A Simple Molecular Orbital Method for Discussing the Electronic Structures of Stereoisomers—The Theoretical Method and ESR Hyperfine Splittings of the Terephthalaldehyde Anion

By Keiji MOROKUMA, Teijiro YONEZAWA and Kenichi FUKUI

(Received May 8, 1962)

The various different properties of the stereoisomers of organic compounds have long excited the interest of chemists in their chemical reactivities, physical properties, spectroscopic data, and so forth.

From the point of view of molecular orbital (MO) treatment, stereoisomers may be divided into two classes, one consisting of geometrical (cis- and trans-) and rotational (gauche- and trans-) isomers, and the other containing optical isomers. The following discussion will be limited to the isomers of the first class.

The electronic structures of these isomers are calculated to be identical when the simple LCAO MO method, in which electronic interactions are formally neglected, is used, for in this method the secular equation of one of the isomers is equal to that of the other. In the discussion of the differences in energy of the first class steroisomers, classical electrostatic calculation has been found useful, as has the ASMO (antisymmetrized MO) calculation, including electronic interactions. In a discussion of their electron distribution the ASMO SCF (self-consistent field) calculation is both necessary and adequate; a typical example would be the strict calculation of the π-electron distribution of trans- and cis-butadiene by Parr and Mulliken[1]. In such non-polar compounds as butadiene, indeed, such a strict but very troublesome calculation is indispensable in order to show any difference of distribution. However, in a compound containing polar groups, some differences of electron distribution between the isomers, which may be sufficient for a qualitative comparison, may be obtained by a simple LCAO MO method, with the parameters modified by considering the electronic interaction between polar groups.

In this paper, such a modified simple molecular orbital method is to be determined for conjugated molecules; it is then to be applied to the interesting differences between terephthalaldehyde anion isomers in the proton hyperfine couplings in ESR (electron spin resonance) spectroscopy recently investigated by Maki[2].

As to the structural isomers, the electronic structures are, of course, different even in the simple LCAO MO calculation. In this simple method, however, it is difficult sufficiently to take into account the effects of near-by polar groups, while actually the electronic interactions cause a considerable change in the electron distribution. The simple MO method with modified parameters which is utilized for geometrical isomers is also of use for this class of isomers. Applications to actual problems of structural isomers—nuclear coupling constants and asymmetric parameters in PQR (pure nuclear quadrupole resonance) spectra, dipole moments, etc.—will be given in the next paper[3].

Theoretical Method

In the Hückel MO theory, by solving the secular equation

$$\sum_{s=1}^{n}(a_{rs}{}^0-\lambda_i\delta_{rs})C_{ir}{}^\pi=0 \qquad (r=1,2,\cdots,n) \qquad (1)$$

molecular orbitals are obtained as a linear combination of atomic orbitals (AO's) as follows:

$$\phi_i{}^\pi=\sum_{r=1}^{n}C_{ir}{}^\pi\chi_r{}^\pi \qquad (i=1,2,\cdots,n) \qquad (2)$$

where n is the number of π AO's, $\chi_r{}^\pi$ is the rth π AO, C_{ir} is the coefficient of the rth AO in the ith MO, λ_i is the ith eigenvalue of Eq. 1, and $a_{rr}{}^0$ and $a_{rs}{}^0$ are the parameters standing for the Coulomb integral of the rth AO and the resonance integral between the rth and the sth AO's, respectively.

The molecular orbitals of σ electrons are similarly calculated as a linear combination of σ atomic orbitals (sp^2 or sp^3 hybridized orbitals on carbon atoms, hydrogen 1s orbitals

---

[1] R. G. Parr and R. S. Mulliken, *J. Chem. Phys.*, **18**, 1182 (1950).

[2] A. H. Maki, ibid., **35**, 761 (1961).

