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Semi-Empirical SCF MO Treatment for Valence Electron Systems. Electronic Structures of trans- and cis-Isomers of Butadiene, Acrolein, and Glyoxal

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Using a semi-empirical ASMO SCF method for all valence electron systems, but a method modified to include one-center exchange integrals and an off-diagonal core integral as estimated by the approximation in our previous treatment, the electronic structures of trans- and cis-isomers of butadiene, acrolein, and glyoxal are calculated. The energy sequence of the molecular orbitals, the charge distributions in lone-pair orbitals and π MO's, and the charge distribution in these compounds are investigated. The n—π^* and π—π^* transition energies are also presented; the agreement between the calculated and observed values is almost entirely satisfactory. Further, the singlet-triplet oscillator strength in the *trans*-glyoxal is estimated by means of the obtained results.

In our previous papers, a semi-empirical ASMO SCF method for all valence electron systems was presented; the calculated results for small molecules[1] and ionic intermediates[2,3] were found to accord fairly well with the experimental results and the other rigorous calculated results. However, it was pointed out that some refinements are necessary if we are to obtain more reasonable results for transition energies especially.

In this paper, we make some of the improvements suggested by our previous results. That is, the one-center exchange integrals neglected in our previous treatment are taken into account, and a modified evaluation of the off-diagonal core integrals is made.[4] By this modified method, the electronic structures of trans- and cis-isomers with the same number of valence electrons, that is, butadiene, acrolein, and glyoxal, are calculated. It will be found that the obtained results for orbital energies, charge distributions, and transition energies are in satisfactory agreement with the other calculated and experimental results.

Method and Parameters Used

The main part of this treatment has already been described in Ref. 1, and only an outline will be given now. The SCF procedure is based on Roothaan's treatment for closed-shell compounds.[5] The Fock operator is:

$$F_{rs} = H_{rs} + \sum_{t,u} P_{tu}[(rs|tu) - (1/2)(rt|su)] \quad (1)$$

The electronic repulsion integral, $(rs|tu)$, is estimated by the Mulliken approximation,[6] and the two-center Coulomb repulsion integral, $(rr|ss)$, by the Ohno approximation.[7]

The diagonal core integrals are expressed as:

$$H_{rr} = U_{rr} + \sum_{B \neq A} (B|rr) \quad (2)$$

By introducing one-center exchange integrals, U_{rr} is approximated as:

$$U_{rr} = -I_r - (N_r - 1)(rr|rr) - \sum_{r'} N_{r'}\{(rr|r'r') - (1/2)(rr'|rr')\} \quad (3)$$

For example, the U_{ss} for the valence 2s atomic orbitals (AO) is:

$$U_{ss} = -I_s - (N_s - 1)(ss|ss) - N_p\{(ss|pp) - (1/2)(sp|sp)\}$$

where N_p is the number of valence p electrons on the atom in question. For the valence 2p AO, U_{pp} is taken to be the average value of the px, py, and pz AO's on the same atom.

The core attraction integral, $(B|rr)$, is:

$$(B|rr) = -\sum_{t}^{\text{on B}} N_t(tt|rr)$$

The off-diagonal core integrals, H_{rs} $(r \neq s)$, are obtained by the following approximate formula:

$$H_{rs} = (S_{rs}/2)\{-(Z_A + Z_B)(C/R_{AB}) - (B|rr) - (A|ss) + H_{rr} + H_{ss}\} \quad (4)$$

where the AO r belongs to the A atom, and AO

1) T. Yonezawa, K. Yamaguchi and H. Kato, This Bulletin, **40**, 536 (1967).
2) T. Yonezawa, H. Nakatsuji and H. Kato, *ibid.*, **39**, 2788 (1966).
3) T. Yonezawa, H. Konishi and H. Kato, *ibid.*, **40**, 1071 (1967).
4) H. Kato, H. Konishi and T. Yonezawa, *ibid.*, **40**, 1017 (1967).
5) C. C. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1961).
6) R. S. Mulliken, *J. Chem. Phys.*, **46**, 497, 675 (1949).
7) K. Ohno, *Theoret. Chim. Acta (Bel.)*, **2**, 219 (1964).

