[Chem. Pharm. Bull. 20(4) 677—681 (1972)]

UDC 547.587.51.03 : 547.812.5.03

The π-Electronic Structures and Spectra of Coumarins and Pyrones Including Sulfur Derivatives

MAMORU KAMIYA and YUKIO AKAHORI

Shizuoka College of Pharmacy[1]

(Received June 16, 1971)

The semiempirical SCF-MO-CI calculations were performed with the aid of the variable β-core procedure for a systematic investigation of the π-electronic structures and spectra of a series of pyrones and coumarins including sulfur derivatives. The calculated results on the π-π^* transitions indicated several significant effects of the heteroatom replacement upon the polarization direction and oscillator strength. The calculated values of the singlet π-π^* transition energies for the compounds excepting the thiothia-derivatives and the polarization directions of the lowest two π-π^* transitions of coumarins and so on were found to be in good agreement with the observed results. Also, the changes in the π-electronic distribution in going from the ground to the lowest $^1(\pi, \pi^*)$ and/or $^3(\pi, \pi^*)$ state were in good correlation with a few experimental facts.

The π-electronic structures of the compounds in the title are of much interest partly because many experimental data suggest that the compounds have pseudo-aromatic character closely related to their topology, and also coumarin itself is known to exhibit an interesting photodimerization reaction and to work as photosensitizing agent in photodynamic actions. In this context, several HMO calculations have been performed recently by Zahradnik, *et al.*[2-4] and by Perelšon, *et al.*[5,6] about the π-electronic properties of these compounds. Consequently, various chemical properties have been predicted successfully. Furthermore, a few spectroscopic studies on the photoexcited states have been carried out particularly for coumarin, and they have provided experimental data available for the assignment of the lowest excited states and direction of polarizations.[7,8] It seems, however, that any systematic SCF calculations have not yet been performed concenrning the π-electronic transitions.

This paper reports a semiempirical SCF-CI calculation on the π-electronic structures of a series of the compounds in the title for a better understanding of the electronic spectra and the electronic structures of the photoexcited states.

Method of Calculation

The present calculations have been performed using the Pariser–Parr–Pople method,[9,10] and the valence- state ionization potential (I) and electron affinity (A) of the π-orbitals are taken as follows with reference to the paper of Pritchard and Skinner;[11]

---

1) Location: *Oshika, Shizuoka-shi.*
2) R. Zahradnik, C. Parkanyi, and J. Koutecky, *Collection Czech. Chem. Commun.*, **27**, 1242 (1962).
3) R. Zahradnik and J. Koutecky, *Collection Czech. Chem. Commun.*, **28**, 1117 (1963).
4) R. Zahradnik and C. Parkanyi, *Collection Czech. Chem. Commun.*, **30**, 3016 (1965).
5) M.E. Perelšon, A.V. Tutkevich, Yu. N. Sheinker, and N.P. Gambaryan, *Teor. Eksp. Khim.*, **2**, 575 (1966).
6) M.E. Perelšon and Yu.N. Sheinker, *Teor. Eksp. Khim.*, **3**, 697 (1967).
7) D.R. Graber, M.W. Grimes, and A. Haug, *J. Chem. Phys.*, **50**, 1623 (1969).
8) P.-S. Song and W.H. Gordon, *J. Phys. Chem.*, **74**, 4234 (1970).
9) R. Pariser and R.G. Parr, *J. Chem. Phys.*, **21**, 466,767 (1953).
10) J.A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).
11) H.O. Pritchard and H.A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

I (=C-)	11.42 eV;	I (=O)	17.28 eV;	I (-O-)	34.10 eV;
I (=S)	12.50 eV:	I (-S-)	22.88 eV		
A (=C)	0.58 eV;	A (=O)	2.70 eV;	A (-O-)	14.77 eV;
A (=S)	2.70 eV;	A (-S-)	10.98 eV		

The two-center repulsion integrals are obtained according to the Mataga–Nishimoto formula.[12] The core-resonance integrals (β_{rs}) are evaluated for neighbouring atomic pairs by the variable β procedure,[13] and the parametrizations are taken as follows;

