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THEORETICAL STUDY OF ISO-CONDENSED THIENOPYRROLES

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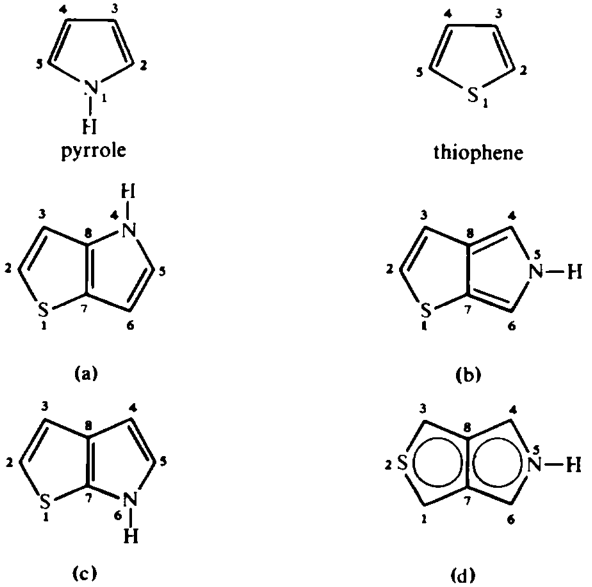
Abstract—SCF MO calculations are reported for isomeric thienopyrroles in the ground and excited states. The main result is that the 1.4- and 1.6-isomers are more stable than the 1.5-isomer. whilst the 2.5-isomer has a triplet state of lower energy than the ground state.

DURING the last few years we have been interested in the properties and stabilities of positional isomers.[1,2] The iso-condensed thiophenes[3,4] and thienopyrroles are good examples of such isomers and in the present paper we report our theoretical studies of ground and excited states of thienopyrroles. There are several reasons why these compounds are important. Firstly, they are interesting from a theoretical point of view because they consist of five-membered rings with well known properties. Secondly, their synthesis is a challenge to organic chemists and thirdly, they occur as constituents of physiologically active compounds.

Apparently, the properties of these molecules largely reflect the presence of π-electrons, therefore, we performed π-molecular orbital calculations for pyrrole.



pyrrole

thiophene

(a)

(b)

(c)

(d)

FIG 1. Atomic skeletal structure and numbering of atoms for pyrrole, thiophene, and the iso-condensed thienopyrroles: 1,4-thienopyrrole (a), 1,5-thienopyrrole (b), 1,6-thienopyrrole (c), and 2,5-thienopyrrole (d) thiophene, 1,4-thienopyrrole (a), 1,5-thienopyrrole (b), 1,6-thienopyrrole (c), and 2,5-thienopyrrole (d). These molecules are presented in Fig 1. We studied these molecules in the ground state and excited states using current molecular orbital methods. In other words, since at present there is no MO method within the π-approximation which can equally well treat molecules in the ground and excited states, we have chosen two variants of the SCF π-MO theory. One belongs to Dewar[5–8] and it is very reliable for calculating the properties of conjugated molecules in their ground states. The other was originated by Pariser and Parr[9] and it is equally good for predicting energies of the excited states of conjugated molecules. The formalism of both variants is well known and has been presented rather extensively in the recent monographs.[10, 11]

Calculations

Ground state properties (heats of atomization, ionization potentials) of pyrrole, thiophene and thienopyrroles were calculated by using a procedure described by Dewar and Harget.[12, 13] It differs from the earlier Dewar procedure[5–8] only in the determination of the key parameter of the theory: one-electron core resonance integral β^c_{ij}. Earlier it was determined by a thermocycle procedure,[14, 15] but in this most recent work[11, 12] it was estimated from a simpler Mulliken approximation

$$\beta^c_{ij} = K_{ij}S_{ij}$$

where K_{ij} is bond constant and S_{ij} is the overlap integral evaluated using Slater–Zener orbitals. Bond constants (K_{ij}) for bonds appearing in molecules studied here are given in Table 1.

TABLE 1. BOND CONSTANTS

Bond (i, j)	Bond constant (K_{ij})
C—C	6·927
C—N	6·9612
C—S	15·7265

Singlet–singlet transition energies are calculated by the standard Pariser–Parr procedure,[9, 10] using parameter set, which has proven to be reliable for various spectroscopic properties of S- or N-heterocycles.[16, 17] We list in Table 2 values of spectroscopic β^c_{ij}'s used in the present work.

