[a] Subscripts C and O mean the carbon and the oxygen atoms, respectively. p_{CC} and p_{CO} are the values for the nearest neighbours.

Table 2. *Effect of the configuration interaction on the first singlet and triplet states (eV)*[a]

Symmetry		M–N β_{near}	M–N β_{all}	P–P β_{near}	P–P β_{all}
		0	0	0	0
${}^1A'_1$	(D.CI)	(−1.702)	(−1.450)	(−1.533)	(−1.289)
${}^1E'_1$	SCF	2.546	2.756	2.731	2.996
	S.CI	2.191	2.451	2.393	2.708
	D.CI	2.705	2.726	2.953	3.026
${}^3E'_1$	SCF	−0.449	−0.135	−0.317	0.055
	S.CI	−0.711	−0.407	−0.497	−0.143
	D.CI	0.911	0.995	0.932	1.059

[a] SCF indicates the lowest excitation energy of the only one singly excited configuration. S.CI means the CI calculation with all the singly excited configurations. D.CI includes the doubly excited configurations in addition to the singly excited configurations. Figures in brackets show the energy depression of the lowest ${}^1A'_1$ state relative to its SCF energy due to D.CI. All other figures are relative to the corresponding.

The effect of configuration interaction upon the lowest energy levels of the ${}^1A'_1$, ${}^1E'_1$ and ${}^3E'_1$ states is examined under four types of approximations and is shown in Table 2. The table shows that if no configuration interaction is taken into consideration (indicated as SCF in Table 2), the first triplet state ${}^3E'_1$ becomes lower than the lowest singlet ${}^1A'_1$ state, except for the case of (β_{all}, P–P). This tendency is enhanced after all the singly excited configurations are taken, since the lowest ${}^1A'_1$ state has no interaction with any of the singly excited states. At the same time, the energy of the ${}^1E'_1$ state tends to deviate from the experimental value 3.40 eV.

When the doubly excited configurations are included, however, the singlet ${}^1A'_1$ state comes out to be always the ground state, because the energy depression for this state is much larger than for any other states. Numerically speaking, the depression is 1.2 ~ 1.7 eV as shown in Table 2, which is quite large compared with the value for the ordinary aromatic hydrocarbons. For example, the energy depression for the ground state of naphthalene due to the doubly excited configurations is about 0.25 eV [14]. Moreover, the experimental value for the first singlet-singlet ${}^1E'_1 \leftarrow {}^1A'_1$ transition (3.40 eV) is best explained in the D.CI calculation (3.026 eV), while the SCF calculation produces the value 2.996 eV[1]. At the same time, Table 2 shows a tendency that the question, which approximation for the basic integrals should be adopted, turns out to be a minor problem if one includes up to doubly excited configurations. Although this is a matter of course from a view-point of configuration interaction, it should be recognized whenever one carries out semiempirical MO calculations.

Table 3 shows the whole results of the configuration interaction calculation for the lower electronic states obtained under the Approximation (β_{all}, P–P). Of the doubly excited configuration species included, Ψ_{ii}^{kk}-type doubly excited configurations play a significant role in the ${}^1A'_1$ state, while Ψ_{ii}^{kl}-type ones contribute much to E'_1 and E'_2 states.

---

[1] A simple SCF calculation with the optimum parameters (variation of effective nuclear charges is not considered) [6] yields the value 3.20 eV for the first singlet-singlet transition and the value 0.45 eV for the first singlet-triplet transition, the latter being considered to be too small.

Table 3. *Energy levels and intensities for croconate anion excited state (eV)*[a]

Singlet state	S.CI	f-number	D.CI	f-number	Exptl.	Triplet state	S.CI	D.CI
	0.0	(Ref.)	0.0	(Ref.)				
$^1A_1'$	8.235	0	5.227	0		$^3A_1'$	4.598	5.887
	8.765	0	7.572	0			8.647	6.684
	(8)		(8 + 14)				(8)	(8 + 10)
$^1E_1'$	2.708	0.571	3.026	0.137		$^3E_1'$	− 0.143	1.059
	5.906	1.417	6.062	0.858	3.40		4.136	5.392
	8.937	0.010	8.628	0.040			8.325	7.126
	(16)		(12 + 12)				(16)	(12 + 14)
$^1E_2'$	4.773	0	4.739	0		$^3E_2'$	3.246	3.954
	5.846	0	6.355	0			4.621	5.521
	7.308	0	9.456	0			6.815	6.585
	(16)		(12 + 12)				(16)	(12 + 14)
$^1A_2'$	7.189	0	6.741	0		$^3A_2'$	7.189	6.791
	10.728	0	9.779	0			10.128	8.631
	(8)		(8 + 14)				(8)	(8 + 10)

