BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1027—1030 (1967)

Calculation of the Electronic Structure of Cinnamic Acid by the Semi-empirical LCAO-SCF-MO Method

Kenichiro NAKAMURA and Shinichi KIKUCHI

Institute of Industrial Science, The University of Tokyo, Azabu, Minato-ku, Tokyo

(Received August 4, 1966)

The photo-isomerization and photo-dimerization of cinnamic acid are discussed from the standpoint of the electronic structures in the ground and excited states. State energies, charge densities, bond orders and free valences are calculated by using the Pariser-Parr-Pople method, including the configuration interaction. The computed transition energies are in good agreement with the experimental results. It is found that the bond order between the α- and β-carbons of cinnamic acid decreases, while the free valences of the α- and β-carbons increases, upon the lowest electronic excitation. It is concluded that the photo-isomerization is due to the smaller bond order, and that the photo-dimerization is due to the larger free valences in the excited state of cinnamic acid.

It is well-known that solid cinnamic acid dimerizes to either α-truxillic acid or β-truxinic acid upon light-irradiation.[1] Various studies on the products of these reactions have been reported.[2,3] Bernstein *et al.*[4] obtained two kinds of products by exposing α- and β-*trans*-cinnamic acid to ultraviolet light. They concluded that α-*trans*-cinnamic acid was converted into α-truxillic acid, and β-*trans*-cinnamic acid into β-truxinic acid. Schmidt *et al.*[5] discussed the products of cinnamic acid topochemically, and explained that in photo-active structures the conformation of the dimer could be correlated with the packing arrangement of nearest-neighbors in the monomer lattice.

In a phase of solution, *trans*-cinnamic acid isomerizes to *cis*-cinnamic acid.[6] Vaidya[7] measured the quantum yields of the trans→cis and cis→trans isomerizations of cinnamic acid. The sum of the two quantum yields was about unity. This fact suggests that the excited states of *cis*- and *trans*-cinnamic acid concerned are the same.

It has been found that *trans*-cinnamic acid has two types of absorption bands, a K-band (4.54 eV) and E-bands (5.58 and 5.74 eV) in the 3.1—6.2 eV region.[8] Tanaka[9] found, by measuring the polarized ultraviolet absorption spectrum, that the K-band of cinnamic acid is the intramolecular charge transfer absorption.

In this report, these reactions will be discussed from the standpoint of the electronic structures of cinnamic acid in the ground and excited states. The state energies, charge densities, bond orders, and free valences of cinnamic acid are calculated by using the Pariser-Parr-Pople method with CI. All of the SCF-MO calculations were carried out on an OKITAC 5090 computer.

Calculation Procedure

The geometry of cinnamic acid with C_s symmetry was taken to be as is shown in Fig. 1. The electronic system of cinnamic acid was treated as 12 electrons with 11 centers. The SCF-MO φ_i and its energy were obtained by the Pariser-Parr-Pople method.

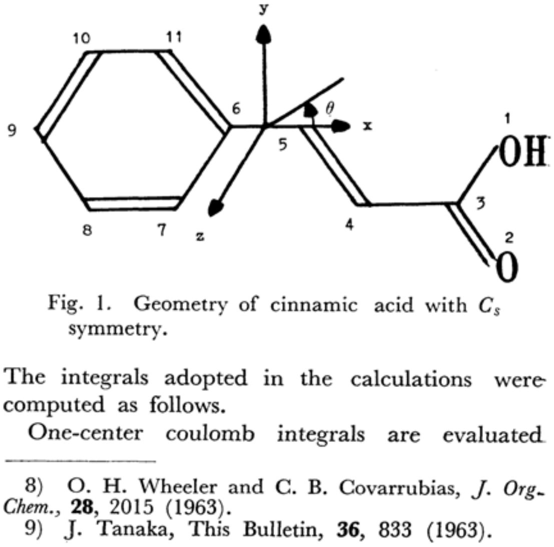


Fig. 1. Geometry of cinnamic acid with C_s symmetry.