$\beta_{C\text{-}C} = -0.51 \quad P_{C\text{-}C} - 1.84$ (eV)
$\beta_{C\text{-}O} = -0.56 \quad P_{C\text{-}O} - 2.20$
$\beta_{C\text{-}S} = -0.33 \quad P_{C\text{-}S} - 1.80$

where $P_{C\text{-}C}$, $P_{C\text{-}O}$ and $P_{C\text{-}S}$ are the usual π-bond orders of the C-C, C-O, and C-S bonds, respectively. In the configuration interaction (CI) procedure all singly excited configurations are allowed to interact. The initial values of all the bond lengths in the aromatic ring are assumed as 1.39 Å, and those of C=O and C=S bond lengths are taken as 1.24 Å and 1.68 Å, respectively. The coordinate axes and numberings of the presently treated compounds are denoted in the molecular diagrams in Fig. 1.

Tabel I. Experimental Data on Electronic Spectra

Compound	ΔE[a] (eV)	log ε[b]
α-Pyrone (I)[c]	4.29	3.67
	5.74	3.36
α-Thiopyrone (II)	3.38	4.80
	4.44	4.87
α-Thiapyrone (III)	—	
α-Thiothiapyrone (IV)	2.99	3.62
	3.89	3.97
	5.12	3.98
γ-Pyrone (V)	3.10	1.19
	5.21	3.99
γ-Thiopyrone (VI)	3.90	1.72
	4.43	4.19
γ-Thiapyrone (VII)	2.32	1.23
	3.76	4.22
	5.39	3.78
γ-Thiothiapyrone (VIII)	2.11	1.43
	3.34	4.32
	5.14	3.34
Coumarin (IX)[d]	3.97	3.70
	{4.41	3.95
	4.57	4.04
Coumarin (IX)[d]	5.21	3.57
Thiocoumarin (X)	3.32	4.11
	{3.99	3.59
	4.20	3.75
	4.44	4.01
	5.04	3.94
Thiacoumarin (XI)	3.67	3.42
	{4.15	3.93
	4.32	3.89
	5.14	4.49
	5.66	4.30
Thiothiacoumarin (XII)	2.98	3.95
	{3.71	3.55
	3.84	3.84
	{4.09	4.15
	4.26	4.14
	4.63	3.98
	5.32	4.47

[a] transition energy of maximum absorption
[b] molar extinction coefficient of maximum absorption
[c] The spectral data (in cyclohexane) on α- and γ-pyrones are taken from the following literatures; R. Mayer, *Chem. Ber*, **90**, 2362 (1957), R. Mayer, *Chem. Tech.*, **10**, 418 (1958); R. Mayer and P. Fischer, *Chem. Ber.*, **95**, 1307 (1962).
[d] The spectral data (in cyclohexane) on coumarins are taken from the literature: A. Mangini and D. Dal Monte, *Atti Accad. Sci. Ist. Bologna*, **5**, 20 (1958).

Table II. Calculated Result of Electronic Spectra

Compound	ΔEs[a] (eV)	ΔEt[b] (eV)	f[c]	α[d]	Main component of CI wave function for $^1(\pi, \pi^*)$ state
α-Pyrone (I)	4.224	1.243	0.392	5	$0.981\phi(4\to3)$
	5.213	2.445	0.106	−71	$0.870\phi(4\to2)-0.457\phi(5\to3)-0.132\phi(4\to3)$
	6.333	3.167	0.389	−59	$0.607\phi(4\to1)-0.598\phi(5\to3)+0.428\phi(6\to3)$
	6.705	4.885	0.319	−82	$0.794\phi(6\to3)+0.501\phi(5\to3)+0.318\phi(4\to2)$
	7.392	5.688	0.166	−81	$0.652\phi(4\to1)+0.580\phi(5\to2)+0.355\phi(5\to3)$

---

[12] N. Mataga and K. Nishimoto, *Z. Phys. Chem.*, **13**, 140 (1957).
[13] K. Nishimoto and L.S. Forster, *Theor. Chim. Acta*, **4**, 155 (1966).

