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Electronic Spectra and Structures of Organic π-Systems. VII. Electronic States of Benzoylium, Acryloylium, and Cinnamoylium Ions[1]

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The electronic states of benzoylium, acryloylium and cinnamoylium ions have been studied by a semiempirical ASMO LCAO SCF CI method including both π- and $\bar{\pi}$-systems.

The results suggest that the contribution of the canonical formula $R^{-}\text{–}\overset{+}{C}O$ or $R\text{–}\overset{+}{C}O$ to the ground state in ketene should be smaller than that in benzoylium, acryloylium or cinnamoylium ion. The longest wavelength singlet-singlet transition of benzoylium or cinnamoylium ion is $\pi-{}^1\pi^*$ as in benzenediazonium ion, and that of acryloylium ion is $\pi-{}^1\bar{\pi}^*$ as in ketene, diazomethane and diazocyclopentadiene.

As a part of our investigations on the electronic states of cumulated systems, we reported on the electronic states of diazomethane, ketene, diazocyclopentadiene, and benzenediazonium ion.[2] This paper deals with the electronic states of benzoylium (isoelectronic with benzenediazonium), cinnamoylium, and acryloylium ions. These systems called oxocarbonium ions are of

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[2] Paper VI: Z. Yoshida and T. Kobayashi, This Bulletin, **45**, 742 (1972).

importance as the reaction intermediates in Friedel-Crafts type acylation.

The method used in this study is a semiempirical ASMO-LCAO-SCF-CI method in which $\bar{\pi}$-systems are duly taken into consideration.

Method of Calculation

The method used in this study being the same as that used in the calculation of diazomethane, ketene, diazocyclopentadiene, and benzenediazonium ion,[2] its details are not given. Four types of approximations NEβ, NTβ, PEβ, and PTβ are used for each molecule.

For the sake of brevity the numberings of the atomic orbitals and the atoms in the molecules are given in Fig. 1.

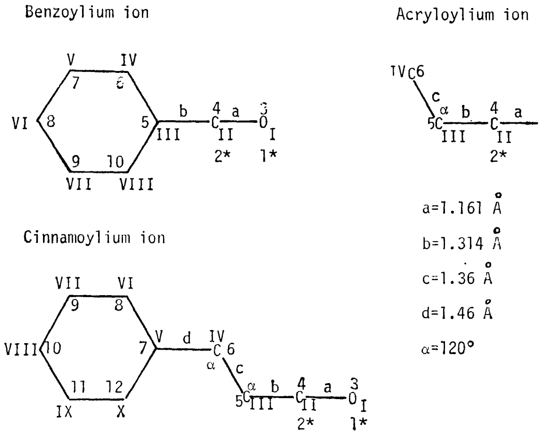

Fig. 1. Assumed structures and numberings of atoms (in Roman numerals) and numberings of atomic orbitals (in Arabic numerals) of benzoylium ion, acryloylium ion, and cinnamoylium ion. ('*' denotes an in-plane $2p_{\bar{\pi}}$-atomic orbital.)

The molecular dimensions of these compounds are assumed to be as shown in Fig. 1. The carbon-oxygen bond length of methyloxocarbonium hexafluoroantimonate is 1.116 Å according to Boer.[3] This is slightly shorter than the carbon-oxygen bond length of ketene (1.161 Å) given by Kox, Thomas, and Sheridan.[4] We assumed the carbon-oxygen bond lengths and the carbon(II)-carbon(III) bond lengths of benzoylium ion, acryloylium ion, and cinnamoylium ion to be equal to those of ketene given by Kox and co-workers as shown in Fig. 1. This is because the CO-groups are in conjugation with other π-systems. The carbon(III)-carbon(IV) bond length of acryloylium ion or cinnamoylium ion is assumed to be 1.36 Å from the structural data of *trans*-acrolein.[5] The carbon(IV)-carbon(V) bond length of cinnamoylium ion is assumed to be 1.46 Å from the data of *syn-p*-chlorobenzaldoxime.[6] The benzene rings of benzoylium ion and cinnamoylium ion are assumed to be regular hexagons with the carbon-carbon bond lengths of 1.397 Å. Carbon (III), carbon(II), and the oxygen atom of each compound are assumed to lie on a straight line according to the structural data of methyloxocarbonium hexafluoroantimonate.[3,7]

The calculated core resonance integrals β_{tu}'s are summarized in Table 1.