We also report the first singlet–triplet transition energies for thienopyrroles. These were calculated by using a recent extension[18, 19] of the "half-electron" method[20] which has proved quite promising in predicting energies and geometries of the triplet states. In essence, this method can be described as follows. In our closed-shell computer program the occupation numbers of the MO's are supplied as data. When calculations are carried out for triplets the occupation numbers of the two singly occupied MO's (m, n) are set equal to unity. But, our program in effect calculates the energy for a system in which each unpaired electron is replaced by two "half-electrons" of opposite spin. The resulting energy (E) is then related to the Roothaan value[21] (E_T) by

$$E_T = E - \tfrac{1}{4}(J_{mm} + J_{nn}) - \tfrac{1}{2}K_{mn}$$

The terms $\frac{1}{4} J_{mm}$ and $\frac{1}{4} J_{nn}$ are corrections for the repulsion between "half-electrons", while the term $\frac{1}{2} K_{mn}$ is a correction to the exchange energy.

In present calculations sulphur is considered without *d*-orbital participation. Reasons for this are several: the experience of various authors in their studies,[22–24] our recent work on sulphur compounds,[3] and finally some recent *ab initio* SCF MO calculations on very small sulphur molecules (H_2S)[25] or ions (α-sulfinyl carbanion)[26] have shown negligible *d*-orbital participation. It is true that contrary opinions have been expressed on the basis of semi-empirical calculations;[27] here, however, the role of 3*d* AO's depends on the choice of parameters.

RESULTS AND DISCUSSIONS

Thienopyrroles consist of pyrrole and thiophene moieties. Therefore, we performed firstly calculations for pyrrole and thiophene. Energy values of pyrrole and thiophene are reported in Table 3. Calculated bond lengths and charge densities are given in Fig 2. Calculated and experimental values for pyrrole and thiophene agree fairly well. Values of aromatic stabilization (A_s) show that these molecules can be regarded as

TABLE 2. ONE-ELECTRON CORE RESONANCE INTEGRALS

$\beta_{CC} = -2{\cdot}395$ eV
$\beta_{CS} = -2{\cdot}000$ eV
$\beta_{CN} = -2{\cdot}490$ eV

TABLE 3. CALCULATED ENERGY VALUES FOR PYRROLE AND THIOPHENE

Molecule	$-\Delta H_a$(eV)	A_s(kcal/mole)	$(IP)_v$[a](eV)	$(IP)_a$[b](eV)	Singlet–singlet transition (eV)
Pyrrole	44·40(44·51)[c]	5·3	9·10(8·97)[d]	8·90(8·22)[e]	5·84; 6·56; 7·64; 7·88 (5·88–6·05; 6·77; 7·21)[f]
Thiophene	40·32(40·32)[g]	6·5	8·93(9·00)[h]	8·68(8·86)[i]	5·35; 6·06; 7·22; 7·35 (5·15; 5·90; 6·80)[j] (5·36)[k]

[a] From Koopmans theorem: T. A. Koopmans, *Physica* 1, 104 (1933)