Compound	ΔEs[a] (eV)	ΔEt[b] (eV)	f[c]	α[d]	Main component of CI wave function for $^1(\pi, \pi^*)$ state
α-Thiopyrone (II)	3.563	0.911	0.380	− 7	$0.971\phi(4\to3)$
	4.502	1.872	0.315	−37	$0.858\phi(4\to2)-0.454\phi(5\to3)+0.158\phi(4\to3)$
	5.827	2.947	0.384	−82	$0.834\phi(5\to3)+0.416\phi(4\to2)+0.255\phi(6\to3)$
	5.903	4.482	0.276	−54	$0.656\phi(6\to3)+0.665\phi(4\to1)-0.255\phi(5\to3)$
	6.750	4.916	0.144	−40	$0.631\phi(5\to2)+0.562\phi(4\to1)-0.505\phi(6\to3)$
α-Thiapyrone (III)	3.947	1.308	0.278	16	$0.974\phi(4\to3)$
	5.073	2.427	0.134	−57	$0.887\phi(4\to3)-0.364\phi(5\to3)-0.243\phi(6\to3)$
	6.046	3.080	0.429	−41	$0.795\phi(5\to3)-0.430\phi(4\to1)-0.318\phi(6\to3)$
	6.391	4.620	0.281	−59	$0.835\phi(6\to3)-0.341\phi(5\to2)+0.287\phi(6\to2)$
	7.039	5.248	0.382	−69	$0.792\phi(4\to1)+0.412\phi(5\to3)+0.245\phi(4\to2)$
α-Thiothiapyrone (IV)	3.300	0.962	0.257	0	$0.963\phi(4\to3)$
	4.382	1.858	0.402	−34	$0.891\phi(4\to2)+0.347\phi(5\to3)+0.177\phi(4\to3)$
	5.595	2.955	0.192	−78	$0.866\phi(5\to3)-0.309\phi(4\to2)+0.258\phi(6\to2)$
	5.703	4.319	0.422	−45	$0.723\phi(6\to3)-0.599\phi(4\to1)-0.182\phi(6\to2)$
	6.421	4.429	0.253	−52	$0.707\phi(4\to1)+0.529\phi(6\to3)-0.392\phi(5\to2)$
γ-Pyrone (V)	4.742	1.530	0.440	90	$0.929\phi(4\to3)$
	4.941	1.925	0.036	0	$0.988\phi(4\to2)$
	5.426	3.018	0.127	0	$0.986\phi(5\to3)$
	6.824	4.630	0.839	90	$0.790\phi(5\to2)-0.552\phi(4\to1)-0.263\phi(4\to3)$
	7.259	5.120	0.377	90	$0.643\phi(4\to1)-0.615\phi(6\to3)+0.377\phi(5\to2)$
γ-Thiopyrone (VI)	4.064	0.901	0.003	0	$0.993\phi(4\to2)$
	4.144	1.808	0.877	90	$0.961\phi(4\to3)$
	5.215	2.692	0.129	0	$0.989\phi(5\to3)$
	6.082	4.299	0.017	90	$0.827\phi(4\to1)-0.529\phi(6\to3)-0.181\phi(5\to2)$
	6.425	4.847	0.741	90	$0.740\phi(5\to2)-0.572\phi(6\to3)-0.269\phi(4\to3)$
γ-Thiapyrone (VII)	4.428	1.540	0.478	90	$0.941\phi(4\to3)$
	4.532	1.937	0.044	0	$0.992\phi(4\to2)$
	5.411	3.002	0.134	0	$0.985\phi(5\to3)$
	6.717	4.378	0.625	90	$0.692\phi(5\to2)-0.687\phi(4\to1)-0.199\phi(4\to3)$