[3] K. Morokuma, T. Masuda and K. Fukui, to be published in this Bulletin.

and σ atomic orbitals on substituents)[4-6]*:

$$\psi_j{}^\sigma=\sum_{t=1}^{N}C_{jt}{}^\sigma\chi_t{}^\sigma \qquad (j=1,2,\cdots,N) \qquad (3)$$

with parameters $b_{tt}{}^0$ and $b_{tu}{}^0$ defined as

$$\left.\begin{array}{ll}\text{Coulomb integral} & \alpha_t{}^\sigma=\alpha_\sigma+b_{tt}{}^0\beta_\sigma\\ \text{resonance integral} & \beta_{tu}{}^\sigma=b_{tu}{}^0\beta_\sigma\end{array}\right\} \quad (4)$$

where N is the number of σ AO's and β_σ is the resonance integral of the standard C–C σ bond of benzene. From these MO's, the π and the σ electron densities, $q_r{}^\pi$ and $q_t{}^\sigma$ respectively, are calculated:

$$\left.\begin{array}{l}q_r{}^\pi=\sum\limits_i^{\text{occ}}\nu_i{}^\pi(C_{ir}{}^\pi)^2\\ q_t{}^\sigma=\sum\limits_j^{\text{occ}}\nu_j{}^\sigma(C_{jt}{}^\sigma)^2\end{array}\right\} \quad (5)$$

where ν_i represents the number of electrons in the ith MO.

Suppose that $q_r{}^\pi$ and $q_t{}^\sigma$ have already been calculated by the use of assumed parameters. We call them the densities and the parameters, respectively, of the zero order. Of course, the results are identical with respect to the cis- and the trans-isomers. If the compound has an even number of electrons (closed shell), Fock's operater of the pth atomic orbital on the Ath atom with electron-electron interaction, which corresponds to the Coulomb integral in the simple MO treatment, may be given as follows[7]:

$$\begin{aligned}F_{pp}=&W_p(q_p)+\frac{1}{2}q_p\gamma_{pp}+(Z_A-1)\xi_{pA}\\ &+\sum_{\substack{r\\(\text{on }A)}}^{\text{all AO's}}q_r\gamma_{pr}+\sum_{\substack{r\\(\text{not on }A)}}^{\text{all AO's}}q_r\gamma_{pr}\\ &+\sum_{\substack{B\\(\neq A)}}^{\text{all cores}}Z_B\xi_{pB}\end{aligned} \qquad (6)$$

The first four terms are concerned with the electrons and the core of atom A, and the last two represent the interactions with electrons and cores on the other atoms; γ_{pr} and ξ_{pB} are the electron repulsion integral and the electron core atraction integral, respectively, which are represented by

$$\left.\begin{array}{l}\gamma_{pr}=\int\chi_p{}^*(1)\chi_p(1)\dfrac{e^2}{r_{12}}\chi_r{}^*(2)\chi_r(2)\mathrm{d}\tau_1\mathrm{d}\tau_2\\ \xi_{pB}=-\int\chi_p{}^*(1)\dfrac{e^2}{r_{1B}}\chi_p(1)\mathrm{d}\tau_1\end{array}\right\} \quad (7)$$

γ_{pp} and ξ_{pA} are the corresponding one-center integrals, and Z_B is the charge of the core B. $W_p(q_p)$ is the energy of an electron on the pth AO in its valence state, which is a function of the electron density, q_p.

If one assumes that, when the rth and the qth AO's belong to the same atom, B, γ_{pr} is equal to γ_{pq} wherever each of them may be directed, and that, further, ξ_{pB} is equal to them (hereafter they are designated by γ_{AB}), then the latter two terms may be written as follows:

$$-\sum_{\substack{B\\(\neq A)}}Q_B\gamma_{AB} \qquad (8)$$

where Q_B is the net charge on atom B

$$Q_B=Z_B-\sum_{\substack{r\\(\text{on }B)}}^{\text{all AO's}}q_r \qquad (9)$$

The assumption is acceptable in this simple qualitative discussion. Because W_p becomes more positive and $-(1/2)q_{pp}$ more negative when q_{pp} is set larger, the sum $W_p{}^0$

$$W_p{}^0=W_p-\frac{1}{2}q_p\gamma_{pp}-\xi_{pA} \qquad (10)$$

might be independent of the density*. Thus, the remainder of the former terms are reduced to

$$-Q_A\gamma_{AA} \qquad (11)$$

Moreover, a simple expression,

$$F_{pp}=W_p{}^0-\sum_B^{\text{all atoms}}Q_B\gamma_{AB} \qquad (12)$$

is obtained, $W_p{}^0$ being a constant, depending only on the kind and the hybridization of the atom (sp^2 carbon, sp^3 carbon, hydrogen, and so forth). We choose a certain atom as the standard, putting 0 on the shoulder as follows:

$$F_{qq}{}^0=W_q{}^0-\sum_B^{\text{all atoms}}Q_B\gamma_{DB} \qquad (13)$$

At this stage, we return to the simple LCAO MO treatment, regarding the F_{pp} as the new Coulomb integral, α_p, modified with electronic interactions, and $F_{qq}{}^0$ as the standard integral, $\alpha_q{}^0$, assumed to be equal to that of the zero order (Eqs. 1 and 4). Therefore, the new Coulomb integrals for the π electrons are:

---

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

5) K. Fukui, H. Kato, T. Yonezawa, K. Morokuma, A. Imamura and C. Nagata, ibid., 35, 38 (1962).