s, to the B atom, and where C is a parameter, which is taken to be 1.0 in this treatment.[4]

Referring to the values estimated by Hinze and Jâffe,[8] the one-center exchange integrals may be approximated as follows:

$$(sp|sp)_A = 0.045\, Z_A\, (ss|pp)_A$$

$$(pp'|pp')_A = 0.011\, Z_A\, (pp|p'p')_A$$

where the subscript A denotes the A atom. For reference, the values obtained by the above approximation are listed in Table 1 together with those of Hinze and Jâffe.

The other integral values and notations appearing in the above equations are the same as in the previous paper.[1]

TABLE 1. THE VALUES OF ONE CENTER EXCHANGE INTEGRAL (eV)

	Present calc.	Ref. 8
$(sp \mid sp)_C$	2.072	2.299
$(pp' \mid pp')_C$	0.477	0.540
$(sp \mid sp)_N$	2.995	2.986
$(pp' \mid pp')_N$	0.710	0.774
$(sp \mid sp)_O$	3.939	3.938
$(pp' \mid pp')_O$	0.906	0.828

The geometries adopted for the treated compounds are cited from Ref. 9; the cis-forms are assumed to have the configurations in which a terminal group rotates 180° around the central C–C bond of the corresponding trans-form.

Results and Discussions

Orbital Energy and Total Energy. All the calculated π molecular orbital (MO) energies and some of the σ MO energies are collected in Table 2, together with those computed by Lipscomb *et al.*[10] and those observed by the photoionization method.[10,11] Our values are also plotted in Fig. 1, together with those in ethylene and formaldehyde as obtained by the same treatment. As to the π MO's, it may be seen that these energies become lower, in the order of butadiene, acrolein and glyoxal, with an increase in the number of oxygen atoms; on the other hand, the lone-pair orbital in acrolein or formaldehyde splits into higher and lower orbitals in glyoxal. By referring to the table, it can also be seen that the obtained first ionization potentials relate to the electron occupying the π-type MO's in butadiene and acrolein, and to the lone-pair MO in

TABLE 2. SOME ORBITAL ENERGIES (eV)

		trans-Butadiene				*tsans*-Acrolein			*trans*-Glyoxal	
		Present calc.	Ref. 10	Ref. 11		Present calc.	Ref. 10	Ref. 11		Present calc.
	π_{bg}	4.87	—	—	π	3.90	—	—	π_{bg}	3.30
LV*	π_{au}	0.89	—	—	π	−0.18	—	—	π_{au}	−0.73
HO*	π_{bg}	−10.39	−7.34	−9.08	π	−11.38	−8.38	−9.99	n_{ag}	−11.22
	π_{au}	−11.84	−13.17	−11.25	n	−11.62	−10.51	−10.82	π_{bg}	−13.32
	σ_{ag}	−12.22	−12.78	−12.14	σ	−13.12	−13.84	−13.19	n_{bu}	−13.87
	σ_{ag}	−13.34	−14.43	−13.23	π	−13.25	−15.02	—	σ_{ag}	−14.05
	σ_{bu}	−13.70	−14.60	—	σ	−13.95	—	—	π_{au}	−14.59
	σ_{bu}	−14.90	−17.20	−15.14	σ	−14.71	—	−14.56	σ_{bu}	−14.75
	σ_{ag}	−14.91	—	—	σ	−15.25	—	−15.95	σ_{ag}	−16.18

		cis-Butadiene			*cis*-Acrolein			*cis*-Glyoxal
		Present calc.	Ref. 10		Present calc.	Ref. 10		Present calc.
	π_{a2}	4.89	—	π	3.99	—	π_{a2}	3.31
LV	π_{b1}	0.95	—	π	0.03	—	π_{b1}	−0.47
HO	π_{a2}	−10.40	−7.03	π	−11.24	−8.19	n_{a1}	−11.07
	π_{b1}	−11.79	−13.27	n	−11.51	−10.70	π_{a2}	−13.13
	σ_{a1}	−12.23	−13.00	σ	−13.04	−13.66	n_{b2}	−13.70
	σ_{b2}	−13.26	—	π	−13.12	−15.08	σ_{a1}	−14.02
	σ_{a1}	−13.74	—	σ	−13.71	—	π_{b1}	−14.41