The integrals adopted in the calculations were computed as follows.

One-center coulomb integrals are evaluated

---

1) C. N. Riiber, *Ber.*, **35**, 2415 (1902).

2) R. Stoermer and E. Laage, *ibid.*, **54**, 77 (1921).

3) H. Stobbe and F. K. Steinberger, *ibid.*, **55**, 2225 (1921).

4) G. I. Bernstein and W. C. Quimby, *J. Am. Chem. Soc.*, **65**, 1845 (1943).

5) M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.*, **1964**, 1966; M. D. Cohen, G. M. J. Schmidt and F. I. Sonntag, *ibid.*, **1964**, 2000; G. M. J. Schmidt, *ibid.*, **1964**, 2014; J. Bregman, K. Osaki, G. M. J. Schmidt and F. I. Sonntag, *ibid.*, **1964**, 2021.

6) R. Stoermer, *Ber.*, **42**, 4869 (1909).

7) B. K. Vaidya, *Proc. Roy. Soc. (London)*, **A129**, 299 (1930).

8) O. H. Wheeler and C. B. Covarrubias, *J. Org. Chem.*, **28**, 2015 (1963).

9) J. Tanaka, This Bulletin, **36**, 833 (1963).

according to the method suggested by Pariser[10]:

$$(rr|rr) = I - E$$

where I and E are the valence-state ionization potential and the electron affinity of the atom respectively. The values of I and E were taken from the values derived by Pritchard *et al.*[11] These values are shown in Table 1.

TABLE 1. THE ADOPTED IONIZATION POTENTIALS AND ONE-CENTER COULOMB INTEGRALS

Atom	I	$(rr\|rr)$
C	11.42 eV	10.84 eV
O (carbonyl)	17.28	14.58
O (hydroxyl)	34.43	19.46

Two-center Coulomb integrals are computed according to the scheme proposed by Pariser and Parr[10]:

for $R \geqq 2.8$ Å

$$(rr|ss) = 7.198 \left\{ \frac{1}{\sqrt{R^2+a}} + \frac{1}{\sqrt{R^2+b}} \right\}$$

for $R < 2.8$ Å

$$(rr|ss) = \frac{1}{2}\{(rr|rr) + (ss|ss)\} + cR + dR^2$$

The constants adopted in the above equation are shown in Table 2. The cinnamic acid crystal has studied by means of X-ray analysis,[12] but the bond distances have not been made clear. Therefore the present authors estimated, from the experimental data for carbonyl compounds, the distances between the nearest carbon atoms to be 1.39 Å, R_{23} to be 1.43 Å, and R_{13} to be 1.28 Å.

TABLE 2. THE ADOPTED CONSTANTS OF TWO-CENTER COULOMB INTEGRALS

Atom	a	b	c	d
C–C	2.00	0	−2.822	0.2458
C–O (carbonyl)	1.47	0.041	−3.91	0.404
C–O (hydroxyl)	1.47	0.041	−8.14	1.055
O (carbonyl)–O (hydroxyl)	—	—	−6.55	0.808

The I_{rr} integral can be expanded by neglecting the penetration integrals[13]:

$$I_{rr} = W_r - \sum_{s \neq r} Z_s(rr|ss)$$

where Z_s is the number of π-electrons contributed by the s atom, 2 for the hydroxyl oxygen and 1 for the others.

The core resonance integrals, I_{rs}'s, are estimated with an exponential fit[10]:

$$I_{rs} = -605 \exp(-3.98\,R)$$

In this report all the resonance integrals were calculated by means of the above equation.