6) K. Morokuma, H. Kato and K. Fukui, to be published in this Bulletin.

* If the compound in question is a conjugated system, sp^2 hybridized orbitals should be used. When the compound is a saturated one, π MO's (Eq. 2) do not appear and the σ MO's are composed of sp^3 hybridized orbitals.

7) J. A. Pople, *Trans. Faraday Soc.*, 49, 1375 (1953).

* In stereoisomers, the assumption expressed by Eq. 10 is unnecessary. The assumption is needed only in structural isomers.

$$\left.\begin{aligned} \alpha_q{}^0 &= \alpha_\pi + a_{qq}{}^0\beta_\pi \\ \alpha_p &= \alpha_p{}^0 + (F_{pp} - F_{qq}{}^0) \end{aligned}\right\} \quad (14)$$

or the new parameters $a_{pp}{}^1$ and $a_{qq}{}^1$ are:

$$\left.\begin{aligned} a_{qq}{}^1 &= a_{qq}{}^0 \\ a_{pp}{}^1 &= a_{pp}{}^0 + (F_{pp} - F_{qq}{}^0)/\beta_\pi \end{aligned}\right\} \quad (15)$$

Also, for σ electrons,

$$\left.\begin{aligned} b_{qq}{}^1 &= b_{qq}{}^0 \\ b_{pp}{}^1 &= b_{pp}{}^0 + (F_{pp} - F_{qq}{}^0)/\beta_\sigma \end{aligned}\right\} \quad (16)$$

With these new parameters of the first order, which do, of course, differ between the two geometrical isomers, are calculated the π and σ electron distributions of the first order, showing the difference between the isomers.

Instead of Eqs. 15 and16, Eq. 17

$$\left.\begin{aligned} a_{pp}{}^1 &= a_{pp}{}^0 + k(F_{pp} - F_{qq}{}^0)/\beta_\pi \\ b_{pp}{}^1 &= b_{pp}{}^0 + k(F_{pp} - F_{qq}{}^0)/\beta_\sigma \end{aligned}\right\} \quad (17)$$

might better be used. The value of k is unity in Eqs. 15 and 16, but this value might lead to an over-estimation of the effects; therefore, so as to get nearer to self-consistency, k might be better settled as $0 < k < 1$.

ESR Hyperfine Splittings of the Terephthalaldehyde Anion

Recently an ESR spectrum of a terephthalaldehyde mononegative ion radical produced by the electrolytic reduction of the aldehyde has been observed by Maki²⁾; it has been found that the hyperfine splittings of the spectrum cannot be interpreted without taking them as rising from two radical species, each of which has three pairs of protons with these coupling constants; species A: 2.08, 0.70 and 3.89 gauss, and species B: 1.54, 1.16 and 3.81 gauss (absolute value). Maki regarded them as cis- and trans-isomers of the anion radical, distinguished in the ESR spectrum because of the restricted rotation of the aldehyde groups; he suggested that species A was the cis isomer, whereas B was the trans isomer.

It would be interesting to apply the method developed in the preceding paragraph and to see which species may be assigned to which isomer and, furthermore, which coupling constant may be assigned to which proton.

As the terephthalaldehyde anion is a radical, Fock's operator in the radical is a little different from that in Eq. 6⁸⁾. For this qualitative discussion, however, the simplified expression, Eq. 12, may rationally be adopted even for a radical; thus, no special notice to its being open shell is paid in this paragraph.

Evaluation of Atomic Integrals.—The electron repulsion integrals necessary to the evaluation of Fock's operator are estimated, in the form used by Mataga et al.⁹⁾, as follows:

$$\gamma_{AB} = \frac{14.39}{a_{AB} + r_{AB}}\,\text{eV}. \qquad (17')$$

where a_{AB} is the distance in Å from atom A to atom B and is constant settled so as to fit experimental values at $r_{AB}=0$ (ionization potential minus electron affinity) if A and B are atoms of the same kind. When A and B are of different kinds, an arithmetical mean may roughly be adopted. The values of a_{AB} are tabulated in Table I.