TABLE 1. CORE-RESONANCE INTEGRALS, β_{ij}'s, IN eV

bond	NEβ	NTβ	PEβ	PTβ
Benzoylium ion				
1—2	−3.043	−3.309	−3.988	−3.559
4—5	−2.731	−2.863	−3.797	−3.270
5—6	−2.378	−2.378	−2.378	−2.378
6—7	−2.378	−2.378	−2.378	−2.378
7—8	−2.378	−2.378	−2.378	−2.378
Acryloylium ion				
1—2	−3.043	−3.309	−3.988	−3.559
4—5	−2.731	−2.863	−3.797	−3.270
5—6	−2.529	−2.586	−2.529	−2.586
Cinnamoylium ion				
1—2	−3.043	−3.309	−3.988	−3.559
4—5	−2.731	−2.863	−3.797	−3.270
5—6	−2.529	−2.586	−2.529	−2.586
6—7	−2.137	−2.049	−2.137	−2.049
7—8	−2.378	−2.378	−2.378	−2.378
8—9	−2.378	−2.378	−2.378	−2.378
9—10	−2.378	−2.378	−2.378	−2.378

The calculation has been carried out on a FACOM 230-60 computer at the computation centre of Kyoto University.

Results

The molecular diagrams of these compounds are shown in Fig. 2. The reported molecular diagrams of ketene are also given. The calculated and the observed transition energies are given in Table 2 together with CI coefficients.

Discussion

In the case of benzoylium ion, the β_{12}- and β_{45}-values calculated by PEβ-approximation are slightly larger than those calculated by PTβ-approximation as shown in Table 1. In N-approximation the β-values given by both methods NTβ and NEβ are similar to each other. The other β_{CC}-values calculated by formulas (6) and (7) in Ref. 2 are in good agreement with each other.

On the whole the four sets of parameters give similar SCF eigenvalues and eigenvectors. The eigenvectors of benzoylium ion are similar to those of benzenediazonium ion.

As is seen in Fig. 2, in the case of benzoylium ion carbon atom II carries a charge of about +0.7—+0.8 and the terminal oxygen I is nearly neutral. The bond

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[3] F. P. Boer, *J. Amer. Chem. Soc.*, **88**, 1572 (1966).

[4] A. P. Cox, L. F. Thomas, and J. Sheridan, *Spectrochim. Acta*, **15**, 542 (1959).

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

[6] B. Jerslev, *Nature*, **180**, 1410 (1957).

[7] G. A. Olah, C. U. Pittman, Jr., and M. C. R. Symons, "Carbonium Ions," Vol. 1, p. 153, ed. by G. A. Olah, and P. von R. Schleyer, Interscience, New York (1968).

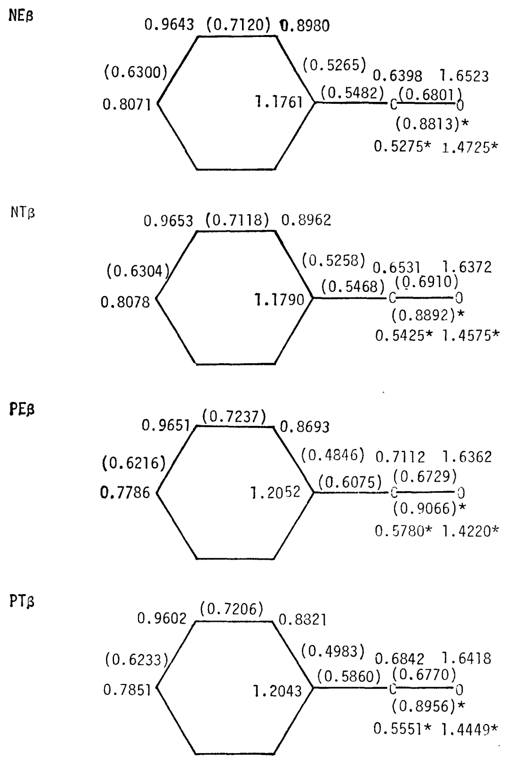

Fig. 2a. Electron densities and bond orders (in parentheses) of benzoylium ion.