* The notations HO and LV indicate the highest occupied and lowest vacant MO, respectively.

8) H. Hinze and H. H. Jâffe, *J. Chem. Phys.*, **38**, 1834 (1963).
9) "Tables of Interatomic Distances and Configuration in Molecules and Ions," ed. by L. E. Sutton, The Chem. Soc., London (1956) and (1965).
10) M. D. Newton, F. P. Boer and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2367 (1966).
11) D. W. Turner, "Advances in Physical Organic Chemistry," Vol. 4, Academic Press, London and N. Y. (1966), p. 31.

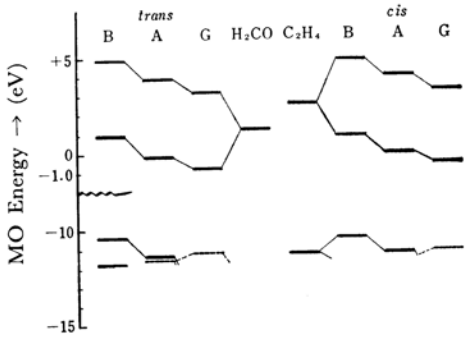


Fig. 1. The energies of the π and lone pair MOs in the *trans*- and *cis*-butadiene (B), acrolein (A) and glyoxal (G). The full lines indicate the π MO levels and the dotted line are lone pair MO levels.

glyoxal. The calculated values of these energies are about 1 eV lower than the observed values in both butadiene and acrolein, whereas the agreement between these values and those observed in glyoxal is excellent. For the lower occupied orbital energies, some discrepancies between the present results and Lipscomb's results are seen in, for example, the energy gap between two occupied π MO's and the order of some MO's. Since the definite assignments of these MO's have not been settled,[10,11] we will here refrain from entering into a detailed discussion.

As to the energy differences between the trans- and cis-forms, the calculated energy differences between the electronic energies, ΔE_n, the core repulsion energies, ΔE_c[3] and the total energies, ΔW, of the trans- and cis-forms in these molecules are listed in Table 3, where the plus sign of ΔW indicates that the total energy of the cis-form is smaller than that of the trans-form. The calculated results indicate that the trans-form is more stable than the cis-form in each pair, and the stabilization energies are mainly contributed by the core repulsion term, not by the electronic term. These results agree with the experimental results and with the results previously obtained by Parr and Mulliken for the π-electron systems in butadiene isomers.[12] The obtained ΔW values, however, seem to be somewhat larger than those obtained in previous experiments.[13]

Table 3. The energy differences between cis- and trans-isomers (eV)

	Butadiene	Acrolein	Glyoxal
ΔE_e	−22.97	−23.51	−19.82
ΔE_c	+23.27	+24.08	+20.37
ΔW	+0.30	+0.57	+0.55

Charge Distributions and Coefficients of Some MO's. The calculated atom populations and atom bond populations are given in Fig. 2.