	7.095	4.601	0.578	90	$0.565\phi(6\to3)-0.553\phi(4\to1)-0.541\phi(5\to2)$
γ-Thiothiapyrone (VIII)	3.767	0.916	0.010	0	$0.997\phi(4\to2)$
	3.903	1.807	0.873	90	$0.960\phi(4\to3)$
	5.190	2.722	0.097	0	$0.979\phi(5\to3)$
	5.905	4.144	0.013	90	$0.827\phi(4\to1)-0.534\phi(6\to3)-0.154\phi(5\to2)$
	6.295	4.331	0.654	90	$0.647\phi(5\to2)-0.638\phi(6\to3)-0.306\phi(4\to1)$
Coumarin (IX)	3.928	1.443	0.264	3	$0.746\phi(6\to5)+0.472\phi(7\to5)-0.303\phi(6\to4)$
	4.283	2.259	0.401	− 8	$0.630\phi(6\to5)-0.550\phi(7\to5)+0.458\phi(6\to4)$
	5.245	2.991	0.127	89	$0.656\phi(7\to5)+0.481\phi(6\to4)-0.322\phi(7\to4)$
	5.328	3.225	0.175	−46	$0.730\phi(6\to3)-0.455\phi(6\to4)-0.323\phi(7\to4)$
	5.727	3.510	0.507	−21	$0.645\phi(8\to5)+0.600\phi(7\to4)+0.335\phi(6\to4)$
Thiocoumarin (X)	3.552	1.013	0.665	−11	$0.949\phi(6\to5)-0.152\phi(8\to5)+0.140\phi(7\to4)$
	4.077	1.996	0.073	−20	$0.608\phi(7\to5)-0.542\phi(6\to4)+0.304\phi(7\to4)$
	4.632	2.613	0.309	−37	$0.603\phi(6\to4)+0.446\phi(8\to5)-0.426\phi(6\to3)$
	4.996	3.169	0.011	48	$0.627\phi(7\to5)+0.622\phi(6\to3)-0.382\phi(7\to4)$
	5.216	3.468	0.508	−43	$0.658\phi(8\to5)-0.519\phi(6\to4)-0.433\phi(7\to4)$
Thiacoumarin (XI)	3.766	1.481	0.226	10	$0.845\phi(6\to5)-0.338\phi(7\to5)+0.281\phi(7\to4)$
	4.277	2.222	0.253	− 7	$0.647\phi(7\to5)-0.518\phi(6\to4)+0.455\phi(6\to5)$
	5.034	2.841	0.060	64	$0.547\phi(7\to5)+0.529\phi(6\to3)+0.456\phi(7\to4)$
	5.175	3.158	0.674	−33	$0.702\phi(6\to4)-0.439\phi(6\to3)+0.337\phi(7\to5)$
	5.550	3.482	0.442	− 3	$0.548\phi(8\to5)-0.544\phi(7\to4)+0.498\phi(6\to3)$
Thiothiacoumarin (XII)	3.359	1.036	0.474	− 7	$0.947\phi(6\to5)+0.160\phi(7\to4)+0.131\phi(8\to5)$
	4.022	1.957	0.020	−19	$0.622\phi(6\to4)-0.577\phi(7\to5)-0.282\phi(7\to4)$
	4.536	2.587	0.739	−30	$0.615\phi(6\to4)+0.412\phi(7\to5)-0.470\phi(6\to3)$
	4.761	3.058	0.012	24	$0.608\phi(7\to5)+0.475\phi(6\to3)-0.457\phi(7\to4)$
	4.990	3.429	0.345	−33	$0.604\phi(8\to5)+0.503\phi(6\to3)+0.385\phi(6\to4)$