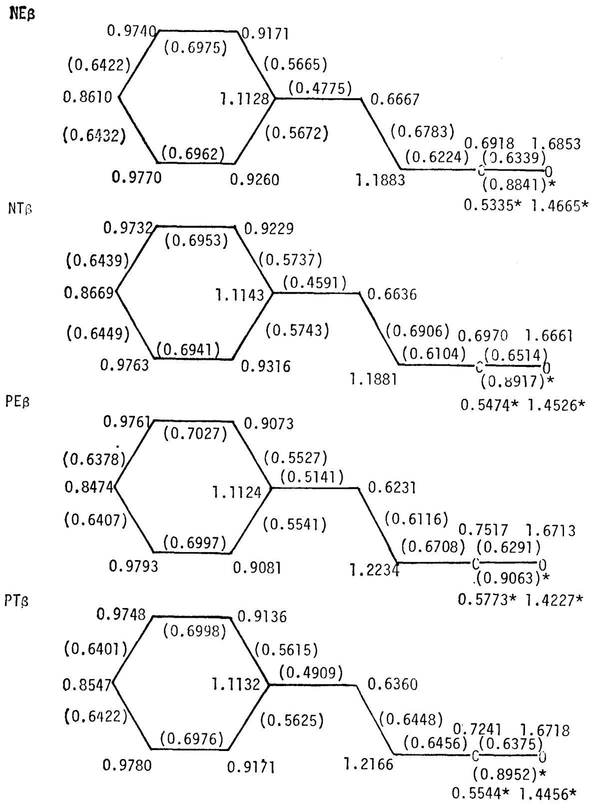

Fig. 2b. Electron densities and bond orders (in parentheses) of cinnamoylium ion.

order of the carbon(II)-oxygen bond is about 1.6. The bond order of the carbon(II)-carbon(III) bond is about 0.54—0.60. A charge of about +0.7 exists on the CO-group. If we compare the molecular diagrams of

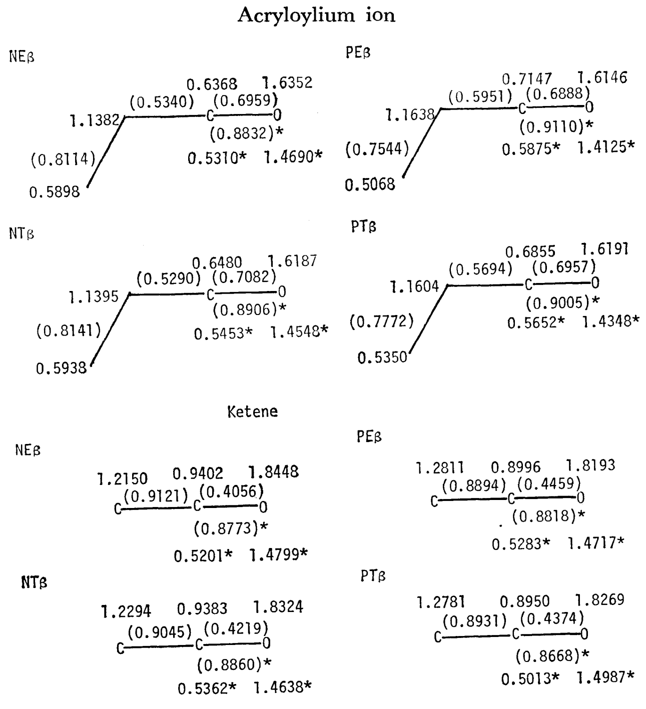

Fig. 2c. Electron densities and bond orders (in parentheses) of acryloylium ion and ketene.

ketene with those of benzoylium ion, the CO bond of benzoylium ion can be anticipated to have a larger triple bond character than the CO bond of ketene, and the C_{II}–C_{III} bond of ketene, a larger double bond character than the C_{II}–C_{III} bond of benzoylium ion. The electron density on the oxygen or carbon atom (I) in ketene is greater than that of the corresponding atom of benzoylium ion. On the whole the extent of contribution of the canonical formula $R-C^+\equiv O$ or $R^--C^+\equiv O$ to the ground state may be greater in the case of benzoylium ion than in ketene.

In the case of acryloylium ion carbon atom II carries a charge of about +0.7—0.8 as in benzoylium ion. The terminal oxygen is nearly neutral as in benzoylium ion. The bond orders of the carbon(II)-oxygen bond and the carbon(II)-carbon(III) bond are about 1.6 and 0.53—0.60, respectively. These values are similar to those of benzoylium ion. The CO-group in acryloylium ion bears a charge of about +0.73—0.67. The extent of contribution of the canonical formula $R-C^+\equiv O$ to the ground state of acryloylium ion might be nearly equal to that in benzoylium ion.

