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Molecular Orbital Calculations for the Three Isomeric Thiophthenes

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Molecular orbital calculations in the framework of the Pariser-Parr and Pople theory is applied to some of the ground state properties and to the UV spectra od 1,4-thiophthene, 1,5-thiophthene, and 1,6-thiophthene. Good agreement was obtained between the observed and calculated values for the first $\pi - \pi^*$ electron transitions in the three molecules studied. An assignement of the spectra is proposed.

In this paper we present results of molecular orbital calculations in the framework of the Pariser-Parr-Pople method[1,2] for three sulphur containing heterocyclics, namely 1,4-thiophthene, 1,5-thiophthene, and 1,6-thiophthene, shown in the Fig. These compounds form a series of three isomeric thiophthenes, referred to as thieno (3,2-*b*) thiophene, thieno (3,4-*b*) thiophene, and thieno (2,3-*b*) thiophene. The syntheses of these three thiophthenes have been reported by several research workers[3-5].

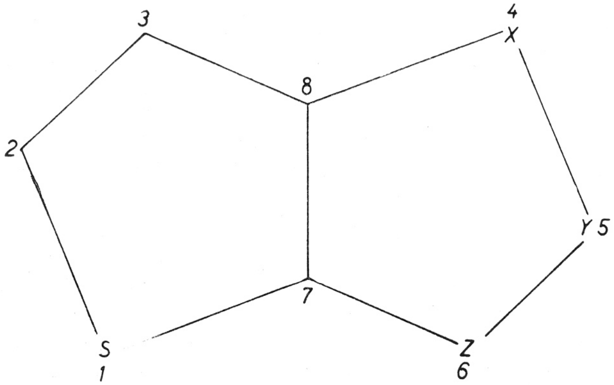

Fig. Atomic skeletal structure and numbering of atoms for the three investigated thiopthenes. 1. X = S, Y = Z = C (1,4-thiophthene). 2. Y = S, X = Z = C (1,5-thiophthene). 3. Z = S, X = Y = C (1,6-thiophthene).

Calculations and Results

Several authors[6-9] have attempted, generally with limited success, to extend the *Zero Differential Overlap* (ZDO) type approximations, typified by the

Pariser-Parr-Pople method*, to molecules in which sulphur contributes electrons to the π system. No explicit account is generally taken of the d orbitals, any such contribution being allowed for in the parameters used.

The problem reduces to the estimation of various parameters involving sulphur, those involving only carbon are regarded as well established.

We have used a parameter set which leads to good agreement with experiment for certain properties.

TABLE I

One electron core integrals. The nomenclature is that of Peacock[11].

$$\beta_{CC} = -2.395 \text{ eV}$$
$$\beta_{CS} = -2.000 \text{ eV}$$
$$\delta W_S = -8.840 \text{ eV}$$

The one electron core integrals used in the calculation are given in Table I. The two electron Coulomb integrals $\gamma_{i,j}$ were evaluated using a relationship of the type[12]

$$\gamma_{i,j} = \frac{14.397}{r_{i,j} + a_{i,j}}$$

where

$$a_{i,j} = \begin{cases} 1.294 & i = j = C \\ 1.376 & i = C;\ j = S \\ 1.471 & i = j = S \end{cases}$$

All C—C bonds were taken to be equal to 1.40 Å, and all C—S bonds to 1.74 Å for purposes of calculation.

The one-body density matrix was made self consistent directly, using the *Steepest Descents* minimisation procedure[13]. Sulphur contributes 2 electrons, carbon 1, to the π systems, and from Table II in which we present the upper triangle and leading diagonal of the self consistent *charge and bond order* matrices, it is seen that sulphur acquires a large positive charge, in every case.

