

A MOLECULAR ORBITAL TREATMENT OF ENOLIZED β -DICARBONYLS

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Abstract—The π -electronic structures of the enol form of β -dicarbonyls such as acetylacetone, benzoylacetone, dibenzoylmethane, and β -keto esters have been investigated in the semi-empirical SCF-LCAO-MO approximation. The calculated values are discussed and compared with observed values of IR, NMR, and UV spectra.

INTRODUCTION

SEVERAL MO calculations have been reported on the electronic structure of the enol form of β -dicarbonyls.¹⁻⁵ Concerning the intramolecular H-bond of β -dicarbonyl, it is particularly interesting whether the vacant 2p orbital of the chelated hydrogen can participate in the π -electron system of the chelate ring. A preliminary extended Hückel MO treatment by Morokuma *et al.* suggested that the participation of the vacant $2p\pi$ orbital of the enolic proton is not possible.⁴ In contrast, Shigorin^{5,6} has stated that construction of a quasi aromatic ring is possible by taking account of the $2p\pi$ orbital of hydrogen associated with the H-bond using a SCF-LCAO-MO calculation.^{5,6} The validity of this result is still questionable. The approximate self-consistent MO method (CNDO/II) has been applied to calculations on the H-bonded system of formaldehyde.⁷ As far as the π -electron system is concerned, the trend is similar to previous work neglecting the σ -electrons.⁸ We have carried out the semiempirical SCF-LCAO-MO calculation in order to elucidate the π -electronic structure of the enol form of the various β -diketones and the substituent effect on the chelate ring.

METHOD

The procedure involving the iteration of the solutions of the eigenvalue problem of the matrix F is as follows;

$$F_{i,i}^{(1)} = -I_i + 1/2 P_{i,i}^{(0)} (I_i - E_i) + \sum_{i \neq j} (P_{j,j}^{(0)} - Z_j) \gamma_{i,j} \quad (1)$$

$$F_{i,j}^{(1)} = \beta_{i,j} - 1/2 P_{i,j}^{(0)} \gamma_{i,j} \quad (2)$$

The index is the same as that used by Pople.⁹ The Coulomb integrals have been evaluated according to the equation proposed.¹⁰

$$\gamma_{i,j} = e^2 / (R_{i,j} + a_{i,j}) \quad (3)$$

The interatomic distances in the calculation were quoted from the crystallographic result reported by Williams.¹¹ The constants $a_{i,j}$ are defined by the following expression

$$\gamma_{i,j} = e^2 / a_{i,j} = I_i - E_i \quad (4)$$

$$e^2/a_{i,j} = 1/2 \cdot (I_i - E_i + I_j - E_j), \quad (5)$$

where I_i and E_i indicate the ionization potential and electron affinity of the i -th atom in valence state, respectively.¹² The $\beta_{i,j}$ integrals were the same as used by Pullman and Pullman.¹³ In order to discuss the electronic spectra except for dibenzoyl-methane configuration interaction treatment has been employed involving one electron excitation.

RESULTS AND DISCUSSION

Figs 1 and 2 illustrate the π -electron charge densities and the bond orders. The C=O, C=C stretching vibrations and the chemical shifts of $-\text{CH}=\text{}$ proton are