The values of β_π and β_σ, standard resonance integrals, are taken as follows:

TABLE I. VALUES OF a_{AB} FOR VARIOUS PAIRS OF ATOMS

B	A: C	H	O
C	1.29	1.20	1.14
H	1.20	1.12	1.05
O	1.14	1.05	0.99

TABLE II. VALUES OF PARAMETERS $a_{rr}{}^0$, $a_{rs}{}^0$, $b_{tt}{}^0$ and $b_{ru}{}^0$ OF THE ZERO ORDER*

$a_{rr}{}^0$: Coulomb integral of π AO's

O	+2
C_{II}	+0.2
C (others)	0

$a_{rs}{}^0$: Resonance integral between π AO's

C_{II}-O	+1.4
C-C	+1

$b_{tt}{}^0$: Coulomb integral of σ AO's

O	+0.3
C	0
H	−0.2

$b_{tu}{}^0$: Resonance integral between σ AO's

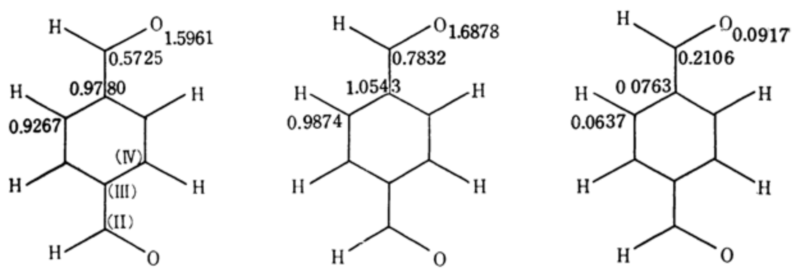
C-O	+1.1
C-H	+0.94
C-C (bonding)	+1
C-C (on the same atom)	+0.38

* As to numbering of AO's, see Fig. 1.

---

8) C. C. J. Roothaan, *Rev. Modern Phys.*, **32**, 179 (1960); J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954).

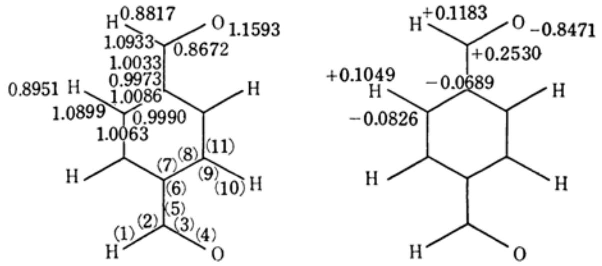
9) N. Mataga and K. Nishimoto, *Z. physik. Chem.*, **13**, 140 (1957).



π Elctron density of the neutral aldehyde (numbering of π AO's)

π Electron density of the aldehyde anion

π Spin density of the anion



σ Electron density (numbering of σ AO's)

Net charge of the anion

Fig. 1. Electron distribution of the zero order (numbering of AO's in parentheses).

$$\left.\begin{aligned}\beta_\pi &= -2.5\text{ eV.}\\ \beta_\sigma &= -8.0\text{ eV.}\end{aligned}\right\} \quad (18)$$

and k is set as unity.

The geometry of the aldehyde and its anion is considered to be planar, with bond lengths of 1.40Å for C–C (aromatic), 1.52Å for C–C (substituent), 1.08Å for C–H, and 1.22Å for C=O and with all bond angles of 120°.

Parameters of the Zero Orders.—The parameters of the zero order for the π and σ electron systems are collected in Table II. The values of a_{rr}^0 and a_{rs}^0 for π electron systems are similar to those popularly used. As to the σ system, the values in the table, except for O and C=O, are taken from a paper by the present authors6). The values of a_{OO}^0 and a_{CO}^0 have been settled anew by referring to the ionization potentials and electron affinities of oxygen, and to the bond energy of the C–O single bond of alcohols or ethers and the ratio of the overlap integrals for C=O and C–O bonds respectively.

Electron Distributions of the Zero Order.—In Fig. 1 are given electron distributions calculated on the basis of the parameters of the zero order. Since, of course, the results are identical for both isomers, the patterns for only the cis isomer are represented in the figure.