[a] Under Approximation (β_{all}, P–P). Figures in brackets indicate the number of functions taken, the first corresponds to the singly excited configurations, the next the doubly excited ones. Note that some of the singly excited configurations are deleted in the case of D.CI.

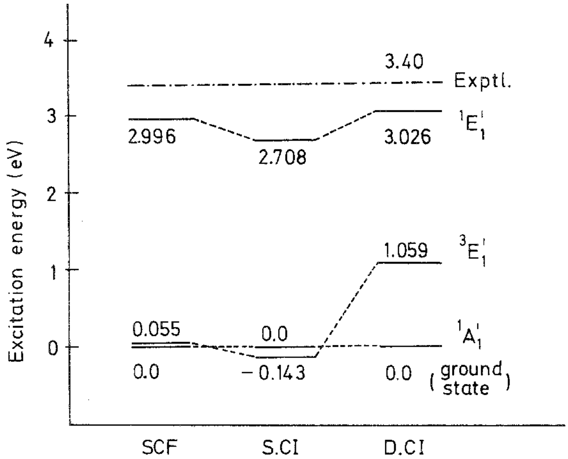

Fig. 2. The lowest excited levels of the E_1' state under approximation (β_{all}, P–P)

Although singly excited configurations can also mix with the doubly excited configurations in the $^1A_1'$ ground state, their contribution is shown to be negligibly small (1%).

It can be tentatively concluded, therefore, that the contribution of the doubly excited configurations is remarkable in certain aromatic hydrocarbons which contain some number of hetero atoms.

Acknowledgement. One of the authors (K. S.) wishes to thank Professor K. Suzuki of Tokyo Kyoiku University for his encouragement.

Appendix A

The Calculation of the Oscillator Strength for the Singlet State Including the Doubly Excited Configurations

The electronic transition moment between the ground ($^1\Phi_G$) and excited ($^1\Phi_E$) states is expressed as

$$M_{GE} = \langle ^1\Phi_G | M | ^1\Phi_E \rangle , \tag{1}$$

where

$$M = e \sum_u r_u + \sum_s e_s r_s$$

the sum u being over all π-electrons and s over all core nuclei. The oscillator strength f is calculated from the following Mulliken-Rieke's formula:

$$f = 1.084 \times 10^{11} \nu M_{GE}^2 . \tag{2}$$

In this equation, ν represents the excitation energy in units of cm^{-1} between $^1\Phi_G$ and $^1\Phi_E$ states. These states consist of the configurational wave functions $^1\Psi_a$ (linear combinations of Slater determinants); $^1\Phi_G$ and $^1\Phi_E = \sum_a A_a \cdot {}^1\Psi_a$. Then the matrix elements for the x-component of the non-zero transition moment are as follows:

(A) $$\langle ^1\Psi_0 | M^x | ^1\Psi_0 \rangle = 2e \sum_f^{\text{occ.}} m_{ff}^x + \sum_s e_s x_s$$

sum f being over all occupied molecular orbitals,

$$m_{ij}^x = \langle \varphi_i(1) | M^x(1) | \varphi_j(1) \rangle = \sum_m C_{mi} C_{mj} (\bar{M}_m^x) ,$$

φ_i and φ_j being LCAO–MO's; $\varphi_i = \sum_m C_{mi} X_m$, the sum m being taken over all the cores donating π-electrons, and $\bar{M}_m^x$ refering to the x-coordinate of m-th core.