The iteration process in the calculation of SCF-MO's was continued for 17 times, at which point the orbital energies converged. Singly-excited configurations were taken into consideration by using the following off-diagonal elements:

$$\langle {}^1\psi_{i\to k}|\mathbf{H}|{}^1\psi_{j\to l}\rangle = 2[jl|ki] - [ji|kl]$$

$$\langle {}^3\psi_{i\to k}|\mathbf{H}|{}^3\psi_{j\to l}\rangle = -[ji|kl]$$

All configurations which have energies lower than 8 eV in the singlet states and 7 eV in the triplet states were included in the diagonalization of the CI matrix. Then the charge density, Q_r, the bond order, P_{rs}, and the free valence, F_r, were calculated.

Results and Discussion

The energies of cinnamic acid as evaluated by the Pariser-Parr-Pople method are given in Fig. 2. The observed energies in Fig. 2 are estimated from the maximum absorption wavelengths of cinnamic acid. The absorption curves measured in an ethanol solution are shown in Fig. 3. The second absorption bands (E-bands) possess two maxima of about equal intensity. The interval between the two peaks is found to be 1300 cm^{-1} in Fig. 3. The peaks of the E-bands may be due to the vibrational structure of cinnamic acid. Therefore in Fig. 2, the second band is written as the

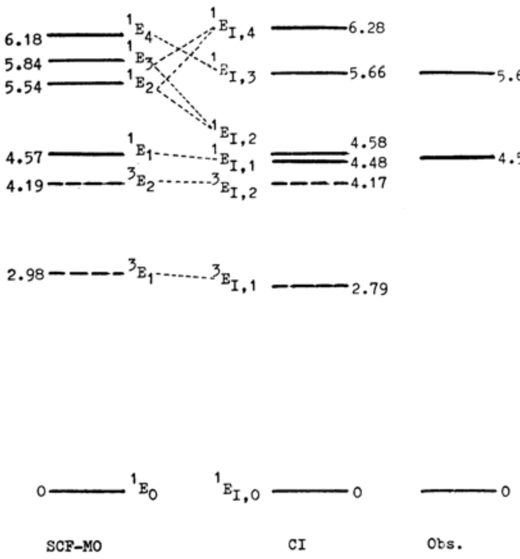


Fig. 2. The calculated and observed energy diagrams of cinnamic acid, eV.

---

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

[11] H. O. Pritchard and H. A. Skinner, *Chem, Revs.*, **55**, 745 (1955).

[12] J. Ladell, T. R. R. Mcdonald and G. M. J. Schmidt, *Acta Cryst.*, **9**, 195 (1956).

[13] M. Goeppert-Mayer and A. K. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

TABLE 3. THE SCF-MO'S COEFFICIENTS C_{ij}'s

i	Orbital energy eV	j 1	2	3	4	5	6	7	8	9	10	11
1	−18.07	0.785	0.364	0.460	0.175	0.0885	0.0374	0.0127	0.0062	0.0047	0.0070	0.0148
2	−15.68	−0.182	0.0676	0.0522	0.183	0.313	0.491	0.377	0.318	0.298	0.323	0.386
3	−14.68	−0.557	0.602	0.361	0.266	0.154	−0.0479	−0.113	−0.154	−0.169	−0.153	−0.111
4	−13.21	0.101	−0.352	−0.122	0.320	0.477	0.334	0.0119	−0.319	−0.460	−0.308	0.0266
5	−11.91	0.0006	0.0037	−0.0006	−0.0081	0.0062	0.0175	0.506	0.493	−0.0088	−0.504	−0.496
6	−10.94	0.0069	0.268	0.0014	−0.520	−0.352	0.389	0.282	−0.171	−0.405	−0.150	0.297
7	−2.09	0.0746	0.275	−0.254	−0.494	0.474	0.279	−0.281	−0.122	0.343	−0.0888	−0.298
8	−0.57	0.0020	0.0080	−0.0081	−0.0103	0.0022	0.0116	−0.505	0.492	0.0162	−0.510	0.492
9	0.23	−0.0754	−0.245	0.316	0.154	−0.405	0.441	−0.106	−0.308	0.495	−0.294	−0.119
10	2.14	0.129	0.387	−0.641	0.396	−0.180	−0.098	0.182	−0.229	0.243	−0.222	0.172
11	2.87	0.0482	0.140	−0.254	0.262	−0.312	0.458	−0.360	0.311	−0.292	0.311	−0.360