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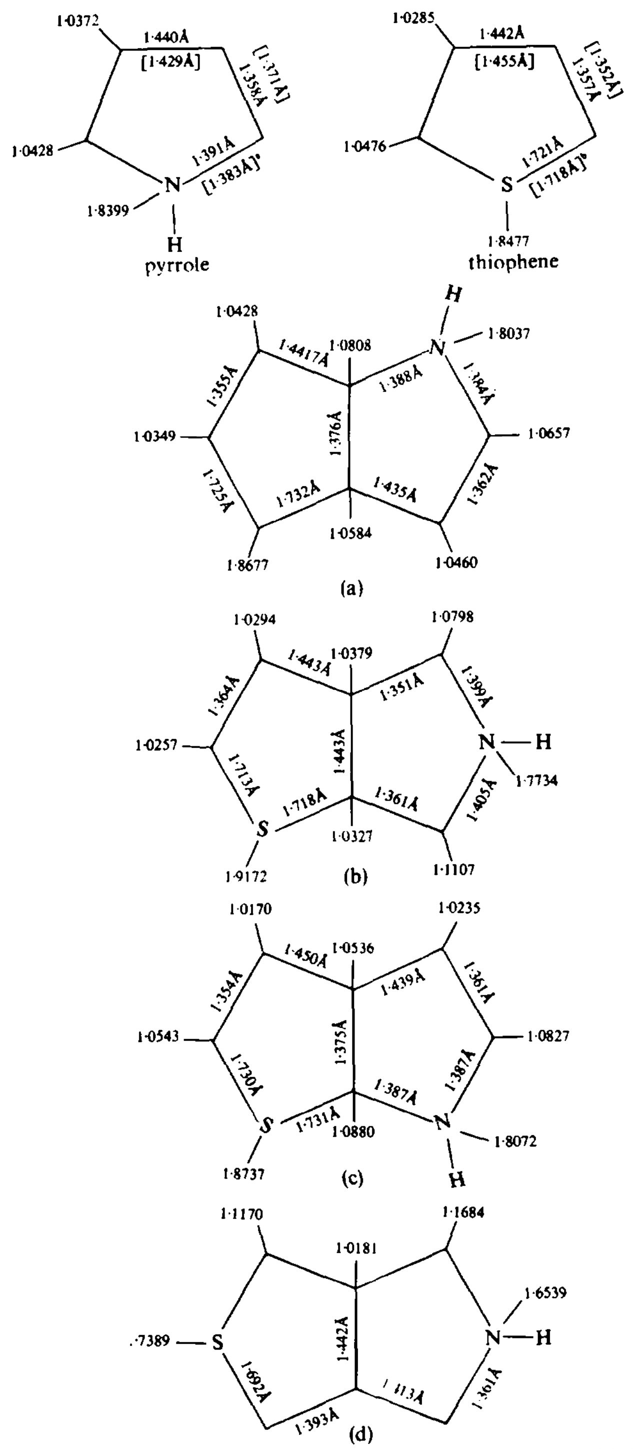

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Fig 2. SCF molecular orbital diagrams for pyrrole, thiophene, and the iso-condensed thienopyrroles in the ground state aromatic, both are inert in Diels–Alder reactions. Only in the last decade it was shown that pyrrole derivatives also possess, in principle, the capacity for taking part in Diels–Alder reactions.[28, 29] It has so far been impossible to react thiophene with dienophiles; in fact with hexachlorocyclopentadiene the thiophene acts as dienophile with the formation of a bisadduct.[30]

Ground state energies of thienopyrroles are reported in Table 4. Calculated bound lengths and charge densities are given in Fig 2. We report in Table 4 total σ-energies, total π-energies, heats of atomization, relative stabilities and vertical ionization potentials of all four theoretically possible thienopyrroles. Experimental data for these molecules are virtually non-existant. 1,4-Thienopyrrole[31, 32] and its N-benzyl derivative[33] have been prepared. N-Ethyl-1,5-thienopyrrole has been recently reported,[34] and similarly, N-benzyl-1,6-thienopyrrole.[35] 2,5-Thienopyrrole has not yet been prepared. This corrolates nicely with our values for relative stabilities of these molecules. Values for relative stabilities are estimated by comparing aromatic stabilization values[11, 36] of pyrrole and thiophene with corresponding values of thienopyrroles. Apparently, the annelation of pyrrole and thiophene at the 2,3 (short) bonds in either *cis* or *trans* position (to heteroatoms) yields a more stable molecule than annelation at the 3,4 (long) bonds. Examples of the first case are 1,4- and 1,6-thienopyrrole, and the second, 2,5-thienopyrrole. When annelation occurs at the 2,3 (short) bond of thiophene and the 3,4 (long) bond of pyrrole, stability is rather low. Thus, 1,5-thienopyrrole is predicted to be less stable than either the 1,4- or 1,6-isomer, this is supported by calculated vertical ionization potentials. Apparently, there is corrolation between the stability and ionization potentials of the positional isomers. This was also observed earlier in our studies on isomeric thiophthenes,[3] isomeric benzopyrroles[1] and benzofurans.[1] No experimental data are as yet available to test this prediction.

TABLE 4. GROUND STATE ENERGY VALUES OF THIENOPYRROLES

Molecule	$-E_\sigma$(eV)	$-E_\pi$(eV)	$-\Delta H_a$(eV)	S(kcal/mole)	$(IP)_v$*(eV)
1,4-Thienopyrrole (a)	31·1025	9·1448	62·0391	12·3	8·40
1,5-Thienopyrrole (b)	31·0500	8·7896	61·6314	0·5	8·04
1,6-Thienopyrrole (c)	31·0979	9·1099	61·9996	11·4	8·61
2,5-Thienopyrrole (d)	31·3209	7·3110	60·4237	−24·9†	6·77

* From Koopmans theorem.