Parameters of the First Orders. — By using the net charge of the anion given in the Fig. 1 and the integrals of γ_{AB}, β_π and β_σ given in the foregoing section, new parameters of the first order have been derived.

As for the π electron system, as the circumstances affecting π AO's C_{II} and C_{III} are not affected by the isomerism, the a_{rr}^1's have been taken to be equal to a_{rr}^0's*. For carbons IV and V, which are indistinguishable in the zero order, new parameters have been estimated by looking tentatively on the $C_V\pi$AO in the trans isomer as a standard; for oxygens, the $O_I\pi$AO in the trans isomer has been taken as a standard.

A similar standardization and calculation of the parameters have also been carried out for σ AO's. The values of the parameters a_{rr}^1 and b_{tt}^1 of the first order thus calculated for both isomers are tabulated in Table III.

Results and Discussion. — The π and σ electron densities and the π spin density of the isomers of the terephthalaldehyde anion have been calculated with the parameters of the first order; the results are given in Fig. 2.

As would be expected from a simple electrostatic consideration, in both isomers the π electron density on C_V is larger than that on C_{IV}, since to the latter the electron-rich and, accordingly, repulsive center of oxygen is located nearer. A similar tendency is found also in σ electron densities on ring hydrogens and ring carbons. The π spin density is

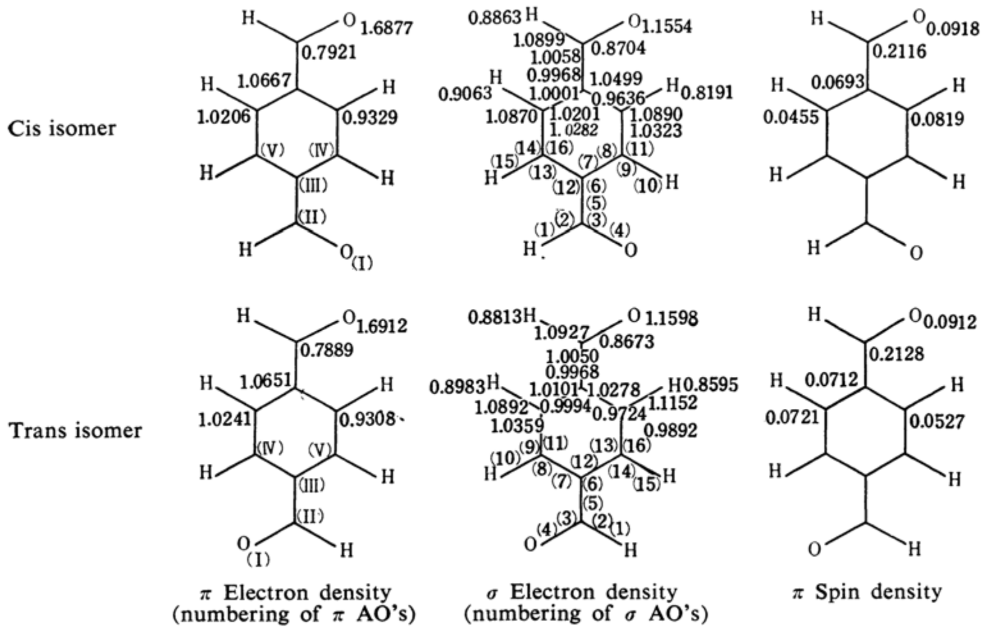
---

* For the numbering of π AO's, see Figs. 1 and 2.

TABLE III. VALUES OF PARAMETERS a_{rr}^1 AND b_{tt}^1 OF THE FIRST ORDER*

Cis		Trans	
a_{rr}^1: Coulomb integral of π AO's		a_{rr}^1: Coulomb integral of π AO's	
O_I	+1.976	O_I	+2.0 (standard)
C_{II}	+0.2 (invariant)	C_{II}	+0.2 (invariant)
C_{III}	0 (invariant)	C_{III}	0 (invariant)
C_{IV}	−0.230	C_{IV}	−0.146
C_V	+0.084	C_V	0 (standard)
b_{tt}^1: Coulomb integral of σ AO's		b_{tt}^1: Coulomb integral of σ AO's	
H_1	−0.193	H_1	−0.2 (standard)
C_2, C_3, C_5	0 (invariant)	C_2, C_3, C_5	0 (invariant)
O_4	+0.292	O_4	+0.3 (standard)
C_6, C_7, C_{12}	0 (invariant)	C_6, C_7, C_{12}	0 (invariant)
C_8, C_9, C_{11}	−0.072	C_8, C_9, C_{11}	−0.046
H_{10}	−0.336	H_{10}	−0.299
C_{13}, C_{14}, C_{16}	+0.026	C_{13}, C_{14}, C_{16}	0 (standard)
H_{15}	−0.164	H_{15}	−0.2 (standard)

* As to numbering of AO's, see Fig. 2.