TABLE 4. THE COEFFICIENTS $C_{I,rs}$'s OF WAVE FUNCTION WITH CI

Configuration wave function	$^1E_{I,1}$	$^1E_{I,2}$	$^1E_{I,3}$	$^1E_{I,4}$	$^3E_{I,1}$
$\psi_{6\to7}$	0.937	−0.0271	0.129	−0.151	0.946
$\psi_{6\to8}$	−0.0867	−0.598	0.171	0.684	0.0268
$\phi_{5\to7}$	0.257	0.636	0.154	0.665	0.0202
$\psi_{5\to8}$	0.175	−0.0571	−0.767	0.221	0.112
$\psi_{4\to7}$	−0.0217	0.0077	−0.351	−0.0088	−0.268
$\psi_{4\to8}$	−0.0609	−0.248	0.0264	0.106	—
$\psi_{5\to9}$	0.110	0.315	−0.0149	−0.0455	−0.0107
$\psi_{6\to9}$	0.0338	−0.0201	−0.464	0.0782	−0.141

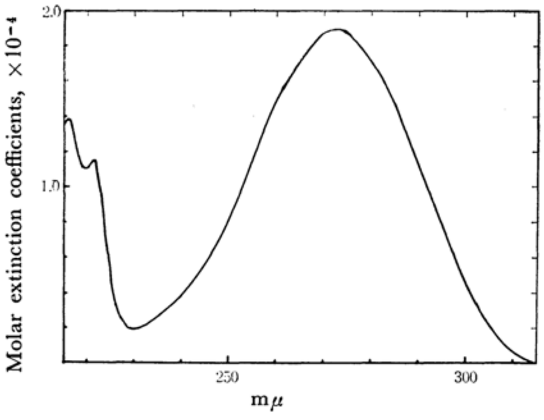


Fig. 3. The ultraviolet absorption spectrum of cinnamic acid.

average value of the two peaks' energies. The energies finally obtained by considering the configuration interaction are also shown in Fig. 2. The energies in the second- and the third-excited singlet states are comparatively greatly changed by CI, while in the first excited state they are almost constant.

The SCF-MO's coefficients, C_{ij}'s, are listed in Table 3. It is found that the molecular orbitals in the benzene ring are fairly well retained in cinnamic acid. The coefficients, $C_{I,rs}$'s, of the wave functions with CI are given in Table 4. In the ground state no excited configuration interacts. In the first-excited singlet and triplet states, the wave functions are mainly contributed by the configuration wave functions, $^1\psi_{6\to7}$ and $^3\psi_{6\to7}$ respectively. In the second and fourth singlet-excited states, the contributions of the configuration wave functions, $^1\psi_{6\to8}$ and $^1\psi_{5\to7}$ are large.

The numerical values of oscillator strengths are evaluated by:

$$f = 8.69 \times 10^{-2} E_{0a} Q_{0a}^2$$

where:

$$Q_{0a} = \int \psi_0 \Sigma \boldsymbol{r}_i \psi_a \mathrm{d}\tau \qquad (\text{Å})$$

and E_{0a} is the excitation energy to a state, a, expressed by eV. The calculated oscillator strengths and the singlet state energies are shown in Table 5. The obtained value of the oscillator strength for the first transition coincides fairly well with the observed value. The calculated directions of the transition moments with respect to the x-axis are shown in the last column of Table 5.