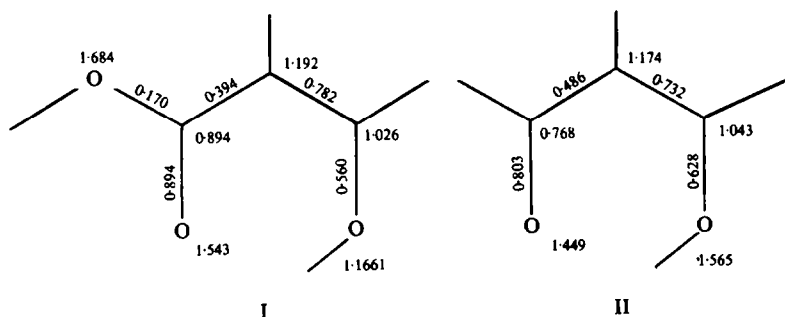


FIG 1. Electron densities (underlined) and Bond orders of I and II

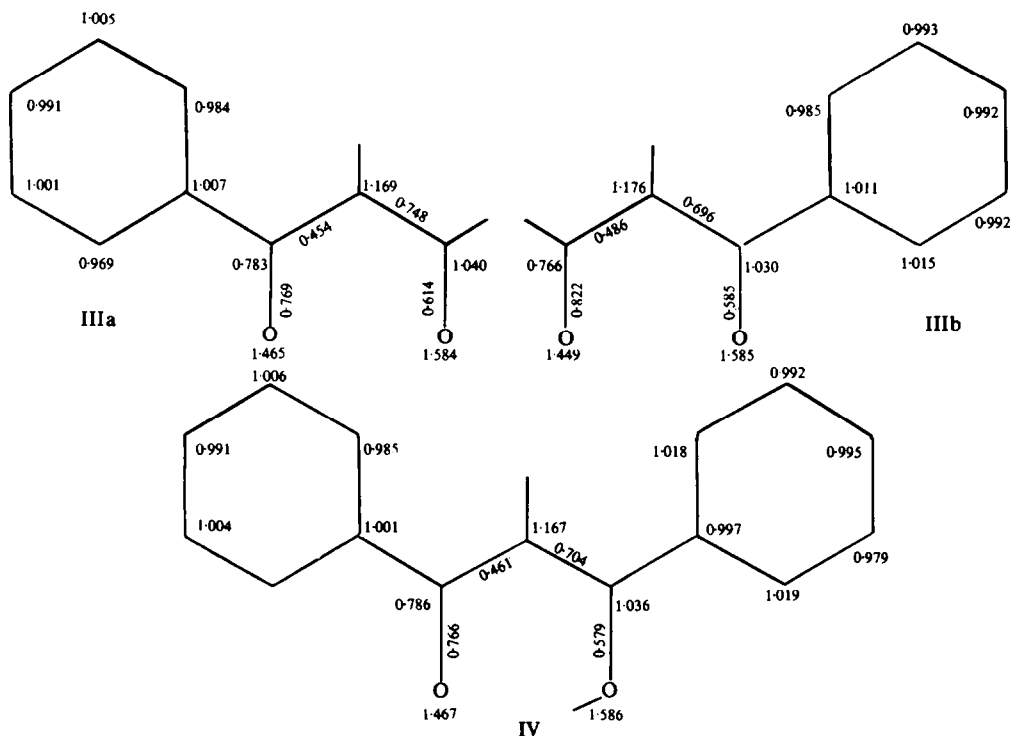


FIG 2. Electron densities (underlined) and Bond orders of IIIa, IIIb and IV

shown in Table 1 as a measure of the π -electron delocalization of β -dicarbonyls at the ground state. In addition, the chemical shift of enolic proton is also listed in this Table to indicate the strength of the intramolecular H-bond. Unfortunately, two

TABLE I. AVERAGED BOND ORDER AND THE CHARACTERISTIC SPECTRA OF IR AND NMR

		$(P_{C=O} + P_{C-O})/2$	Obsd freq (cm^{-1}) $\nu(\text{C=O}), \nu(\text{C=C})$	Chemical shift (ppm)	
				$\tau_{\text{CH=}}$	τ_{OH}
I	Ethylacetoacetate	0.838	1650, 1632	4.97	-2.16
II	Acetylacetone	0.768	1618	4.44	-5.56
III	Benzoylacetone	0.750(a)	1605	4.05	-6.33
		0.758(b)			
IV	Dibenzoylmethane	0.735	1600	3.64	-7.00

frequencies assigned to $\nu(\text{C=O})$ and $\nu(\text{C=C})$ are overlapped, whereas the β -keto-ester shows two absorptions. Therefore, the average values of the bond orders of the C=O and the C=C are compared with the observed frequencies as shown in Table 2. The frequency ($\nu(\text{C=O}) + \nu(\text{C=C})$) shifts slightly to lower frequency region as the π -electron delocalization is enhanced. Strictly speaking, the calculated bond order must be compared with the force constants of the C=C and C=O instead of the observed frequencies.

This trend accords with the changes in the chemical shift of the $-\text{CH=}$ protons. Collman¹⁴ and Hester¹⁵ have explained that an appearance of the chemical shift of the $-\text{CH=}$ at lower magnetic field is attributed to the ring current of metal acetylacetonate. The concept of ring current in quasiaromatic rings may provide an explanation about the chemical shift as has been stated by Shigorin. However, Kuhr and Musso have proposed that the enolic ring does not show an aromaticity based on the non existence of ring current in the NMR spectral measurement.¹⁶ Therefore, it is possibly interpreted that changes in the chemical shift of the $-\text{CH=}$ are essentially attributed to the magnetic environment resulting from delocalization of the $-\text{CO}-\text{CH}=\text{CO}-$ π -electron system. The enhanced delocalization of the $-\text{CO}-\text{CH}=\text{CO}-$ π -electron system causes a down-field shift of the $-\text{CH=}$ proton as is shown in Table 1.