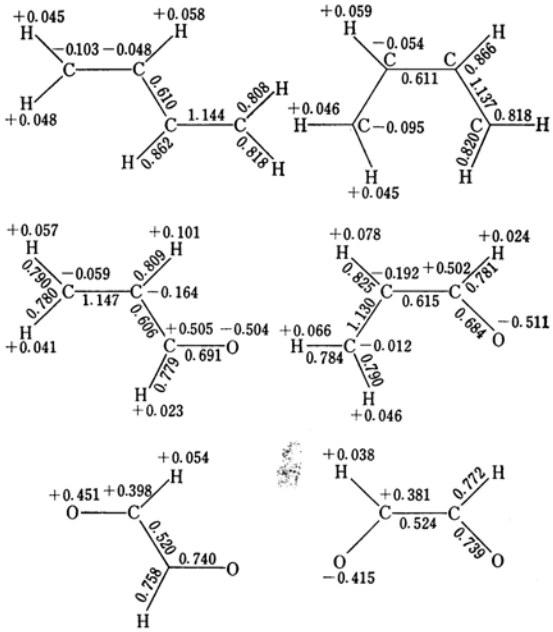


Fig. 2. The net charges and atom bond populations.

The calculated atom populations indicate that the oxygen atoms bear considerably large negative charges; for instance, in acrolein, the net charges of the oxygen atoms as determined by Mulliken population analysis are −0.504 in the trans-form and −0.511 in the cis-form, while they are −0.225 and −0.208 respectively in Ref. 10. The dipole

Table 4. The dipole moments (in Debye unit)

	trans-A	*cis*-A	*cis*-G	*cis*-B
$\mu_{Q\parallel}$	3.18	2.92	4.35	0.20
$\mu_{Q\perp}$	0.28	0.59	0	0
μ_{QT}	3.19	2.97	4.35	0.20
$\mu_{A\parallel}$	0.37	0.68	0.75	0.11
$\mu_{A\perp}$	0.01	0.07	0	0
μ_{AT}	0.37	0.69	0.75	0.11
μ_T	3.56	3.66	5.10	0.31
Ref. 10	1.572	1.628	—	—
Obs* $\mu_\parallel$	3.06	—	—	—
Obs* $\mu_\perp$	0.54	—	—	—
Obs* μ_T	3.11	—	—	—

* R. Wagner, J. Fine, J. W. Simmons and J. H. Goldstein, *J. Chem. Phys.*, **26**, 634 (1957).

** The notation μ_Q refers to the moment by charges and μ_A to the atomic moment, and μ_T to the total moment.

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

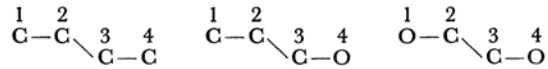
13) R. Wagner, J. Fine, J. W. Simmons and J. H. Goldstein, *ibid.*, **26**, 634 (1957).

TABLE 5. THE COEFFICIENTS OF π MO's

MO		AO: trans 1**	trans 2	trans 3	trans 4	cis 1	cis 2	cis 3	cis 4
B*	π_4	0.523	−0.721	0.721	−0.523	0.524	−0.722	0.722	−0.524
	π_3	0.626	−0.485	−0.485	0.626	0.627	−0.480	−0.480	0.627
	π_2	0.516	0.414	−0.414	−0.516	0.519	0.413	−0.413	−0.519
	π_1	0.382	0.453	0.453	0.382	0.374	0.459	0.459	0.374
	N_π***	1.028	0.972	0.972	1.028	1.018	0.982	0.982	1.018
A*	π_4	0.538	−0.738	0.694	−0.479	0.552	−0.739	0.689	−0.472
	π_3	0.627	−0.441	−0.504	0.601	0.636	−0.413	−0.509	0.605
	π_2	0.592	0.550	−0.237	−0.395	0.579	0.572	−0.215	−0.394
	π_1	0.204	0.299	0.561	0.550	0.175	0.296	0.570	0.553
	N_π	0.983	1.000	0.929	1.088	0.929	1.047	0.933	1.091
G*	π_4	0.512	−0.703	0.703	−0.512	0.519	−0.697	0.697	−0.519
	π_3	0.596	−0.481	−0.481	0.596	0.608	−0.467	−0.467	0.608
	π_2	0.517	0.425	−0.425	−0.517	0.510	0.435	−0.435	−0.510
	π_1	0.411	0.447	0.447	0.411	0.393	0.461	0.461	0.393
	N_π	1.052	0.948	0.948	1.052	1.007	0.993	0.993	1.007

* B: butadiene, A: acrolein, G: Glyoxal.