It can be seen from Fig. 2 that the computed first singlet-singlet transition energy is in good agreement with the experimental results. Table 3 and Table 4 show that the total electron densities of the lower unpaired orbital and the upper unpaired orbital localized in the substitutional acrylic acid group are 0.415 and 0.584 respectively in the first-excited singlet state. This fact and the wave functions shown in Table 3, suggest that the first singlet-singlet transition absorption is the intramolecular charge transfer absorption. This suggestion agrees with the experimental result obtained by Tanaka.(9)

TABLE 5. THE STATE ENERGIES AND THE OSCILLATOR STRENGTHS

State energy		Oscillator strength, f		θ_{calcd}
Calcd.	Obs.	Calcd.	Obs.	
4.48	4.52	0.745	0.473	−23.7°
4.58		0.149		74.6°
5.66	5.67	0.138		−20.5°
6.28		0.223		85.1°

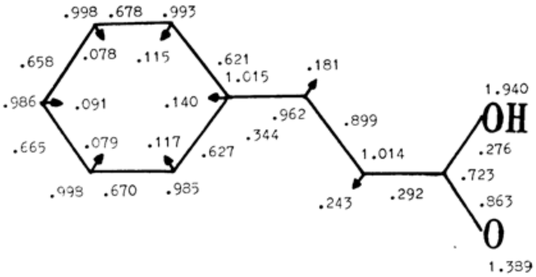
The computed second singlet-singlet transition could not be found by experimentation. The calculated transition energy and direction of the transition moment in Table 5 show that this second transition corresponds to the benzene $^1B_{2u}$ band (4.75 eV). It seems reasonable to say that it is covered in the very strong and broad charge transfer band (half width, 5500 cm^{-1}), as in the case of *p*-substituted benzene derivatives. A similar conclusion was obtained by Inuzuka,(14) who calculated the electronic structure of cinnamaldehyde by a simple LCAO-MO method with CI and reported that the B_2^- transition of cinnamaldehyde was due to the transition localized in the benzene ring.

In the third singlet state, the configuration wave function, $^1\psi_{5\rightarrow8}$, makes a larger contribution. The SCF-MO's φ_5 and φ_8, are the orbitals localized in the benzene ring, as is shwon in Table 3, Therefore it may be concluded that this thrid transition corresponds to the benzene $^1B_{1u}$ band (5.96 eV).

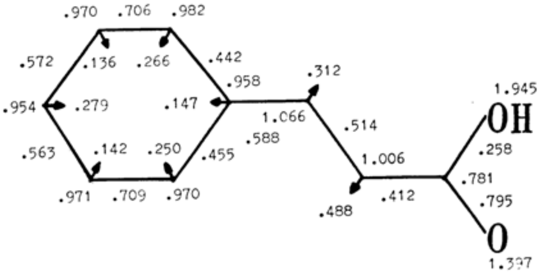
The charge densities, bond orders, and free valences in the ground state and the first-excited singlet state are shown in Fig. 4. The free valence, F_r, is estimated according to the usual equation:

$$F_r = N_{max} - N_r$$

Coulson *et al.*(15) reported that, for a trigonal carbon atom, N_{max} has the value of $3+\sqrt{3}$ or $3+\sqrt{2}$, according as the atom in question is attached to three or two other trigonal carbon atoms.



in the ground state



in the first excited singlet state

Fig. 4. Molecular diagrams of cinnamic acid.

Figure 4 shows that the electronic structure of the excited state is different from that in the ground state. It is found that the bond order between α- and β-carbons decreases, and the free valences of α- and β-carbons increase, in the excited state in comparison with those in the ground state. The former fact about the bond order suggests that the bond between α- and β-carbons approaches a single bond and that cinnamic acid is isomerized by the electronic excitation of ultraviolet light. From the standpoint of the latter fact about the free valences, it may be concluded that cinnamic acid dimerizes at the positions of α- and β-carbons.

The authors wish to thank Dr. H. Hosoya for many helpful discussions and suggestions during this work.

---

14) K. Inuzuka, This Bulletin, **34**, 1557 (1961).

15) F. H. Burkitt, C. A. Coulson and H. C. Longuet-Higgins, *Trans. Faraday Soc.* **47**, 553 (1951).