† Relative to the classical structures used for (a), (b) and (c).

The molecules were also studied in the triplet state; results are listed in Table 5. These calculations are performed by the extension of the "half-electron" method to triplet states. An interesting result is obtained in the case of 2,5-thienopyrrole. The triplet state of 2,5-thienopyrrole is the most stable state for this molecule. A similar result was obtained earlier[3] for isomeric thiophthenes, where 2,5-thiophthene was predicted to have a triplet state as the lowest state. Apparently there is some experimental evidence for this theoretical prediction; Cava and Pollack[37] have found that 2,5-thiophthene exist only as a transient and very reactive intermediate.

We report in Fig 3 the geometry of 2,5-thienopyrrole in its triplet state, which differs from its geometry in the ground state, but is similar to that of the other isomers in the ground state.

Table 5. Triplet energies of thienopyrroles

Molecule	Singlet–triplet transition energy (eV)
1,4-Thienopyrrole (a)	1·34
1,5-Thienopyrrole (b)	1·84
1,6-Thienopyrrole (c)	1·93
2,5-Thienopyrrole (d)	−0·12

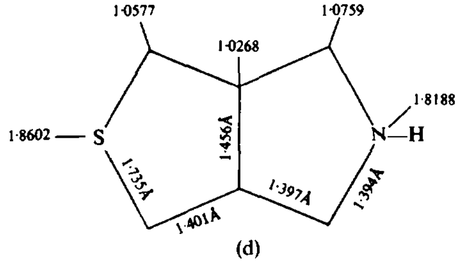

Fig 3. Triplet state geometry of 2,5-thienopyrrole

Finally, we have calculated lower singlet transition energies (Δ*E*) and transition moments of 1,4-, 1,5-, and 1,6-thienopyrrole. These results are reported in Table 6. Experimental UV spectra of 1,4-thienopyrrole,[32] N-ethyl-1,5-thienopyrrole,[34] and N-benzyl-1,6-thienopyrrole[35] are given in Table 7. Agreement between calculated and experimental values is fairly good; the average deviation from the experimental values for the first transition is only 0·19 eV and for the second transition is even better (0·08 eV). Calculated transition moments are in agreement with the intensities of the first two bands in the UV spectra of 1,4- and 1,6-thienopyrrole. In the case of the N-ethyl-1,5-thienopyrrole the experimental intensity of the second UV band is twice

Table 6. Calculated transition energies (ΔE) and transition moments (M^2) of thienopyrroles

Molecule	ΔE (eV)	$M^2 = M_x^2 + M_y^2$
1,4-Thienopyrrole	5·70	0·18
	5·27	0·30
	4·47	1·06
1,5-Thienopyrrole	5·81	0·71
	5·17	0·40
	4·48	0·97
1,6-Thienopyrrole	5·89	0·65
	5·10	0·44
	4·50	1·03

TABLE 7. EXPERIMENTAL UV SPECTRA OF THIENOPYRROLES

Molecule	λ_{max} (eV)	$\varepsilon \times 10^3$
1,4-Thienopyrrole[a]	5·32	4·9
	4·77	11·8
1,5-Thienopyrrole, N-ethyl[b]	5·25	12·1
	4·35	5·6
1,6-Thienopyrrole, N-benzyl[c]	5·22	5·6
	4·64	12·0

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[c] R. K. Olsen and H. R. Snyder, *J. Org. Chem.* **30**, 184 (1960)

as intense as the first, while the theoretical transition moments predict the reverse. Since this is a substituted molecule the result is not dissapointing because it is known that substitution sometimes alters the position and intensity of the π–π^* bands in a UV spectra.[38]

CONCLUSIONS

Annelation of pyrrole and thiophene leads to various isomeric thienopyrroles, which differ in their properties and stabilities. This apparently depends where annelation occurs. Annelation at short (2,3) bonds in either *cis* or *trans* position produces a more stable molecule than annelation at long (3,4) bonds. The intermediate case is when annelation occurs at the short (2,3) bond of thiophene and the long (3,4) bond of pyrrole. The order of relative stability (based on calculated values: heats of atomization, relative stabilities, and ionization potentials) of isomeric thienopyrroles is then obtained as: 1,4-thienopyrrole $\sim$ 1,6-thienopyrrole $>$ 1,5-thienopyrrole $\gg$ 2,5-thienopyrrole. We found that 2,5-thienopyrrole should have a triplet state as its lowest state.

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