** The numbers refer to the one of π AO.



*** The notation, N_π is the π atomic orbital population.

moment calculated by the approximations described in Ref. 14 is 3.56 D in *trans*-acrolein; this value is close to the observed value, 3.11 D.[13,15] For reference, all the obtained dipole moment values are collected in Table 4; the moments produced by the charges, μ_Q, and the atomic dipoles, μ_A, are also indicated, together with their two components, which are parallel and perpendicular to the terminal bonds. The angles of the orientation of the moment from the C=O axis are calculated to be 6° in *trans*-acrolein and 11° in *cis*-acrolein, whereas the observed value is estimated as 14° for the trans-form.[13] Unfortunately, there are no observed values for the other compounds to be compared.

Table 5 lists the obtained values of the coefficients of the π MO's and the π AO populations. For butadienes, the tendencies of these values between cis- and trans-forms are similar to those presented by Parr and Mulliken,[12] but the π charges do not agree; *i. e.*, our finding is that the negative charges are on the terminal carbon atoms, −0.28 in the trans form and −0.18 in the cis-form, while, on the contrary, the terminal carbon atoms show positive charges in Ref. 12.

In Table 6 the coefficients of the lone-pair MO's are collected, (a) those of the two lone-pair MO's in trans-glyoxal, and (b) those of the *cis*- and *trans*-acroleins. Roughly speaking, the electrons in these MO's are delocalized as follows: 65—60%.

TABLE 6. THE COEFFICIENTS OF LONE PAIR MOs'

(a) *trans*-Glyoxal*

n_{ag} $-0.12(s_{C_1}+s_{C_2})+0.14(x_{C_1}-x_{C_2})+0.29(y_{C_1}-y_{C_2})$
$-0.03(s_{O_1}+s_{O_2})-0.11(x_{O_1}-x_{O_2})-0.59(y_{O_1}-y_{O_2})$
$+0.27(h_3+h_4)$

n_{bu} $0.19(x_{C1}+x_{C_2})+0.08(y_{C1}+y_{C2})-0.12(s_{O1}-s_{O2})$
$-0.39(x_{O1}+x_{O2})+0.48(y_{O1}+y_{O2})-0.24(h_3-h_4)$

(b) *cis*-Acrolein*

n $0.05s_{C1}-0.02x_{C1}-0.11y_{C1}-0.13s_{C_2}-0.24x_{C_2}$
$+0.41x_{C_2}-0.06s_{C_3}+0.09x_{C_3}-0.16y_{C_3}-0.03s_O$
$-0.12x_O+0.78y_O+0.32h_1+0.10h_2-0.18h_3$
$+0.07h_4$

trans-Acrolein*

n $-0.04s_{C_1}-0.10x_{C_1}+0.02y_{C_1}+0.13s_{C_2}+0.25x_{C_2}$
$-0.40y_{C_2}+0.06_{C_3}-0.09x_{C_3}+0.16y_{C_3}+0.03s_O$
$+0.12x_O-0.78y_O-0.32h_1-0.11h_2+0.17h_3$
$-0.07h_4$

* The molecular plane is xy plane and the C=O bonds are parallel to the x direction. The numbers in suffix refer to the ones in Table 3, and the number in the 1s AO of hydrogen atom is increased as the increase of the distance from the oxygen atom.

14) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, s 136 (1965).

15) Generally speaking, when these approximations are connected with the Mulliken populations, the obtained dipole values are quite larger, as may be seen in Ref. 1. The details will be published in the near future.