(B) $$\langle ^1\Psi_0 | M^x | ^1\Psi_t^u \rangle = \sqrt{2}\, m_{tu}^x ;$$

(C) $$\langle ^1\Psi_0 | M^x | ^1\Psi_{pq}^{mn} \rangle = 0 ;$$

(D) $$\langle ^1\Psi_r^s | M^x | ^1\Psi_t^u \rangle = \delta_{rt} \left\{ \delta_{su} \left(2 \sum_f^{\text{occ.}} m_{ff}^x - m_{rr}^x + m_{ss}^x + \sum_s e_s x_s \right. \right.$$
$$\left. + (1 - \delta_{su})\, m_{su}^x \right\} + (1 - \delta_{rt})\, \delta_{su} (- m_{rt}^x)$$

(E) $$\langle ^1\Psi_r^s | M^x | ^1\Psi_{pq}^{mn} \rangle ;$$

(i) $$\langle ^1\Psi_r^s | M^x | ^1\Psi_{pp}^{mn} \rangle = \delta_{rp} [\delta_{mn} \delta_{sm} (\sqrt{2}\, m_{rs}^x) + (1 - \delta_{mn}) \{ \delta_{sm} (m_{rn}^x) + \delta_{sn} (m_{rm}^x) \}] ;$$

(ii) $$\langle ^1\Psi_r^s | M^x | ^1\Psi_{pq}^{mm} \rangle = \delta_{sm} \{ \delta_{rp} (- m_{sq}^x) + \delta_{rq} (- m_{sp}^x) \} \qquad (p \neq q) ;$$

(iii) $$\langle ^1\Psi_r^s | M^x | ^1\Psi_{pq}^{mn}(\mathrm{I}) \rangle = \delta_{rp} \delta_{sm} \left(\frac{\sqrt{6}}{2} m_{qn}^x \right) + \delta_{rq}\, \delta_{sn} \left(\frac{\sqrt{6}}{2} m_{pm}^x \right) ;$$

$$\langle ^1\Psi_r^s | M^x | ^1\Psi_{pq}^{mn}(\mathrm{II}) \rangle = \delta_{rp} \left\{ \delta_{sm} \left(\frac{\sqrt{2}}{2} m_{qn}^x \right) + \delta_{sn} (- \sqrt{2} m_{qm}^x) \right\}$$
$$+ \delta_{rq} \left\{ \delta_{sm} (- \sqrt{2}\, m_{pn}^x) + \delta_{sn} \left(\frac{\sqrt{2}}{2} m_{pm}^x \right) \right\} \qquad (p \neq q \quad \text{and} \quad m \neq n) ;$$

(F)

(i) $\langle {}^1\Psi_{ii}^{kl}|M^x|{}^1\Psi_{pp}^{mn}\rangle$ type

$$\begin{aligned}
&= \delta_{ip}\Biggl[\delta_{kl}\Biggl\{\delta_{mn}\,\delta_{km}\Biggl(2\sum_{f}^{\text{occ.}}\mathrm{m}_{ff}^x - 2\mathrm{m}_{ii}^x + 2\mathrm{m}_{kk}^x + \sum_s \mathrm{e}_s\mathrm{x}_s\Biggr) + (1-\delta_{mn})\\
&\quad\cdot(\delta_{km}\sqrt{2}\,m_{kn}^x + \delta_{kn}\sqrt{2}\,m_{km}^x)\Biggr\} + (1-\delta_{kl})(1-\delta_{mn})\Biggl\{(\delta_{km}\,\delta_{ln} + \delta_{kn}\,\delta_{lm})\\
&\quad\cdot\Biggl(2\sum_{f}^{\text{occ.}} m_{ff}^x - 2m_{ii}^x + m_{kk}^x + m_{ll}^x + \sum_s e_s x_s\Biggr) + \delta_{km}(1-\delta_{ln})\,m_{ln}^x\\
&\quad + \delta_{kn}(1-\delta_{lm})\,m_{lm}^x + \delta_{lm}(1-\delta_{kn})\,m_{kn}^x + \delta_{ln}(1-\delta_{km})\,m_{km}^x\Biggr\}\\
&\quad + \delta_{mn}(1-\delta_{kl})(\delta_{km}+\delta_{lm})\sqrt{2}\,m_{kl}^x\Biggr]\,;
\end{aligned}$$