In the case of cinnamoylium ion carbon atom II bears a charge of about +0.7—0.8 as in benzoylium ion and acryloylium ion. The terminal oxygen is nearly neutral also in this system. The bond order of the carbon(II)-oxygen bond is about 1.53 which is slightly smaller than those in benzoylium ion and acryloylium ion. The bond order of the carbon(II)-carbon(III) bond is about 0.61—0.67 which is slightly larger than those of acryloylium ion and benzoylium ion. The results suggest that the triple bond character of the carbon(II)-oxygen bond is slightly smaller than those of benzoylium ion and acryloylium ion, and the double bond character of the carbon(II)-carbon(III) bond is slightly larger than those of the other two com-

TABLE 2. CALCULATED TRANSITION ENERGIES IN eV

Sym.	E	f	CI Composition[a)]		Sym.	E	f	CI Composition[a)]		Obsd	
										E	log ε
Benzoylium ion											
NEβ approximation					NTβ approximation						
$^1B_2$	3.706	0.099	5—6	0.961	$^1B_2$	3.769	0.105	5—6	0.957	4.03	3.57[7)]
$^1A_2$	4.216	0.0	3—7	0.463	$^1A_2$	4.428	0.0	4—7	0.876	4.75	4.23
			4—7	0.872				3—7	0.459		
$^1A_1$	4.373	0.384	4—6	0.894	$^1A_1$	4.444	0.372	4—6	0.892		
			5—8	0.349				5—8	0.371		
$^1B_1$	5.127	0.0	5—7	1.0	$^1B_1$	5.321	0.0	5—7	1.0		
$^1A_1$	5.997	0.293	3—6	−0.467	$^1A_1$	6.146	0.544	3—6	−0.429		
			2—7	−0.356				5—8	0.685		
			5—8	0.611				4—10	−0.427		
			4—9	−0.441							
$^3B_2$	2.628		5—6	0.958	$^3B_2$	2.663		5—6	0.960		
PEβ approximation					PTβ approximation						
$^1B_2$	3.876	0.143	5—6	0.957	$^1B_2$	3.811	0.128	5—6	0.959	4.03	3.57[7)]
$^1A_1$	4.694	0.324	4—6	0.874	$^1A_1$	4.607	0.355	4—6	0.880	4.75	4.23
			5—8	−0.445				5—8	−0.422		
$^1A_2$	5.266	0.0	4—7	0.844	$^1A_2$	4.788	0.0	4—7	0.848		
			3—7	−0.522				3—7	−0.514		
$^1B_1$	6.471	0.0	5—7	1.0	$^1B_1$	5.910	0.0	5—7	1.0		
$^3B_2$	2.562		5—6	0.975	$^3B_2$	2.562		5—6	0.970		
Acryloylium ion											
NEβ approximation					NTβ approximation						
$^1A''$	4.516	0.0	3—5	0.976	$^1A''$	4.766	0.0	3—5	0.980	(5.28~6.20)[7)]	
$^1A'$	5.009	0.488	3—4	0.953	$^1A'$	5.193	0.540	3—4	0.966		
$^1A'$	6.859	0.209	2—5	0.655	$^1A'$	7.295	0.177	1—4	−0.562		
			1—4	−0.589				2—5	0.649		
			3—6	0.342				3—6	0.427		
$^3A'$	2.701		3—4	0.990	$^3A'$	2.828		3—4	0.990		
PEβ approximation					PTβ approximation						
$^1A''$	5.492	0.0	3—5	0.987	$^1A''$	5.052	0.0	3—5	0.984	(5.28~6.20)[7)]	
$^1A'$	5.578	0.682	3—4	0.986	$^1A'$	5.471	0.644	3—4	0.976		
$^1A'$	8.328	0.070	1—4	0.497	$^1A'$	7.607	0.137	1—4	0.542		
			2—5	0.636				2—5	0.664		
			3—6	0.541				3—6	0.427		
$^3A'$	2.974		3—4	0.996	$^3A'$	2.918		3—4	0.996		
Cinnamoylium ion											
NEβ approximation					NTβ approximation						
$^1A'$	3.356	0.046	5—7	0.417	$^1A'$	3.374	0.044	6—7	0.898	3.80	4.471[7)]
			6—7	0.855				5—7	0.316		
$^1A'$	3.570	0.954	5—7	0.844	$^1A'$	3.585	0.906	5—7	0.886		
			6—7	−0.419				6—7	−0.320		
$^1A''$	3.830	0.0	4—8	−0.621	$^1A''$	4.057	0.0	4—8	−0.621		
			5—8	−0.679				5—8	0.702		
$^1A'$	5.255	0.215	4—7	0.709	$^1A'$	5.333	0.287	4—7	0.685		
			6—10	0.500				6—10	0.557		
$^3A'$	2.099		4—7	−0.375	$^3A'$	2.178		4—7	−0.375		
			5—7	0.830				5—7	0.867		
			6—7	−0.364							
PEβ approximation					PTβ approximation						
$^1A'$	3.307	0.053	6—7	0.958	$^1A'$	3.279	0.047	6—7	0.955	3.80	4.471[7)]
$^1A'$	3.726	0.923	5—7	0.942	$^1A'$	3.654	0.915	5—7	0.937		
$^1A''$	4.904	0.0	3—8	−0.316	$^1A''$	4.423	0.0	3—8	0.345		
			4—8	0.664				4—8	0.644		
			5—8	0.675				5—8	−0.679		