π Electron density (numbering of π AO's)

σ Electron density (numbering of σ AO's)

π Spin density

Fig. 2. Electron densities of the first order of the aldehyde anion isomers (numbering of AO's in parentheses).

calculated as the density of the half-occupied level of the anion.

In order to compare these findings in the calculations, the experimental proton hyperfine coupling constants, a_H, have been converted into spin densities on the adjacent carbons, ρ_C, by the equation

$$a_H = Q\rho_C \tag{19}$$

where the constant, Q, is equal to −23 gauss[10]. Strictly speaking, the constancy of Q would not hold in this case, for the different polarity of each C–H bond, as may be seen in Fig. 2, would yield a different value of Q; in a qualitative discussion like this, however, such a slight difference is of little significance.

On collating the calculated spin densities with the experimental findings indicated in Table IV, we find a good mutual agreement, thus obtaining the following assignments:

(1) The A species is the cis isomer and the B species is the trans isomer, in agreement with Maki's proposition.

---

[10] H. M. McConnell, *J. Chem. Phys.*, **24**, 632, 764 (1956).

TABLE IV. CALCULATED AND EXPERIMENTAL SPIN DENSITIES AND ASSIGNMENT OF COUPLING CONSTANTS OF TEREPHTHALALDEHYDE ANION

Calculated (cis isomer)		Experimental (species A)
Position	Spin density	Spin density
C_{II}	0.212	0.169
C_{IV}	0.082	0.090
C_V	0.046	0.030

Calculated (trans isomer)		Experimental (species B)
Position	Spin density	Spin dencity
C_{II}	0.213	0.166
C_{IV}	0.053	0.050
C_V	0.072	0.067

(2) In each isomer, the largest (in absolute value) and nearly invariant coupling constant originates from the aldehyde proton.

(3) In the trans isomer, the order of the spin density on ring carbons is $C_V > C_{IV}$. On the other hand, in the cis isomer, the spin density on C_{IV} is much larger than that on C_V. This result is of great interest because the order of the spin density is inverse to that of the total π electron density and is contradictory to a simple electrostatic presumption. On inspecting the calculated electron distribution of each molecular orbital (Table V), such a presumption seems to be attributable to the total density and to the distribution of molecular orbitals of a lower energy, but not necessarily to a distribution molecular orbitals of a higher energy or of a less bonding or antibonding nature, as the half-occupied orbital of the anion discussed here.

Summary

A new simple molecular orbital method with parameters modified by electronic interactions was developed so as to discuss simply the difference in electron distributions between stereoisomers. An application was made to the proton hyperfine coupling constants of the cis- and trans-isomers of the terephthalaldehyde anion radical, and the assignment of the constants was proposed on the basis of molecular orbital calculations.

TABLE V. ELECTRON DENSITY OF EACH OCCUPIED π MO

1. Cis isomer

Orbital energy λ_i	Symmetry**	Electron density	
		C_{IV}	C_V
−0.1498*	A'	0.0819	0.0455
+0.9204	A'	0.2662	0.2253
+1.1815	A''	0.0493	0.0652
+1.9686	A'	0.1001	0.1838
+2.8555	A''	0.0015	0.0017
+2.8876	A'	0.0085	0.0117

* Half occupied level
** Symmetry in C_{1h} group

2. Trans isomer

Orbital energy λ_i	Symmetry**	Electron density	
		C_{IV}	C_V
−0.1383*	A	0.0527	0.0721
+0.9240	B	0.2661	0.2255
+1.1872	B	0.0291	0.0922
+1.9597	A	0.1334	0.1469
+2.8716	B	0.0014	0.0016
+2.9021	A	0.0090	0.0097

* Half occupied level
** Symmetry in C_2 group

Most of the numerical calculations were carried out on the KDC-I digital computor of Kyoto University.

Faculty of Engineering
Kyoto University
Sakyo-ku, Kyoto