(ii) $\langle {}^1\Psi_{ii}^{kl}|M^x|{}^1\Psi_{pq}^{mm}\rangle$ type $(p \neq q)$

$$= \delta_{kl}\,\delta_{km}\{\delta_{ip}\sqrt{2}\,m_{iq}^x + \delta_{iq}\sqrt{2}\,m_{ip}^x\}\ ;$$

(iii) $\langle {}^1\Psi_{ii}^{kl}|M^x|{}^1\Psi_{pq}^{mn}\rangle$ type $(k \neq l, p \neq q$ and $m \neq n)$;

Case 1: ${}^1\Psi_{pq}^{mn} = {}^1\Psi_{pq}^{mn}(\mathrm{I})$;

$$\{\delta_{km}\,\delta_{ln} + \delta_{kn}\,\delta_{lm}\}\left\{\delta_{ip}\left(-\frac{\sqrt{6}}{2}\,m_{iq}^x\right) + \delta_{iq}\left(-\frac{\sqrt{6}}{2}\,m_{ip}^x\right)\right\},$$

Case 2: ${}^1\Psi_{pq}^{mn} = {}^1\Psi_{pq}^{mn}(\mathrm{II})$;

$$\{\delta_{km}\,\delta_{ln} + \delta_{kn}\,\delta_{lm}\}\left\{\delta_{ip}\left(\frac{\sqrt{2}}{2}\,m_{iq}^x\right) + \delta_{iq}\left(\frac{\sqrt{2}}{2}\,m_{ip}^x\right)\right\};$$

(iv) $\langle {}^1\Psi_{ij}^{kk}|M^x|{}^1\Psi_{pq}^{mm}\rangle$ type $(i \neq j$ and $p \neq q)$

$$\begin{aligned}
&= \delta_{km}\Biggl\{(\delta_{ip}\,\delta_{jq} + \delta_{iq}\,\delta_{jp})\Biggl(2\sum_{f}^{\text{occ.}} m_{ff}^x - m_{ii}^x - m_{jj}^x + 2m_{kk}^x + \sum_s e_s x_s\Biggr)\\
&\quad + \delta_{ip}(1-\delta_{jq})(-m_{jq}^x) + \delta_{iq}(1-\delta_{jp})(-m_{jp}^x) + \delta_{jp}(1-\delta_{iq})(-m_{iq}^x)\\
&\quad + \delta_{jq}(1-\delta_{ip})(-m_{ip}^x)\Biggr\}\,;
\end{aligned}$$

(v) $\langle {}^1\Psi_{ij}^{kk}|M^x|{}^1\Psi_{pq}^{mn}\rangle$ type $(i \neq j, p \neq q$ and $m \neq n)$;

Case 1: ${}^1\Psi_{pq}^{mn} = {}^1\Psi_{pq}^{mn}(\mathrm{I})$;

$$(\delta_{ip}\,\delta_{jq} + \delta_{iq}\,\delta_{jp})\left\{\delta_{km}\left(-\frac{\sqrt{6}}{2}\,m_{kn}^x\right) + \delta_{kn}\left(-\frac{\sqrt{6}}{2}\,m_{km}^x\right)\right\},$$

Case 2: ${}^1\Psi_{pq}^{mn} = {}^1\Psi_{pq}^{mn}(\mathrm{II})$;

$$(\delta_{ip}\,\delta_{jq} + \delta_{iq}\,\delta_{jp})\left\{\delta_{km}\left(\frac{\sqrt{2}}{2}\,m_{kn}^x\right) + \delta_{kn}\left(\frac{\sqrt{2}}{2}\,m_{km}^x\right)\right\};$$

(vi) $\langle {}^1\Psi_{ij}^{kl}|M^x|{}^1\Psi_{pq}^{mn}\rangle$ type $(i \neq j, k \neq l, p \neq q$ and $m \neq n)$,

