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An Approach for Calculation of n,π^* State Energies of Some Carbonyl Molecules Within the Framework of the Semi-Empirical SCF-MO-CI Method

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Electronic state energies (π,π^*) of many organic molecules have been calculated by the Pariser-Parr and Pople SCF–MO–CI methods.[1,2] Such approaches have proven successful for the electronic properties of π,π^* states, but their application to n,π^* state energy calculations is scarce. One reason is the difficulty of obtaining good values for the electronic repulsion integrals between n and π electrons. Lindner *et al.*[3] used the Ohno approximation[4] for such integrals to calculate n,π^* state properties of nitrogen-heterocyclics. However, the state energies were not in agreement with experiment. Sidman[5] carried out n,π^* state energy calculations for several carbonyl molecules within the framework of the P–P–P SCF–MO–CI method. The assumption was made that the n-orbital energy of the carbonyl molecules is constant, and the value, -10.50 eV, was assigned to it throughout the calculations. The electronic repulsion integral between n and π electrons was obtained by the Pariser-Parr approximation.[1] The assumption that the n-orbital energy of carbonyl group is constant appeared reasonable since it is known that there is not such a large variation in the n-orbital energy as in the π-orbital energy within similar carbonyl molecules. However, such an assumption may not give good calculated results when we use the SCF–MO's and the energies obtained using different approximations for the electronic repulsion integrals. In addition, it may not be valid for different values of the parameters such as resonance integral, ionization potential, electron affinity or effective nuclear charge of the atomic orbital.

On the other hand, Plotnikov[6] carried out SCF–MO calculation for n,π^* and π,π^* state energies of different kinds of organic molecules taking into account their n-orbital energies and using proper approximation for repulsion integrals between n and π electrons. His calculated results were in good agreement with experimental values. In view of the difficulties encountered in calculating n,π^* transition energies in agreement with experiment, we have examined different approximations for the two-center repulsion integrals in order to obtain better absolute agreement for the π,π^* and n,π^* state energies, particularly for the latter. In this paper, the n-orbital energies and n,π^* state energies were calculated using both Mataga-Nishimoto (M–N)[7] and Pariser-Parr (P–P)[1] approximations.

Methods of Calculation

All calculations were carried out by means of the usual semi-empirical SCF–MO–CI method:

$$\sum_{\nu} F_{\mu\nu} c_{i\nu} = \varepsilon_i c_{i\mu} \tag{1}$$

$$F_{\mu\mu} = -I_\mu + (1/2)P_{\mu\mu}\gamma_{\mu\mu} + \sum_{\nu\neq\mu}(P_{\nu\nu}-1)\gamma_{\mu\nu} \tag{2}$$

$$F_{\mu\nu} = \beta_{\mu\nu} - (1/2)P_{\mu\nu}\gamma_{\mu\nu} \tag{3}$$

$$\gamma_{\mu\mu} = I_\mu - A_\mu \tag{4}$$

where I_μ and A_μ are the ionization potential and electron affinity of atom μ, and $P_{\mu\mu}$ is the electron charge density on atom μ. $\beta_{\mu\nu}$ is the resonance integral for the nearest neighbor atoms μ and ν. Numerical values used for the skeletal structures of *trans*-acrolein,[8] *trans*-2,4-pentadienal, benzaldehyde, and *trans*-cinnamaldehyde were, respectively, 1.36 Å for the carbon double bond, 1.46 Å for the single bond, 1.22 Å for the carbonyl group, and 1.39 Å for the benzene ring. The value 120° was assigned to the C–C–C and C–C–O bond angles.

The n,π^* and π,π^* transition energies were calculated by the following equations.

$$^1E_{jk} = \varepsilon_k - \varepsilon_j - J_{jk} + 2K_{jk} \tag{5}$$

$$^3E_{jk} = \varepsilon_k - \varepsilon_j - J_{jk} \tag{6}$$

where ε_k is the energy of k-th molecular orbital, J_{jk} Coulomb integral over the MO's j and k, and K_{jk} an exchange integral. The n,π^* and π,π^* state energies were calculated including all singly excited configurations.

The SCF–MO's and π,π^* transition energies of these four molecules were calculated using the Pariser-Parr approximation[1] for the electronic repulsion integral between π electrons with $Z_c=3.25$ and $Z_o=4.55$. The resonance integral β_{co} of the carbonyl group was obtained by Kon's equation,[9] and the value -2.67 eV was used for the four molecules. The value of β_{cc} for the nearest neighbour carbon atoms was treated as a parameter and adjusted for each molecule to fit the calculated π,π^* state energy to the experimental value.

