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ELECTRONIC SPECTRA AND STRUCTURES OF THIOPYRYLIUM AND PYRYLIUM CATIONS

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Abstract—The electronic spectra and structures of thiopyrylium and pyrylium cations have been investigated by the SCF–MO–CI method in which only the π electrons are explicitly considered. The calculated spectra agree with those observed. More delocalization of the positive charge in the thiopyrylium cation than in the pyrylium cation has been shown from the ground state SCF MO.

MONOCYCLIC CARBONIUM ions are formed from five sp^2 carbons and one 6th group element, X, (X: S, O) giving thiopyrylium (I, X: S) and pyrylium (II, X: O) cations. The ground state structures for both the cations are shown as the Kekulé structures and carbonium ion structures (Fig. 4). We have studied the reactions[1–3] and the CT complex formation of this interesting system.[4] This paper deals with features of the electronic spectra and the structures of both cations which are iso-π-electronic with benzene. From simple Hückel molecular orbital (HMO) calculations, the highest occupied and the lowest vacant orbitals of benzene are doubly degenerate due to symmetry; six π-electrons occupy three bonding orbitals. Despite such a simple appearance of the electronic state of benzene, its electronic spectrum is more complicated than expected from HMO methods. This is explained by a more accurate theoretical treatment taking electronic repulsion terms into consideration. Since the replacement of a —CH= group of benzene with a hetero-atom reduces the symmetry of the molecule and hetero-atoms have much larger electronegativities, the π-electronic states of I and II cannot be expected to be similar to that of benzene. In order to investigate the character of the electronic transitions of I and II in comparison with those of benzene, the SCF–MO–CI method with a Pariser–Parr–Pople approximation was applied.

The charge distributions and the π-bond orders for I and II were obtained from their ground state SCF–MO's. The difference between the electronic states of I and II is discussed.

Thiopyrylium fluoroborate [Ia], perchlorate [Ib] and iodide [Ic] were prepared according to Degani *et al.*[5] and purified by recrystallization from MeCN–Et_2O; pyrylium perchlorate (II) was similarly prepared.[5]

The UV spectra of I and II were recorded on a Hitachi EPS-3T spectrophotometer in MeCN between 210 and 360 mμ. The observed spectra were analyzed by assuming that the absorption bands are approximated by Gaussian curves, thus two peaks were obtained for I and II, respectively. Cation I gave another absorption maximum in the vacuum UV (λ_{max} = 195 mμ), measured in water under N_2. No such absorption maximum was observed for the pyrylium cation at wavelengths higher than 190 mμ. All observed absorption bands and oscillator strengths (calculated by the usual method) are shown in Table 1.

TABLE 1. UV SPECTRA OF THIOPYRYLIUM (I) AND PYRYLIUM (II) IONS

I		II	
λ_{max} (mμ)	f	λ_{max} (mμ)	f
285	0·019	270	0·118
246	0·038	219	—
195	—		

Calculations. These were carried out using the general basic approximations developed by Pariser, Parr and Pople[6]: (i) neglect of zero differential overlaps, (ii) I–A approximation for one center Coulomb integrals, (iii) neglect of non-nearest neighbour core resonance integrals. Under these simplifications, the best ground state molecular orbitals were obtained by the self-consistent field method described by Pople.[7]

For a system with an even number of electrons, the molecular orbital (ψ_i) is expressed as a linear combination of atomic orbitals (χ_p),

$$\psi_i = \sum_p C_{ip}\chi_p, \tag{1}$$

where the coefficients are the solutions of the Roothaan equation,

$$\sum_q F_{pq}C_{iq} = \varepsilon_i C_{ip}, \tag{2}$$

The F_{pq}'s are the matrix elements of the self-consistent field Hamiltonean and are given by

$$F_{pp} = \alpha_p + \tfrac{1}{2}P_{pp}(pp|pp) + \sum_{r \neq p} P_{rr}(pp|rr). \tag{3}$$

$$F_{pq} = \beta_{pq} - \tfrac{1}{2}P_{pq}(pp|qq), \tag{4}$$

$$P_{pq} = 2\sum_i^{occ} C_{ip}C_{iq}, \tag{5}$$

where α and β are Coulomb and resonance integrals, respectively, and $(pp|qq)$ is an atomic integral.