$$\left.\begin{array}{l}\langle {}^1\Psi_{ij}^{kl}|M^x|{}^1\Psi_{iq}^{kl}\rangle \\ \langle {}^1\Psi_{ij}^{kl}|M^x|{}^1\Psi_{qi}^{lk}\rangle \\ \langle {}^1\Psi_{ji}^{kl}|M^x|{}^1\Psi_{qi}^{kl}\rangle \\ \langle {}^1\Psi_{ji}^{kl}|M^x|{}^1\Psi_{iq}^{lk}\rangle\end{array}\right\} = \left\{\begin{array}{ll}\langle \mathrm{I}|\mathrm{I}\rangle & = -m_{jq}^x \\ \langle \mathrm{I}|\mathrm{II}\rangle = \langle \mathrm{II}|\mathrm{I}\rangle & = 0 \\ \langle \mathrm{II}|\mathrm{II}\rangle & = -m_{jq}^x\end{array}\right.$$

$$\left.\begin{array}{l}\langle {}^1\Psi_{ij}^{kl}|M^x|{}^1\Psi_{qi}^{kl}\rangle \\ \langle {}^1\Psi_{ij}^{kl}|M^x|{}^1\Psi_{iq}^{lk}\rangle \\ \langle {}^1\Psi_{ji}^{kl}|M^x|{}^1\Psi_{iq}^{kl}\rangle \\ \langle {}^1\Psi_{ji}^{kl}|M^x|{}^1\Psi_{qi}^{lk}\rangle\end{array}\right\} = \left\{\begin{array}{ll}\langle \mathrm{I}|\mathrm{I}\rangle & = -\frac{1}{2}m_{jq}^x \\ \langle \mathrm{I}|\mathrm{II}\rangle = \langle \mathrm{II}|\mathrm{I}\rangle & = \frac{\sqrt{3}}{2}m_{jq}^x \\ \langle \mathrm{II}|\mathrm{II}\rangle & = \frac{1}{2}m_{jq}^x\end{array}\right.$$

$$\left.\begin{array}{l}\langle {}^1\Psi_{ij}^{kl}|M^x|{}^1\Psi_{ij}^{kn}\rangle \\ \langle {}^1\Psi_{ij}^{lk}|M^x|{}^1\Psi_{ij}^{nk}\rangle \\ \langle {}^1\Psi_{ij}^{lk}|M^x|{}^1\Psi_{ji}^{kn}\rangle \\ \langle {}^1\Psi_{ij}^{kl}|M^x|{}^1\Psi_{ji}^{nk}\rangle\end{array}\right\} = \left\{\begin{array}{ll}\langle \mathrm{I}|\mathrm{I}\rangle & = m_{ln}^x \\ \langle \mathrm{I}|\mathrm{II}\rangle = \langle \mathrm{II}|\mathrm{I}\rangle & = 0 \\ \langle \mathrm{II}|\mathrm{II}\rangle & = m_{ln}^x\end{array}\right.$$

$$\left.\begin{array}{l}\langle {}^1\Psi_{ij}^{kl}|M^x|{}^1\Psi_{ij}^{nk}\rangle \\ \langle {}^1\Psi_{ij}^{lk}|M^x|{}^1\Psi_{ij}^{kn}\rangle \\ \langle {}^1\Psi_{ij}^{lk}|M^x|{}^1\Psi_{ji}^{nk}\rangle \\ \langle {}^1\Psi_{ij}^{kl}|M^x|{}^1\Psi_{ji}^{kn}\rangle\end{array}\right\} = \left\{\begin{array}{ll}\langle \mathrm{I}|\mathrm{I}\rangle & = \frac{1}{2}m_{ln}^x \\ \langle \mathrm{I}|\mathrm{II}\rangle = \langle \mathrm{II}|\mathrm{I}\rangle & = -\frac{\sqrt{3}}{2}m_{ln}^x \\ \langle \mathrm{II}|\mathrm{II}\rangle & = -\frac{1}{2}m_{ln}^x\end{array}\right.$$

$$\left.\begin{array}{l}\langle {}^1\Psi_{ij}^{kl}|M^x|{}^1\Psi_{ij}^{lk}\rangle \\ \langle {}^1\Psi_{ij}^{kl}|M^x|{}^1\Psi_{ji}^{kl}\rangle\end{array}\right\} = \left\{\begin{array}{ll}\langle \mathrm{I}|\mathrm{I}\rangle & = \frac{1}{2}m_o^x \\ \langle \mathrm{I}|\mathrm{II}\rangle = \langle \mathrm{II}|\mathrm{I}\rangle & = -\frac{\sqrt{3}}{2}m_o^x \\ \langle \mathrm{II}|\mathrm{II}\rangle & = -\frac{1}{2}m_o^x\end{array}\right.$$