[a] singlet π-π^* transition energy

[b] triplet π-π^* excitation energy

[c] oscillator strength

[d] the angle of polarization direction measured counterclockwise to the x-axis

Result and Discussion

Electronic Spectra

The theoretical results obtained here are listed in Table II. As for a series of coumarins excepting (XII), fairly good agreement is found between the theoretical and experimental values of the lowest $^1(\pi,\pi^*)$ transition energies. The lowest transitions of coumarins are polarized considerably close to the long molecular axis. In the case of coumarin, such property of polarization direction can be supported experimentally by the polarized fluorescence spectrum obtained by Song and Gordon.[8] The phosphorescent state of coumarin has been assigned to $^3(\pi,\pi^*)$ state by Song and Gordon.[8] The theoretical value of the $^3(\pi,\pi^*)_1$ excitation energy for coumarin, however, is too low as compared with the observed value of 2.71 eV.[8]

As for a series of α-pyrones excepting (IV), fairly good agreement is found between the theoretical and experimental spectra. The increasing order of the theoretical $^1(\pi,\pi^*)_1$ transition energies of α-pyrones is IV<II<III<I just in agreement with the corresponding order for coumarins, but the ordering of the theoretical values of oscillator strengths is dissimilar to that for coumarins in which the intramolecular charge-transfer interaction upon the $^1(\pi,\pi^*)_1$ excitation is partly induced through the CI mixing. The polarization direction of the $^1(\pi,\pi^*)_1$ transition of α-pyrones is also close to the x-axis.

The theoretical values of the $^1(\pi,\pi^*)_1$ transition energies of γ-pyrones are not in so good agreement with the observed values excepting the $^1(\pi,\pi^*)_1$ transition for γ-thiopyrone.

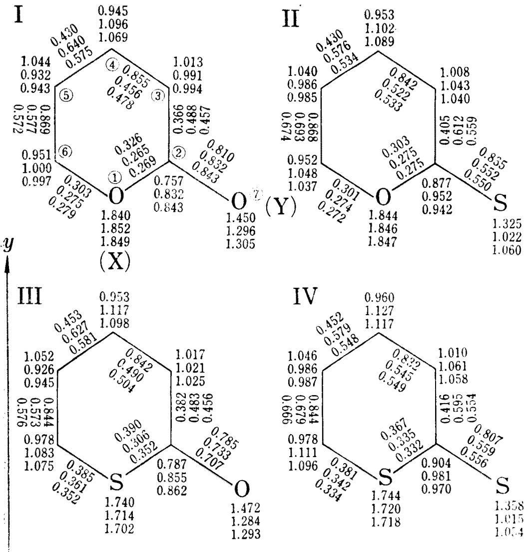

Fig. 1. Molecular Diagrams at the Ground, Lowest singlet and triplet (π, π*) states

Top, middle and bottom numbers at each molecular diagram refer to the ground, lowest singlet and triplet (π, π*) states, respectively. Endocyclic and exocyclic heteroatoms are denoted as X and Y, respectively.