TABLE 7. THE TRANSITION ENERGIES (ΔE) AND TRANSITION MOMENTS (Q)

(a) Butadiene

		ΔE calc.	Q calc.	ΔE calc.[a]	ΔE obs.[a]
trans					
$\pi_2-\pi_3$	^1B_u	6.38	1.367	6.21	6.0
$\pi_1-\pi_3$	^1A_g	7.37	0	7.87	7.2
$\pi_2-\pi_4$	^1A_g	9.87	0	8.51	—
$\pi_1-\pi_4$	^1B_u	10.62	0.433	9.50	—
$\pi_2-\pi_3$	^3B_u	4.18	0	3.92	—
$\pi_1-\pi_3$	^3A_g	5.51	0	4.61	—
$\pi_2-\pi_4$	^3Ag	8.06	0	8.16	—
$\pi_1-\pi_4$	^3B_u	9.18	0	8.74	—
cis					
$\pi_2-\pi_3$	$^1B_1$	6.03	0.948	5.91	—
$\pi_1-\pi_3$	$^1A_1$	7.48	0.803	8.29	—
$\pi_2-\pi_4$	$^1A_1$	10.01	0.794	8.34	—
$\pi_1-\pi_4$	$^1B_1$	10.41	0.658	9.25	—
$\pi_2-\pi_3$	$^3B_1$	4.11	0	3.96	—
$\pi_1-\pi_3$	$^3A_1$	5.44	0	4.62	—
$\pi_2-\pi_4$	$^3A_1$	8.00	0	7.95	—
$\pi_1-\pi_4$	$^3B_1$	9.08	0	8.61	—

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

(b) Acrolein

		ΔE calc.	Q calc.	ΔE calc.[a,c]	ΔE obs.[a,b]
trans					
$n-\pi_3$	$^1A''$	4.24	0.066	3.85[a]	3.71[a] 3.76[b]
$n-\pi_4$	$^1A''$	8.41	0.055	6.53[a]	—
$\pi_2-\pi_3$	$^1A'$	6.25	1.272	6.08[a] 6.62[c]	5.96[a] 6.32[b]
$\pi_1-\pi_3$	$^1A'$	7.39	0.247	7.76[a]	—
$\pi_2-\pi_4$	$^1A'$	9.64	0.326	7.76[a]	— 8.35[b]
$\pi_1-\pi_4$	$^1A'$	10.82	0.574	9.44[a]	— 8.46[b]
$n-\pi_3$	$^3A''$	3.76	0	2.85[a]	—
$n-\pi_4$	$^3A''$	7.97	0	6.00[a]	—
$\pi_2-\pi_3$	$^3A'$	3.85	0	4.17[a]	—
$\pi_1-\pi_3$	$^3A'$	5.28	0	5.85[a]	—
$\pi_2-\pi_4$	$^3A'$	7.97	0	5.85[a]	—
$\pi_1-\pi_4$	$^3A'$	9.32	0	7.53[a]	—
cis					
$n-\pi_3$	$^1A''$	4.21	0.068	—	—
$n-\pi_4$	$^1A''$	8.34	0.058	—	—
$\pi_2-\pi_3$	$^1A'$	5.92	0.922	6.20[c]	
$\pi_1-\pi_3$	$^1A'$	7.51	0.744	—	—
$\pi_2-\pi_4$	$^1A'$	9.68	0.748	—	—
$\pi_1-\pi_4$	$^1A'$	10.62	0.208	—	—
$n-\pi_3$	$^3A''$	3.73	0	—	—
$n-\pi_4$	$^3A''$	7.91	0	—	—
$\pi_2-\pi_3$	$^3A'$	3.77	0	—	—
$\pi_1-\pi_3$	$^3A'$	5.24	0	—	—
$\pi_2-\pi_4$	$^3A'$	7.60	0	—	—
$\pi_1-\pi_4$	$^3A'$	9.24	0	—	—

a) K. Inuzuka, This Bulletin, **34**, 6 (1961).
b) A. D. Walsh, *Trans. Faraday Soc.*, **41**, 498 (1945).
c) M. Klessinger and W. Lüttke, *Z. Electrochem.*, **65**, 707 (1961).