The relationship between bond order $P_{i,j}$ and bond length $r_{i,j}$ is

$$r_{i,j} = A + BP_{i,j}{}^{14} \tag{1}$$

where A, B are different for different pairs i, j, but constant for a series of similar pairs. The bond lengths of 1,4-thiophthene have been measured accurately[15], and are presented in Table III, together with the calculated bond lenghts, computed using relation (1) above. For C—C bonds, $A = 1.517$ and $B = -0.180$ were used[16], giving good agreement with experimental values whilst for C—S bonds we propose the use of $A = 1.8896$ and $B = -0.4106$, which reproduce the observed bond lengths reasonably well. We also predict the bond lengths of 1,5-thiophthene and 1,6-thiophthene, and these are also, recorded in Table III. These A and B parameters which have been used for the C—S bonds have also been checked on thiophene and 1,4-dithiathiene for which we have used results[6] obtained by the P-method, and have predicted bond lengths very close to the experimentally observed[17,18]**.

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* Recently[10] referred to as the P-method.

** Research on establishing the bond length/bond-order curve for a large class of molecules containing S(II)—C(sp^2) bonds is in progress.

TABLE II

The upper triangle and leading diagonals of the charge and bond order *matrices. Numbering as in the Fig.*

(*a*) 1,4-thiophthene

1	2	3	4	5	6	7	8
1.7596	0.4066	—0.2543	0.1045	—0.0888	—0.0954	0.3612	—0.1861
	1.0627	0.8210	—0.0893	0.1957	—0.0052	—0.3205	—0.0880
		1.0904	—0.0951	—0.0054	0.0128	—0.0427	0.4921
			1.7596	0.4066	—0.2543	—0.1861	0.3612
				1.0627	0.8210	—0.0880	—0.3205
					1.0904	0.4921	—0.0427
						1.0874	0.6871
							1.0874

(*b*) 1,5-thiophthene

1	2	3	4	5	6	7	8
1.8064	0.3558	—0.2650	0.1048	0.0114	—0.1868	0.3054	—0.1180
	1.0466	0.8672	—0.2482	0.1258	—0.0148	—0.1940	—0.0632
		1.0798	—0.0372	—0.0412	0.0570	—0.0358	0.4048
			1.0918	0.4532	—0.4382	—0.0584	0.7188
				1.7058	0.4284	—0.2170	—0.2196
					1.1280	0.7530	—0.0498
						1.0688	0.4954
							1.0728

(*c*) 1,6-thiophthene

1	2	3	4	5	6	7	8
1.7644	0.3854	—0.2458	0.0430	0.0844	—0.1444	0.3804	—0.1788
	1.0796	0.8388	—0.1148	0.0730	0.0844	—0.3278	—0.0926
		1.0678	—0.0168	—0.1148	0.0430	—0.0510	0.4620
			1.0678	0.8388	—0.2458	—0.0510	0.4620
				1.0796	0.3854	—0.3276	—0.0926
					1.7644	0.3806	—0.1788
						1.0840	0.6954
							1.0924

TABLE III

Calculated and observed bond lengths, all in Angströms.

Bond	1,4-thiophthene		1,5-thiophthene	1,6-thiophthene
	Measured	Calculated	Calculated	Calculated
1,2	1.72	1.723	1.744	1.731
2,3	1.36	1.369	1.361	1.366
3,8	1.41	1.428	1.444	1.434
8,7	1.36	1.393	1.428	1.392
1,7	1.74	1.741	1.764	1.733
4,8			1.388	
4,5			1.704	
5,6			1.714	
6,7			1.381	

All singly excited states were used for the configuration interaction calculations. The experimental uv. spectra (λ_{max}, ε) of the three isomeric thiophthenes which have been reported elsewhere[6,19] are in Table IV.

TABLE IV

Experimental UV spectra of 1,4-thiophthene, 1,5-thiophthene, and 1,6-thiophthene.

	λ_{max} (eV)	$\varepsilon \times 10^3$
1,4-thiophthene	4.767 4.615 4.449 4.149	12.3 12.0 10.9 0.2
1,5-thiophthene	5.322 4.848 4.690 4.519 4.192	16.9 3.4 3.7 3.7 5.4
1,6-thiophthene	5.526 4.615 4.449	24.0 2.0 1.0

The wave functions for 1,4-thiophthene transform as representation of the group C_{2h}: the π orbitals are b_g if there is a change in sign on reflection in the yz plane, a_u otherwise. Clearly, only transitions between A_u and B_g states are formally allowed. We attribute the calculated value of 4.9 eV to the first π—π^* transition (B_u). There is also a very weak band at 4.1 eV in the uv. spectrum, which has low intensity and may be attributed to the $n - \pi^*$ transition.