Table 2. Calculated transition eneregies in eV (continued)

Sym.	E	f	CI Composition[a]	Sym.	E	f	CI Composition[a]	Obsd E	Obsd log ε
$^1A'$	5.530	0.433	4—7 −0.685	$^1A'$	5.485	0.424	4—7 −0.661		
			6—9 0.625				5—9 −0.319		
			5—10 0.316				6—10 0.621		
$^3A'$	2.259		5—7 0.939	$^3A'$	2.183		5—7 0.921		
							4—7 −0.319		

a) The transition, indicated by i—j, refers to a one electron excitation from orbital i to virtual orbital j. The second column gives the CI coefficient of the configuration i—j.

pounds. The bond order of the carbon(III)-carbon(IV) bond in acryloylium ion is 0.75—0.80 which is greater than that of cinnamoylium ion, 0.61—0.69. This suggests that the double bond character of the carbon(III)-carbon(IV) bond of acryloylium ion is larger than that of cinnamoylium ion. The CO-group of cinnamoylium ion bears a charge of about +0.58—0.64. The value is smaller than those in benzoylium and acryloylium ions. On the whole the triple bond character of the carbon(II)-oxygen bond of benzoylium ion, acryloylium ion or cinnamoylium ion is more enhanced than that of ketene. The double bond character of the carbon(II)-carbon(III) bond of ketene may be larger than those of benzoylium, acryloylium, and cinnamoylium ions. Contribution of the canonical formula $R^{-}\text{–}\overset{+}{C}O$ or $R\text{–}\overset{+}{C}O$ to the ground state of benzoylium ion, acryloylium ion, or cinnamoylium ion might be larger than in ketene.

Calculated transition energies are summarized in Table 2. In the case of benzoylium ion P-approximation gives better results than the other. This is consistent with the molecular diagram. Calculated 4.788 eV and 5.910 eV transitions (PTβ-approximation) are π—$^1\bar{\pi}^*$ transitions and are the so-called intramolecular charge-transfer transitions. The character of the transitions of this system is similar to that of benzenediazonium ion.

In the case of acryloylium ion P-approximation gives a better result as in the case of benzoylium ion. This is also consistent with the molecular diagrams. The calculated 5.052 eV transition has the character of the so-called intramolecular charge-transfer transition. This is π—$^1\bar{\pi}^*$ transition.

In the case of cinnamoylium ion the four methods give similar results but P-approximation gives slightly better results. The calculated 4.423 eV transition by PTβ-approximation has the character of the so-called intramolecular charge-transfer transition, and is π—$\bar{\pi}^*$ transition.

Conclusion

The triple bond character of the CO bond of benzoylium ion, acryloylium ion or cinnamoylium ion may be larger than that of ketene. The double bond character of the carbon(II)-carbon(III) bond of ketene may be larger than that of acryloylium ion, cinnamoylium ion or benzoylium ion. The contribution of the canonical formula $R^{-}\text{–}\overset{+}{C}O$ (or $R\text{–}\overset{+}{C}O$) to the ground state in ketene may be smaller than in benzoylium ion, acryloylium ion, and cinnamoylium ion.

The longest wavelength singlet-singlet transitions of benzoylium and cinnamoylium ions are π—π^* as in benzenediazonium ion, and that of acryloylium ion is π—$\bar{\pi}^*$ as in diazomethane, ketene, and diazocyclopentadiene.