TABLE 7. Continued

(c) Glyoxal

		ΔE calc.	Q calc.	ΔE calc.[a,b,c]	ΔE obs.[a]
trans					
$n_{ag}-\pi_3$	^1A_u	3.22	0.062	3.1[a] 2.6[b]	2.72[a]
$n_{bu}-\pi_3$	^1B_g	5.81	0	—	4.50[a]
$n_{ag}-\pi_4$	^1B_g	7.20	0	(8.0)[a]*	—
$n_{bu}-\pi_4$	^1A_u	9.83	0.059	—	—
$\pi_2-\pi_3$	^1B_u	7.27	1.167	7.4[a] 7.6[b] 7.8[c]	7.2—7.6[a]
$\pi_1-\pi_3$	^1A_g	7.92	0	8.0[a]	—
$\pi_2-\pi_4$	^1A_g	10.55	0	9.0[a]	—
$\pi_1-\pi_4$	^1B_u	11.28	0.634	10.2[a]	—
$n_{ag}-\pi_3$	^3A_u	2.68	0	2.3[a]	2.42[a]
$n_{bu}-\pi_3$	^3B_g	5.22	0	—	—
$n_{ag}-\pi_4$	^3B_g	6.69	0	(8.0)[a]	—
$n_{bu}-\pi_4$	^3A_u	9.38	0	—	—
$\pi_2-\pi_3$	^3B_u	4.59	0	2.5[a]	—
$\pi_1-\pi_3$	^3A_g	5.91	0	4.3[a]	—
$\pi_2-\pi_4$	^3A_g	8.60	0	8.9[a]	—
$\pi_1-\pi_4$	^3B_u	9.75	0	10.5[a]	—
cis					
$n_{a1}-\pi_3$	$^1B_1$	3.18	0.065	2.5[b]	—
$n_{a1}-\pi_4$	$^1A_2$	7.08	0.006	—	—
$n_{b2}-\pi_3$	$^1A_2$	5.68	0.034	—	—
$n_{b2}-\pi_4$	$^1B_1$	9.65	0.050	—	—
$\pi_2-\pi_3$	$^1B_2$	6.94	0.805	7.2[b] 6.4[c]	—
$\pi_2-\pi_4$	$^1A_1$	10.60	0.714	—	—
$\pi_1-\pi_3$	$^1A_1$	8.08	0.714	—	—
$\pi_1-\pi_4$	$^1B_2$	10.98	0.117	—	—
$n_{a1}-\pi_3$	$^3B_1$	2.60	0	—	—
$n_{a1}-\pi_4$	$^3A_2$	6.56	0	—	—
$n_{b2}-\pi_3$	$^3A_2$	5.07	0	—	—
$n_{b2}-\pi_4$	$^3B_1$	9.17	0	—	—
$\pi_2-\pi_3$	$^3B_2$	4.50	0	—	—
$\pi_2-\pi_4$	$^3A_1$	8.41	0	—	—
$\pi_1-\pi_3$	$^3A_1$	5.90	0	—	—
$\pi_1-\pi_4$	$^3B_2$	9.61	0	—	—

a) J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957).
b) A. Julg and J. C. Donadini, *Compt. Rend.*, **252**, 1798 (1961).
c) M. Klessinger and W. Lüttke, *Z. Electrochem.*, **65**, 707 (1961).
* The assignments for these transitions were not given in the Ref. a.

on the oxygen atoms, 20—25% on the carbon atoms, and 15% on the hydrogen atoms. In trans-glyoxal, the higher lone-pair MO's show more $p\pi'$ nature ($p\pi'$ AO in the molecular plane) and less s and $p\sigma$ natures than do the lower ones. Further, it may be pointed out that the unstabilization in the upper lone-pair MO is due to antibonding interaction between the $p\pi'$ AO's of the oxygen and neighboring carbon atoms. In the lower lone-pair MO, the stabilization is mainly due to the bonding interaction between the $p\sigma$ AO's of the C–O bonds. Accordingly, it may be noticed that the splitting between these two lone-pair MO's in glyoxals is largely dependent on the interactions between two neighboring atoms, not on those between the localized lone-pair AO's of the two oxygen atoms.