$$(pp|qq) = \iint \chi_p^*(1)\chi_p(1)\frac{1}{r_{12}}\chi_q^*(2)\chi_q(2)\,dv_1\,dv_2. \tag{6}$$

The energies ε_i corresponding to the molecular orbital ψ_i are the solutions of the secular equation,

$$\mathrm{Det}|F_{pq} - \varepsilon_i\delta_{pq}| = 0. \tag{7}$$

For the electronic transitions, four kinds of low-lying singlet-singlet one electron excitations were considered and the configuration interaction among these excited states carried out. Let $V(i\text{–}j)$ be the determinantal wave function in which one electron is excited from an occupied molecular orbital ψ_i to a vacant molecular orbital ψ_j with spin antiparallel, then the excitation energy can be written using SCF–MO energy,

$$\Delta E(i - j) = \varepsilon_j - \varepsilon_i - J_{ij} + 2K_{ij}. \tag{8}$$

where J_{ij} and K_{ij} are molecular Coulomb integrals and molecular exchange integrals, respectively.

$$J_{ij} = \iint \psi_i^*(1)\psi_i(1)\frac{1}{r_{12}}\psi_j^*(2)\psi_j(2)\,\mathrm{d}v(1)\,\mathrm{d}v(2) \tag{9}$$

$$K_{ij} = \iint \psi_i^*(1)\psi_j(1)\frac{1}{r_{12}}\psi_i^*(2)\psi_j(2)\,\mathrm{d}v(1)\,\mathrm{d}v(2) \tag{10}$$

The excited state of the molecule is expressed as a linear combination of singly excited state configurations after the configuration interaction.

$$\Psi_{exc} = \sum_{i,k} C_{ik}\, V\,(i\text{–}k) \tag{11}$$

The coefficients C_{ik} and the singlet-singlet excitation energies are obtained by diagonalizing configuration interaction matrices with the element given by

$$[V(i\text{–}j)|H|V(k\text{–}l)] = 2[jl|ki] - [ji|kj] \tag{12}$$

where

$$[ij|Kl] = \iint \psi_i^*(1)\psi_j(1)\frac{1}{r_{12}}\psi_k^*(2)\psi_1(2)\,\mathrm{d}v_1\,\mathrm{d}v_2. \tag{13}$$

The entire procedure was programmed and run on an HITAC 5020 computer.

Structural models for I and II are shown in Fig· 1, in which I and II are reasonably assumed to have C_{2v} symmetry and the interatomic distances are taken as follows;

$\overline{C_2C_3} = \overline{C_3C_4} = \overline{C_4C_5} = \overline{C_5C_6} = 1{\cdot}39\text{Å}$

$\overline{C\text{—}S} = 1{\cdot}70\text{Å}$

$\overline{C\text{—}O} = 1{\cdot}41\text{Å}$

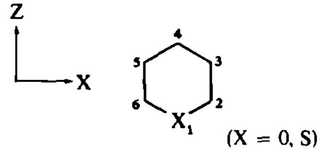

FIG 1

The sulphur atom in the thiopyrylium cation has not only 3s and 3p but also 3d orbitals in the valence state. However, in the electron deficient species such as the thiopyrylium cation, little participation of 3d-orbital is expected. In this calculation the 3d-orbitals of the sulphur atom were not taken into account. Effect of the counter anion was also neglected.

According to the Pariser approximation, one centre Coulomb integrals were derived from the valence state ionization potentials (I) and the electron affinities (A)

$$(pp|pp) = I_p - A_p. \tag{14}$$

Values for I_p and A_p can be found in the compiled table by Hinze and Jaffe.[8] In the case of carbon atoms, the atomic orbitals mix to give sp^2 hybridization, but because of poor knowledge of the valence states for sulphur and oxygen atoms the values given in Table 2 were taken for their atomic hybridization.[8b]

TABLE 2. VALENCE STATE IONIZATION POTENTIALS AND ELECTRON AFFINITIES

Atom	State	Orbital	I	A
C	*trtrtr* π	π	11·16 eV	0·03 eV
S^+	te^2tete π	π	23·74	11·65
O^+	tr^2trtr π	π	34·08	15·30