All $\pi - \pi^*$ electronic transitions in 1,5-thiophthene are formally allowed, since the wave functions of this molecule must transform as representation of the group C_1. The band observed at about 5.3 eV corresponds to the first strong $\pi - \pi^*$ transition. The three bands at 4.8, 4.7 and 4.5 eV, respectively, are probably the vibronic structure of the same band, whilst the band observed at about 4.2 eV may also be a π—π^* transition. If this so, then our results for the π—π^* transitions (at 4.6 eV and 5.8 eV) are in good agreement with the experimental values (at 4.2 eV and 5.3 eV). The uv. spectrum of 4-6-dimethyl-1,5-thiophthene reported by Dann and Dimmling[20] is very similar to that of 1,5-thiophthene, except that the bands are red shifted. This red shift is probably due to the mesomeric effect of the methyl groups.

The wave functions for 1,6-thiophthene transform as representation of the group C_{2v}: the π molecular orbitals belong either to a_2 or b_2 irreducible representations. Only transitions between A_2 and B_2 states are symmetry allowed. We have attributed the value of 5.9 eV to the first $\pi - \pi^*$ transition (B_1) in the spectrum. Weak bands at 4.6 and 4.4 eV are probably due to $n - \pi^*$ electronic transitions.

In Table V we present our predicted uv. spectra with transition moments along the x and y axes, for the three investigated isomeric thiophthenes.

The calculations were performed on the ICT *Atlas* computer, at Harwell, England. We are grateful to SRC for making computing facilities available.

TABLE V

Calculated transition energies (eV) and oscillator strengths M$_x$ *and* M$_y$, *for the three molecules studied. Only transitions below 8 eV are recorded. The transitions are classified by symmetry, except for 1,5-thiophthene.*

(*a*) 1,4-thiophthene

Δ E (eV)	M_x	M_y	$M^2=M_x^2+M_y^2$	Symmetry
7.797	0.817	—0.069	0.672	B_u
7.324	—0.040	0.915	0.838	B_u
7.140	0.004	0.004	0.000	A_g
6.782	—0.001	—0.003	0.000	A_g
5.942	0.000	0.004	0.000	A_g
5.293	—0.253	—0.759	0.640	B_u
4.918	1.393	—0.114	1.952	B_u

(*b*) 1,5-thiophthene

Δ E (eV)	M_x	M_y	$M^2=M_x^2+M_y^2$
7.629	—0.292	—0.552	0.390
7.016	0.861	—0.188	0.776
6.801	—0.355	—0.280	0.205
6.208	—0.148	—0.229	0.075
5.750	—1.213	—0.207	1.515
5.081	0.451	—0.028	0.204
4.589	—0.505	0.947	1.153

(*c*) 1,6-thiophthene

Δ E (eV)	M_x	M_y	$M^2=M_x^2+M_y^2$	Symmetry
7.870	—0.262	0.000	0.069	B_1
7.569	0.009	0.000	0.000	A_1
6.846	0.000	0.143	0.020	A_1
6.184	0.000	0.862	0.743	A_1
5.919	—1.579	0.000	2.494	B_1
5.609	0.000	0.393	0.155	A_1
5.135	—0.221	0.000	0.049	B_1

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IZVOD

Račun molekularnih orbitala za tri izomerna tioftena

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Račun molekularnih orbitala u okviru teorije Parisera, Parra i Poplea je primjenjen na izračunavanje nekih svojstava osnovnog stanja i UV spektara, 1,4-tioftena, 1,5-tioftena i 1,6-tioftena. Postignuto je dobro slaganje između eksperimentalnih i računskih dobivenih rezultata za prvi π—π* prijelaz elektrona kod triju ispitivanih molekula. Također je predložena asignacija spektara.

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