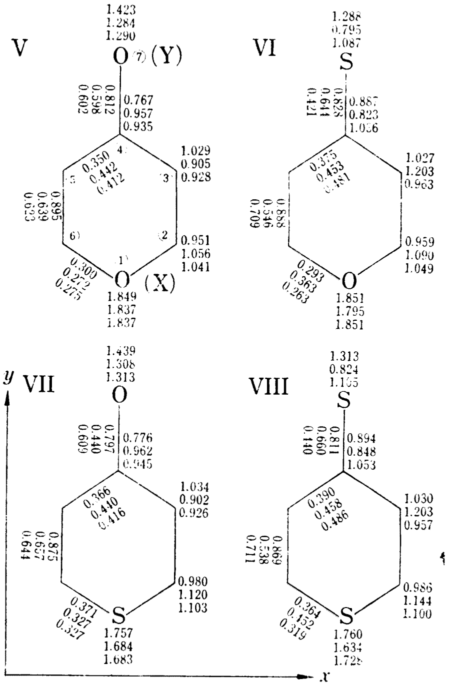

Fig. 2

π-Electronic Distributions

The changes in the π-electronic distributions upon excitations to the $^1(\pi,\pi^*)_1$ and $^3(\pi,\pi^*)_1$ states are known from the molecular diagrams in Fig. 1—3. As for a series of coumarins, the exocyclic heteroatoms release π-electrons upon the excitations unlike many other aromatic carbonyls and thiocarbonyls. This electronic distribution change appears to take place in the order of $^1(\pi,\pi^*)_1<^3(\pi,\pi^*)_1$ for coumarin, and of $^3(\pi,\pi^*)_1<^1(\pi,\pi^*)_1$ for other sulfur-containing coumarins. Also, the mobile π-bond-order of the C(3)-C(4) bond in the α-pyrone moiety exhibits a remarkable decrease upon the excitations. This takes place in the order of $^1(\pi,\pi^*)_1<^3(\pi,\pi^*)_1$ for coumarins with the carbonyl group, and of $^3(\pi,\pi^*)_1<^1(\pi,\pi^*)_1$ for coumarins with the thiocarbonyl group. These theoretical results mentioned above are in good correlation with the experimental facts that not the singlet but triplet excited coumarin molecule undergoes a photodimerization reaction yielding trans head-to-head dimer efficiently,[14] and that the vibrational structure due to C–C stretching appears in the phosphorescence of coumarin.[8] In the case of α-pyrones, such changes in the π-electronic distribution generally takes place in the order of $^3(\pi,\pi^*)_1<^1(\pi,\pi^*)_1$ in a way reverse to coumarin. In the case of γ-pyrones also, excitations to the $^1(\pi,\pi^*)_1$ and/or $^3(\pi,\pi^*)_1$ state causes a remarkable decrease in the mobile π-bond-order of the C(2)-C(3) bond. This takes place in the order of $^1(\pi,\pi^*)_1<^3(\pi,\pi^*)_1$ for γ-pyrones with the carbonyl group, and of $^3(\pi,\pi^*)_1<^1(\pi,\pi^*)_1$ for γ-pyrones with the thiocarbonyl group. This decrease of the π-bond-order may cause a large geometrical change upon the excitations. In fact it has been reported that the 0–0 transition in the vibrational structure of the first intense bands are forbidden in the case of the γ-pyrone and γ-thiapyrone spectra.[15]

IX

X

XI

XII

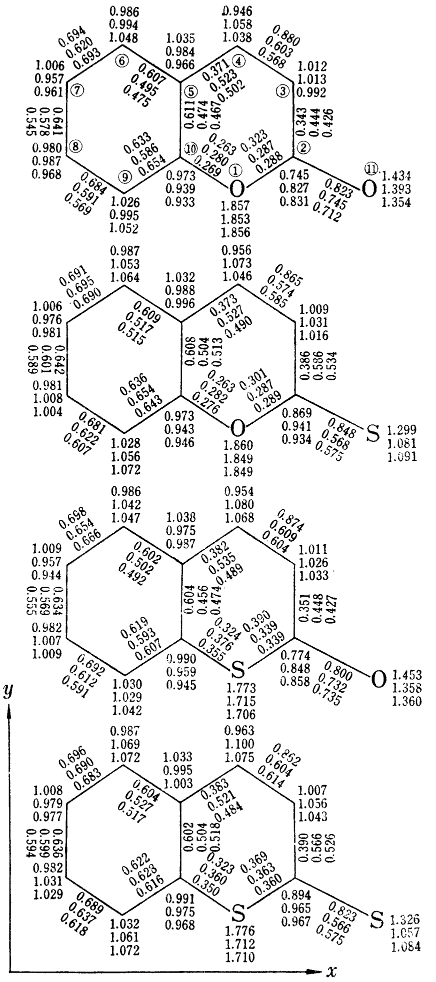

Fig. 3.

Acknowledgement The present calculations were performed with a HITAC 5020-E computer at the Computation Center of the University of Tokyo, to which the authors express their gratitude. This work was supported in part by a Grant-in-Aid from the Ministry of Education.

---

[14] G.S. Hammond, C.A. Stout, and A.A. Lamola, *J. Am. Chem. Soc.*, **86**, 3103 (1964).

[15] M. Rolla and P. Franzosini, *Ann. Chim.*, **47**, 346 (1957).