The two centre repulsion integrals were calculated by a parabolic equation of type,

$$(pp|qq) = \tfrac{1}{2}\{(I_p - A_p) + (I_q - A_q)\} + bR + aR^2. \tag{15}$$

where R is an interatomic distance and the coefficients, a and b, were determined by utilizing theoretical multipole interaction of Slater atomic orbitals at 3·5 and 5·0Å. In the parallel type of p-orbital, multipole interaction is of the form,

$$(pp|qq) = e^2\{1/R - (Q_p + Q_q)/4R^3 + (3Q_pQ_q/16R^5), \tag{16}$$

where Q is the scalar quadrapole for the p-orbital and is expressed by

$$Q = 24\ a_0/Z^2 \text{ for 2p-orbital,}$$

$$Q = 144\ a_0/Z^2 \text{ for 3p-orbital.} \tag{17}$$

(a_0 is the Bohr Radius)

Effective nuclear charges (Z) of sulphur 3p and oxygen 2p were set to be 5·80 and 4·90, respectively, according to the Slater rule. Coefficients of the parabolic equation are summarized in Table 3.

TABLE 3. THE COEFFICIENTS (a AND b) FOR TWO-CENTRE REPULSION INTEGRALS

	z	a	b
C–C	3·25	0·253	−2·920
C–S	5·80	0·294	−3·224
C–O	4·90	0·522	−4·930

Atomic core integrals were evaluated by the Goepert-Mayer and Sklar[9] method neglecting the penetration integrals,

$$\alpha_p = W_p - \sum_{p \neq q} (pp|qq) \tag{18}$$

where W_p is the valence state orbital energy and can be expressed by

$$W_p = -I_p. \tag{19}$$

Ionization potentials were quoted from the Table by Hinze and Jaffe.[8a]

$$W_C(trtrtr\ \pi) = -11{\cdot}16 \text{ eV}$$

$$W_S(tr^2tr^2tr\ \pi) = -12{\cdot}70 \text{ eV}$$

$$W_O(tr^2tr^2tr\ \pi) = -17{\cdot}70 \text{ eV}$$

In the evaluation of α, the neglect of penetration integrals for the carbon atom seems to be applicable, but might not be negligible for the positively charged hetero-atom, because in the onium structure the penetration integral between the electron of a carbon 2p-orbital and that of a hetero-atom 2p-orbital is roughly estimated to be summation of the repulsion between the 2p-electron in the carbon and three valence electrons in the hetero-atom, and the attraction between an electron in the carbon and in the hetero-atom core which is charged by +4e. For the nearest carbon-hetero-atom, this value might be *ca.* 10 eV. In spite of this state of affairs we neglected the penetration integrals, because the considered cations were not purely onium in structure but a resonance hybrid between an onium structure and a carbonium ion structure, and for W_p we formally set it to be a negative sign of the first ionization potential of the appropriate valence state.

Semiempirical values were given for the core resonance integrals of the adjacent carbon–carbon bonds, and the values estimated by Mulliken's approximation[10] for those of the bonds containing the hetero-atom,

$$\beta_{C-X} = S_{C-X}K/2(W_C + W_X). \tag{20}$$

where S_{C-X} are overlap integrals and variable K's were chosen to be 0·86 and 1·00 for C—S and C—O bonds, respectively. Values for resonance integrals are shown in Table 4.

Table 4. Core resonance integral

Bond	β_{C-X} (eV)
C—C	−2·39
C—S	−1·75
C—O	−2·27

RESULTS AND DISCUSSION

The self-consistent orbitals and the energies for thiopyrylium and pyrylium cations are summarized in Tables 5 and 6, respectively.

Table 5. SCF-MO's and energies for thiopyrylium ion (I)

SCF MO	Symmetry	χ_1	$\chi_2 + \chi_6$	$\chi_3 + \chi_5$	χ_4	Energy (eV)
ψ_1	b_2	0·3249	0·3547	0·4505	0·4867	−14·401
ψ_2	a_2	0	−0·4891	−0·5107	0	−11·464
ψ_3	b_2	0·6837	0·3081	−0·2224	−0·4937	−10·978
ψ_4	b_2	0·5936	−0·3800	−0·2001	0·5280	−1·006
ψ_5	a_2	0	−0·5107	0·4891	0	0·059
ψ_6	b_2	−0·2732	0·3672	−0·4556	0·4904	2·779

Theoretical transition energies, oscillator strengths and wave functions were obtained after the configuration interaction. These results are presented in Tables 7 and 8.