The n-orbital on the oxygen atom is assumed to be a pure $2p\pi$ atomic orbital. The n-orbital energy ε_n was obtained from the following equation.[3]

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Table 1. Calculated and observed lowest singlet and triplet state energies and calculated n-orbital energies of carbonyl molecules (eV in unit)

Approx. for γ_{ij} integral	Config.	Sym.	Singlet		Triplet		ε_n
			Calcd	Obsd	Calcd	Obsd	
trans-Arcolein							
P–P	π-π^*	A'	5.960	5.96[a]	2.935	3.05[b]	
M–N	n-π^*	A''	3.917	3.71[a]	3.405	3.01[c]	−12.037
P–P	n-π^*	A''	3.292		2.771		−12.955
trans-2,4-Pentadienal							
P–P	π-π^*	A'	4.745	4.79[d]	2.048		
M–N	n-π^*	A''	3.801	3.81[d]	3.311		−11.897
P–P	n-π^*	A''	3.221		2.714		−12.783
Benzaldehyde							
P–P	π-π^*	A'	4.675	4.50[e]	3.082		
M–N	n-π^*	A''	3.900	3.66[f]	3.404	3.22[f]	−11.890
P–P	n-π^*	A''	3.286		2.780		−12.803
trans-Cinnamaldehyde							
P–P	π-π^*	A'	4.366	4.41[g]	2.314		
M–N	n-π^*	A''	3.822	3.49[h]	3.332		−11.874
P–P	n-π^*	A''	3.233		2.727		−12.757

a) See Ref. 13 and 17. b) See Ref. 13 and 16. c) See Ref. 12 and 13. d) See Ref. 18. e) See Ref. 19. f) See Ref. 15. g) See Ref. 20. h) The value was obtained in the n-hexane solution. It corresponds to $\lambda_{\max}$ value.

$$\varepsilon_n = U_n + \sum_{\mu \neq o}(P_{\mu\mu}-1)\gamma_{\mu n} + (P_{oo}-1)(\gamma_{no}-\delta_{no}/2) \tag{7}$$

where U_n is treated as a parameter for the n-electron, and the value −14.75 eV[10] was used. The two one-center integrals concerning the oxygen atom, γ_{no} and δ_{no} represent $\langle n_o\pi_o|r_{12}^{-1}|n_o\pi_o\rangle$ and $\langle n_o\pi_o|r_{12}^{-1}|\pi_o n_o\rangle$, respectively. The value 12.865 eV[5] was used for the former integral and the value 0.903 eV[11] for the latter one. The $\gamma_{\mu n}$ is a two-center atomic repulsion integral between the π-electron of the carbon atom μ and the n-electron of the oxygen atom. The $\gamma_{\mu n}$ was calculated by the usual Matage-Nishimoto and Pariser-Parr approximations.

Results and Discussion

The calculated results are shown in Table 1. The data show that the n,π^* state energies calculated by M–N approximation are higher than those by P–P approximation, and somewhat higher than the corresponding observed values. However, the calculated n,π^* state energies using the P–P approximation are lower than the corresponding observed values.

The lowest singlet state of the molecules is assigned as the n,π^* state as shown in Table 1. The relative order of the calculated lowest n,π^* and π,π^* singlet state by both approximations is in accordance with the observed order (*cf.* Table 1).

The observed lowest triplet states of acrolein[12–14] and benzaldehyde[15] are assigned to be n,π^* states. The calculated n,π^* triplet state energies by M–N approximation are higher than the calculated π,π^* triplet states, but the corresponding states by P–P approximation are lower than the calculated π,π^* triplet state energies. The relative order of n,π^* and π,π^* triplet states of acrolein and benzaldehyde using P–P approximation is in harmony with the observed order; however, the values of calculated n,π^* triplet states, 2.771 eV (acrolein) and 2.780 eV (benzaldehyde) differ slightly form the observed values 3.01 eV[12,13] and 3.22 eV[15] for acrolein and benzaldehyde, respectively. In the case of *trans*-2,4-pentadienal, the theoretical n,π^* triplet state energy by both approximations, M–N (3.311 eV) and P–P (2.714 eV) is higher than the corresponding π,π^* triplet state energy (2.048 eV). We can not compare the theoretical values with experimental values (no data) for 2,4-pentadienal. However, the theoretical result and the small energy difference between the n,π^* and π,π^* triplet states of acrolein[12,16] suggest that the lowest triplet state of polyenals with polyene chains longer than acrolein may be assigned to the π,π^* triplet state. It is interesting that our calculated n,π^* state energies of acrolein and 2,4-pentadienal using M–N approximation show a good correspondence with those of crotonaldehyde and sorbaldehyde by Plotnikov.[6] Parallel state energy ordering is obtained for *trans*-cinnamaldehyde (n,π^* states higher than π,π^* states). Judging from the present calculated results, the lower triplet state of cinnamaldehyde may be assigned to the π,π^* state.

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The calculated *n*-orbital energies of the molecules are shown in Table 1. The energies are almost the same for all molecules by means of either M–N or P–P approximation although the absolute values depend upon the choice of approximation. The result is in agreement with the assumption by Sidman[5] that the *n*-orbital energy in carbonyl group is approximately constant, although our absolute magnitude is greater.

If the value of U_n in Eq. (7) and/or the numerical values in the Mataga-Nishimoto and Pariser-Parr's electronic repulsion integrals between the *n*- and π-electrons are taken as parameters and adjusted properly, better calculated results for the n,π^* state energy and the *n*-orbital energy may be expected. The method is also applicable to n,π^* state energy calculations for *N*-heterocyclics.

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