Transition Energy. Some $\pi-\pi^*$ and $n-\pi^*$ transition energies are summarized in Table 7 (a)—(c), together with the other calculated and the observed values where the numbers in subscripts increase from the lower to the higher MO. The agreement between the sets is fairly satisfactory. The lowest singlet transition in *trans*-glyoxal is predicted to be the Au–Ag transition; the next $n-\pi$ transition is a B_g–A_g transition. These assignments were not attempted in Sidman's paper,[16] where the lone-pair MO's were treated as localized

16) J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957).

on the oxygen atom. It may be noted that, in acrolein, the lowest transition becomes the $n-\pi^*$ transition; neverthless, the highest-occupied MO is a π-type MO, as may be seen in Table 2.

The calculated transition moments (in Å) are also indicated in Table 7. These values are calculated by the Mulliken approximation and include one-center terms. The obtained values, however, are seen to be considerably larger than the observed values; for instance, the oscillator strength value for the lowest $\pi-\pi^*$ transition in trans-butadiene is 0.98, while the observed value is 0.53.[17]

To examine the validity of the obtained results, the S-T oscillator strength in trans-glyoxal was also calculated. The perturbed transition adopted for the lowest triplet $n-\pi^*$ transition is the singlet $\pi_2-\pi_3^*$ transition;[18] the symmetries of these transitions are given in Table 7(c). Thus, the S-T oscillator strength, $f_{T\text{-}S}$, is estimated to be approximately as follows:[19]

$$f_{T\text{-}S} \doteqdot f_{s1-s0}\frac{E_{n-\pi}}{E_{\pi-\pi}}\left|\frac{\langle n \mid H_{so} \mid \pi_2\rangle}{E_{n-\pi}-E_{\pi-\pi}}\right|^2 \qquad (5)$$

where the notations are as follows: f_{s1-s0} refers to the oscillator strength of the singlet $\pi_2-\pi_3$ transition; $E_{n-\pi}$ and $E_{\pi-\pi}$ are the transition energies of the lowest triplet $n-\pi^*$ and singlet $\pi_2-\pi_3$ transitions, and $\langle n \mid H_{so} \mid \pi_2\rangle$ is the matrix element between the highest n MO and the π_2 MO. The matrix element, $\langle n \mid H_{so} \mid \pi_2\rangle$, is computed by considering only the one-center terms, which are given two set values. The other quantities in Eq. (5) are calculated by this treatment. The values obtained are 0.71×10^{-7} for $\zeta_c=27\ cm^{-1}$, and $\zeta_o=104\ cm^{-1}$,[20] and 1.68×10^{-7} for $\zeta_c=28\ cm^{-1}$, and $\zeta_o=152\ cm^{-1}$,[21] whereas the value estimated by Kanda *et al.* using the results of Sidman[15] was 0.78—1.8×10^{-7}.[18] The accordance between two results is fairly good. The effect on the transition energy of including a certain amount of configuration interaction (CI) is now under study. These results show that the lower transition energies are not seriously changed by the CI treatment. More details on this point will be published in the near future

The calculations have been carried out on an HITAC 5020 Computer at the computation center of the University of Tokyo.

17) E. g., C. M. Moser, *J. Chem. Soc.*, **1954**, 3455.
18) Y. Kanda, R. Shimada and H. Shimada, Preprints for the 19th Annual Meeting of the Chem. Soc. of Japan (1966), p. 144.
19) *E. g.*, J. W. Sidman, *J. Chem. Phys.*, **29**, 644 (1958).
20) These values are calculated by using the exponents determined from the Slater rule.
21) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).