TABLE 6. SCF-MO'S AND ENERGIES FOR PYRYLIUM ION (II)

SCF MO	Symmetry	χ_1	$\chi_2 + \chi_6$	$\chi_3 + \chi_5$	χ_4	Energy (eV)
ψ_1	b_2	0·6099	0·4169	0·3168	0·2821	−15·188
ψ_2	b_2	−0·5198	−0·1290	0·3929	0·6277	−12·164
ψ_3	a_2	0	−0·4718	−0·5268	0	−10·983
ψ_4	b_2	0·4738	−0·3374	−0·2875	0·6185	0·090
ψ_5	a_2	0	−0·5267	0·4718	0	0·515
ψ_6	b_2	−0·3651	0·4424	−0·4033	0·3874	3·622

TABLE 7. CALCULATED AND OBSERVED RESULTS FOR I

Wave function	State	Transition energy (eV)			
		Calc.	f	Obs.	f
0·782 V(2–4) + 0·624 V(3–5)	B_1	4·47	0·016	4·35	0·019
0·801 V(3–4) − 0·599 V(2–5)	A_1	4·94	0·091	5·06	0·038
−0·624 V(2–4) + 0·782 V(3–5)	B_1	6·55	1·000	6·35	—
0·599 V(3–4) + 0·801 V(2–5)	A_1	7·06	1·523		

TABLE 8. CALCULATED AND OBSERVED RESULTS FOR II

Wave function	State	Transition energies (eV)			
		Calc.	f	Obs.	f
0·859 V(3–4) − 0·512 V(2–5)	B_1	4·81	0·093	4·59	0·118
0·607 V(2–4) + 0·795 V(3–5)	A_1	5·46	0·029	5·69	
0·512 V(3–4) + 0·859 V(2–5)	B_1	7·31	1·053		
0·795 V(2–4) − 0·607 V(3–5)	A_1	7·63	1·104		

I and II were reasonably assumed to have C_{2v} symmetry in this calculation, and the calculated transition energies and oscillator strengths were in good agreement with those observed. All the π-π^* transitions of I and II are shown to be allowed due to their C_{2v} symmetry, which was also supported by the experimental molecular extinction coefficients of the absorption bands.

The electronic transition is compared with that of benzene, which is isoelectronic with I and II. The transition to the lowest energy level is the state A_1–B_1 of which direction of transition moment is the x-axis, and this corresponds to the A_{1g}–B_{2u} transition of benzene. The transition to the second lowest energy levels of the state A_1–A_1 of which polarization is in the Z-direction corresponds to the A_{1g}–B_{1u} of benzene. The A_{1g}–E_{1u} transition of benzene is split to give A_1–A_1 and A_1–B_1 transitions of both the cations. These cation transitions and the removal of degeneracy are permitted due to a decrease of the symmetry elements from D_{6h} to C_{2v}. The difference in the electronic state between I and II is found in the character of the occupied SCF molecular orbitals. The symmetries of the MO's ψ_2 and ψ_3 for I are a_2 and b_2, but

b_2 and a_2 for II. The inversion of the symmetry originated from the lowering of MO ψ_2 in II. The occupied MO's belonging to a_2 (ψ_2 in I, and ψ_3 in II) are not affected by the hetero-atoms, since they have no components of the atomic p-orbitaals on the hetero-atoms, the sulphur and the oxygen. On the other hand, MO ψ_3 in I and ψ_2 in II have the component of the p-orbitals on the hetero-atoms, and the lower p-orbital energy of the oxygen than for the sulphur results in lowering the energy of the ψ_2 in II. For the same reason, the energy of ψ_1 in II is lower than that of ψ_1 in I. The transition energies for π-π^* excitation thus far discussed were obtained by the configuration interaction among four low-lying electronic configurations. The small change in transition energies was caused by the configuration interaction among all the one-electron excitations (Table 9). The transition energies above 7·5 eV are not given in Table 10. The configuration interaction took place mainly between the state $V(2\text{–}4)$ and $V(3\text{–}5)$ for B_1 state of I and for A_1 state of II, and between the state $V(3\text{–}4)$ and $V(2\text{–}5)$ for A_1 state of I and for B_1 state of II as shown in Fig. 2. Therefore, the limited configuration interaction is sufficient for the calculation of the transition energies for I and II.