$$\left.\begin{array}{l}\langle {}^1\Psi_{ij}^{kl}|M^x|{}^1\Psi_{ij}^{kl}\rangle \\ \langle {}^1\Psi_{ij}^{kl}|M^x|{}^1\Psi_{ji}^{lk}\rangle\end{array}\right\} = \left\{\begin{array}{ll}\langle \mathrm{I}|\mathrm{I}\rangle & = m_o^x \\ \langle \mathrm{I}|\mathrm{II}\rangle = \langle \mathrm{II}|\mathrm{I}\rangle & = 0 \\ \langle \mathrm{II}|\mathrm{II}\rangle & = m_o^x ,\end{array}\right.$$

where $m_0^x = 2\sum_f^{\text{occ.}} m_{ff}^x - m_{ii}^x - m_{jj}^x + m_{kk}^x + m_{ll}^x + \sum_s e_s x_s$,

$$\langle \mathrm{I} | \mathrm{II} \rangle = \langle \Psi_{ij}^{kl}(\mathrm{I}) | M^x | \Psi_{pq}^{mn}(\mathrm{II}) \rangle .$$

The pair of independent singlet functions constructed from the $i \to j, k \to l$ type excitations is:

$$^1\Psi_{ij}^{kl}(\mathrm{I}) = \frac{1}{2\sqrt{3}} \{ -|i\bar{j}k\bar{l}| - |\bar{i}j\bar{k}l| - |\bar{i}\bar{j}kl| - |ij\bar{k}\bar{l}| + 2|i\bar{j}\bar{k}l| + 2|\bar{i}jk\bar{l}| \} ,$$

$$^1\Psi_{ij}^{kl}(\mathrm{II}) = \frac{1}{2} \{ + |i\bar{j}k\bar{l}| + |\bar{i}j\bar{k}l| - |\bar{i}\bar{j}kl| - |ij\bar{k}\bar{l}| \} .$$

Appendix B

The Determination of the Symmetry of the Degenerate MO's

The pair of the degenerate MO's φ_i and φ_j of the form

$$\varphi_i = \sum_r a_{ir} \chi_r \tag{1}$$

is transformed by a symmetry operator R into

$$R\begin{pmatrix} \varphi_i \\ \varphi_j \end{pmatrix} = \begin{pmatrix} \alpha\beta \\ \gamma\delta \end{pmatrix} \begin{pmatrix} \varphi_i \\ \varphi_j \end{pmatrix} = \begin{pmatrix} \varphi_i' \\ \varphi_j' \end{pmatrix} \tag{2}$$

where α, β, γ and δ are the corresponding transformation matrix elements. The transformed functions φ_i' and φ_j' can then be written in a form

$$\varphi_i' = R\varphi_i = \sum_r a_{ir} R\chi_r = \sum_r a_{ir}' \chi_r . \tag{3}$$

Substituting (1) and (3) into (2), we obtain

$$\begin{aligned} a_{ir}' &= \alpha a_{ir} + \beta a_{jr} \\ a_{jr}' &= \gamma a_{ir} + \delta a_{jr} . \end{aligned} \tag{4}$$

The two groups of atoms $C_1 \sim C_5$ and $O_6 \sim O_{10}$ numbered as in Fig. 1 belong to the same D_{5h} symmetry and can not be superimposable one another, we only have to consider the carbon skeleton to simplyfy our discussion.

If we apply operation $\hat{C}_5$ to the degenerate MO's φ_2 and φ_3, that is a rotation of angle $2\pi/5$ about the principal axis, we find that:

$$\begin{aligned} \varphi_2 &= -0.41891\chi_1 - 0.21016\chi_2 + 0.28903\chi_3 + 0.38879\chi_4 - 0.04875\chi_5 + \cdots \\ \varphi_3 &= -0.08486\chi_1 + 0.37219\chi_2 + 0.31488\chi_3 - 0.17758\chi_4 - 0.42463\chi_5 + \cdots , \end{aligned} \tag{5}$$

$$\begin{aligned} \varphi_2' &= \hat{C}_5\varphi_2 = -0.21016\chi_1 + 0.28903\chi_2 + 0.38879\chi_3 - 0.04875\chi_4 - 0.41891\chi_5 + \cdots \\ \varphi_3' &= \hat{C}_5\varphi_3 = +0.37219\chi_1 + 0.31488\chi_2 - 0.17758\chi_3 - 0.42463\chi_4 - 0.08486\chi_5 + \cdots . \end{aligned} \tag{6}$$