Burdett and Rogers have reported that the phenyl group in III and IV acts as an electron-withdrawing group in the enolic form.¹⁷ To the contrary, it has been proposed that an electron-supplying effect of the phenyl group through resonance increases in electron density on the carbonyl oxygen resulting in a stronger intramolecular H-bond.^{18, 19} As far as the π -electrons are concerned, MO calculation shows charge migration from the phenyl ring of the carbonyl side to the enolic ring. On the other hand, the change in the electron densities of the phenyl ring of the enol side is quite small relative to the former one. A crystallographic investigation on IV shows that the phenyl ring is almost coplanar with the enolic ring.¹¹ Consequently, the charge separation through resonance would be expected between the phenyl ring and the enolic ring.

We have proposed that the O-D out-of-plane deformation can be related to the double bond character of the C-O bond being evaluated from the extent of π -electron delocalization.²⁰ The linear relationship between the $\pi(\text{OD})$ or $\nu(\text{C=O})$,

and τ_{OH} shows that the intramolecular H-bond strongly associates with π -conjugation of the enolic ring. Therefore, the order of the double bond character of the C—O bond is expected to be I < II < III < IV. However, the order of $P_{C=O}$ calculated here does not agree with its bond order estimated from the IR spectra. This disagreement is probably ascribed to neglecting the H-bonding system in the calculation. The π -electron charge displacement from the proton acceptor to the proton donor in the intermolecular H-bond⁷ would be redistributed through the counter-migration of the π -electrons in the intramolecularly H-bonded system.²¹ Thus, it is explained that the stronger H-bond causes the larger value of $P_{C=O}$ owing to the redistribution of the π -electrons through resonance.

In order to elucidate electronic spectra, the configuration interaction (CI) involving singly-excited configuration is considered for these molecules, I, II, IIIa and IIIb. Table 2 shows the observed maxima of absorptions in n-heptane and the calculated

TABLE 2. THE CALCULATED AND OBSERVED TRANSITION ENERGIES OF β -DICARBONYLS (ENERGY IN eV)

Molecule	E_{cal} (f)	E_{exp} (f)	E_{exp} (log ϵ)
I	4.51 (0.02)	5.00 (—*)	5.10 (4.00) ^a
	4.55 (0.76)		
	5.54 (0.06)		
II	4.61 (0.48)	4.58 (0.42)	4.55 (3.99) ^b
	6.25 (0.30)	6.42 (—*)	6.42 (2.92) ^b
	6.80 (0.35)		
IIIa	3.97 (0.32)	4.05 (0.57)	4.00 (4.36) ^a
	4.41 (0.00)		
	4.89 (0.91)	5.05 (—*)	4.98 (3.75) ^a
	4.93 (0.13)		
IIIb	5.44 (0.24)		
	4.01 (0.44)	4.05 (0.57)	4.00 (4.36) ^a
	5.09 (0.01)		
	5.27 (0.17)	5.05 (—*)	4.98 (3.75) ^a

* Strength of absorption were not determined due to poorly resolved spectra

^a Ref. 22

^b Ref. 23

transition energies with oscillator strength. The strong absorption at around 250–300 $m\mu$ is due to the $\pi \rightarrow \pi^*$ transition. The calculated transition energies show a good agreement with the observed values except for β -keto ester. From the comparison of the coefficients of atomic orbitals, the 250 $m\mu$ and 300 $m\mu$ bands of III are demonstrated to be the characteristic intramolecular charge transfer band from the enolic ring to the phenyl group. Both two enolic isomers (IIIa and IIIb) can exist in the ground state because of the low energy barrier of the proton migration between two forms. Another complication arises from the possible proton transfer in the excited state. Therefore, the observed values of III have been tentatively assigned to overlapping of $\pi \rightarrow \pi^*$ transition of IIIa and IIIb. The observed maximum of I at 193 $m\mu$

has been assigned to $n \rightarrow \sigma^*$ transition from the polarity effect of solvent on the spectrum.²³ This trend may not conform to the general observation for $n \rightarrow \sigma^*$ transition. However, the calculation indicates that this absorption is attributed to the $\pi \rightarrow \pi^*$ transition involving higher transition energy. As has been pointed out by Sidman²⁴ and Allinger *et al.*,²⁵ an explicit calculation including of the σ and n electrons will be required for more accurate prediction in this region.

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