TABLE 9. TRANSITION ENERGIES AND OSCILLATOR STRENGTHS AFTER CONFIGURATION INTERACTION AMONG ALL THE SINGLY EXCITED STATES

	I eV (f)	eV (f)
B_1	4·50 (0·016)	4·81 (0·078)
A_1	4·83 (0·084)	5·27 (0·033)
B_1	6·53 (0·940)	7·29 (1·096)
A_1	7·04 (1·498)	7·47 (0·881)

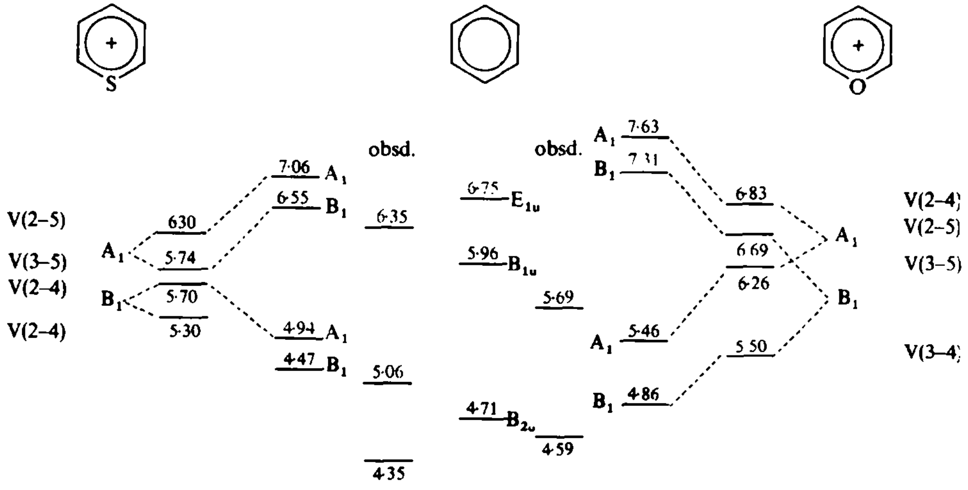

FIG. 2. Diagram of configuration interaction for I and II.

From the SCF MO calculated for I and II, the electronic distributions and π-bond orders are obtained (Fig. 3).

FIG 3. π-Electron distributions and π-bond orders.

It is obvious from Fig. 3 that the positive charge is not localized at the hetero-atom, but delocalization to C_2, C_6 and C_4 takes place. This means that I and II are the resonance hybrids of Kekulé structures (onium structures) and carbonium ion structures shown in Fig. 4. From the amount of decrease of the positive charge on the hetero-atom, the contributions of the carbonium ion structures to resonance hybrids are found to be 14·6% and 28·4% for I and II, respectively, i.e. carbonium ion character is larger in the latter than in the former. This accords with the fact that II is more reactive to nucleophilic reagents than I. The order of positive charge population in I is C_2, C_6 > C_4 > C_3, C_5, suggesting that nucleophilic attack predominantly occurs at the α-carbon atom, this agrees well with our experimental results on the reactions of I with active methylene compounds in the presence of bases[1] and amines.[11]

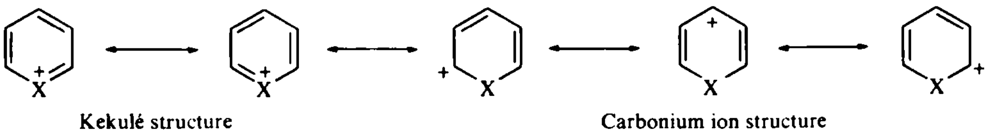

FIG 4. Resonance structures for I and II.

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