From (4), (5) and (6), the transformation matrix is obtained as follows:

$$\begin{pmatrix} \cos(2\pi/5) & 0.9510 \\ -0.9510 & \cos(2\pi/5) \end{pmatrix} \subset \hat{C}_5 .$$

In the like way, we have

$$\begin{pmatrix} \cos(4\pi/5) & 0.5878 \\ -0.5878 & \cos(4\pi/5) \end{pmatrix} \subset \hat{C}_5^2 , \quad \begin{pmatrix} -0.9211 & -0.3892 \\ -0.3892 & 0.9211 \end{pmatrix} \subset \hat{C}_2 ,$$

$$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \subset \hat{\sigma}_h , \quad \begin{pmatrix} -\cos(2\pi/5) & -0.9510 \\ 0.9510 & -\cos(2\pi/5) \end{pmatrix} \subset \hat{S}_5 ,$$

$$\begin{pmatrix} -\cos(4\pi/5) & -0.5878 \\ 0.5878 & -\cos(4\pi/5) \end{pmatrix} \subset \hat{S}_5^2 , \quad \begin{pmatrix} 0.9211 & 0.3892 \\ 0.3892 & -0.9211 \end{pmatrix} \subset \hat{\sigma}_v .$$

Examing these characters, we can determine that the MO's φ_2 and φ_3 belong to the e_1'' symmetry. The other degenerate MO's are determined in the same way:

$$(\varphi_4, \varphi_5) \subset e_2'', \quad (\varphi_7, \varphi_8) \subset e_1'', \quad (\varphi_9, \varphi_{10}) \subset e_2'' .$$

The numbering of MO's is in the order of orbital energies; φ_1 (lowest), φ_2 and φ_3, φ_4 and φ_5 (two pairs of degenerate MO's), φ_6 (highest occupied), φ_7 and φ_8, φ_9 and φ_{10} (two pairs of degenerate MO's, unoccupied).

References

1. Yamada, K., N. Mizuno, and Y. Hirata: Bull. chem. Soc. Japan **31**, 543 (1958).
2. Ito, M., and R. West: J. Amer. chem. Soc. **85**, 2580 (1963).
3. Baezinger, N. C., J. J. Hegenbarth, and D. G. William: J. Amer. chem. Soc. **85**, 1539 (1963).
4. West, R., and D. L. Powell: J. Amer. chem. Soc. **85**, 2577 (1963).
5. Baezinger, N. C., and J. J. Hegenbarth: J. Amer. chem. Soc. **86**, 3250 (1964).
6. Cignitti, M.: Theoret. chim. Acta (Berl.) **5**, 169 (1966).
7. West, R., and H. Y. Niu: J. Amer. chem. Soc. **85**, 2586 (1963).
8. Brown, R. D., and M. L. Heffernan: Trans. Faraday Soc. **54**, 757 (1958).
9. Matsuoka, O., and Y. I'Haya: Molecular Physics **8**, 455 (1964).
10. I'Haya, Y.: Recent Developments in the Generalized Hückel Method, Advances in Quantum Chemistry, Löwdin ed., p. 211. New York: Academic Press Inc. 1964.
11. Pariser, R., and R. G. Parr: J. chem. Physics **21**, 767 (1953).
12. Flurry, R. L., Jr., E. W. Stout, and J. J. Bell: Theoret. chim. Acta (Berl.) **8**, 203 (1967).
13. Mataga, N., and K. Nishimoto: Z. physik. Chem. **13**, 140 (1957).
14. Ito, H., and Y. I'Haya: Theoret. chim. Acta (Berl.) **2**, 247 (1964).

Professor Y. J. I'Haya
Department of Materials Science
The University of Electro-Communications
Chofu-Shi
Tokyo 182, Japan