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Molecular Orbital Calculations for Some Bithiophenes and Bifurans

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Molecular orbital calculations in the framework of Pariser-Parr-Pople theory are applied to some of the ground state properties and to the UV spectra of 3,3'-bithiophene, 3,3'-bifuran, 2,2'-bithiophene and 2,2'-bifuran. Good agreement has been obtained between the observed and calculated values for the first $\pi-\pi^*$ electronic transition in all the molecules examined.

Recent interest in the chemistry and spectral properties of bithiophene and bifuran ring systems, both experimental¹⁻⁷ and theoretical⁸ prompt us to report some results of MO (molecular orbital) calculations, within the framework of the Pariser-Parr-Pople (PPP)^{9,10} approximations, for 3,3'-bithiophene (I), 3,3'-bifuran (II), 2,2'-bithiophene (III) and 2,2'-bifuran (IV), whose skeletal structures, and numbering of atoms are shown in Fig. 1.

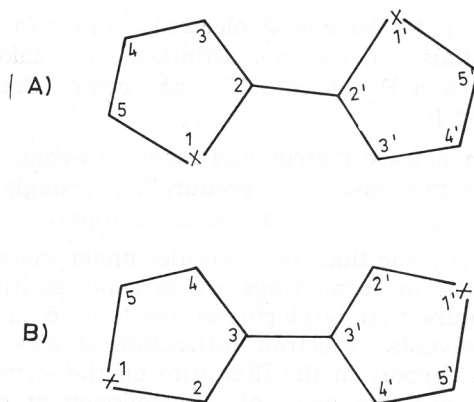


Fig. 1. The skeletal structure and numbering of atoms for the investigated molecules. A) if X=S, 2,2'-bithiophene (III); if X=O, 2,2'-bifuran (IV). B) if X=S, 3,3'-bithiophene (I); if X=O, 3,3'-bifuran (II).

Calculations

Several authors^{8,11,12} have attempted to extend the PPP method to molecules in which oxygen and sulphur contribute electrons to the π system. It has been emphasized that this is rather difficult, because of the uncertainties

involved in the parameter choice for the heteroatom. However, with the increasing body of experimental data, the application of the PPP method to the ground state properties and the UV spectra of oxygen and sulphur containing molecules is becoming standard¹³⁻²⁶.

No explicit account is generally taken of the *d* orbitals of sulphur, any such contribution being allowed for in the parameters used*. The problem reduced to the estimation of various parameters involving oxygen or sulphur atoms, parameters involving the carbon atom being regarded as well established. We have used a parameter set which leads to good agreement with experiment for certain properties (reactivities¹⁷, bond lengths²², UV spectra^{16,18}, spin density distributions¹⁹); the core integrals used in the calculation are given in Table I (part A), and the two center Coulomb integrals were evaluated using the Mataga-Nishimoto-type approximation²⁶:

$$\gamma_{ij} = \frac{e^2}{a_{ij} + r_{ij}}$$

where

	i=j=C	i=C, j=S	i=C, j=O	i=j=S	i=j=O
a _{ij}	1.3281	1.3001	1.0952	1.2741	0.9318

In the calculation all C—C bonds were taken to be 1.40 Å, the C—S bonds to be 1.74 Å, and the C—O bonds to be 1.37 Å. The one center Coulomb integrals were evaluated in the following way:

$$\gamma_{ii} = I_i - A_i$$

where *I* is ionisation potential and *A* electron affinity for atom *i*. Values for the ionisation potentials and electron affinities were taken from Zahradnik *et al.*¹³ and Skinner and Pritchard²⁷. The one center Coulomb integrals are given in Table I (part B).

The one-electron density matrix was made self-consistent directly, using a »Steepest Descent« minimisation procedure²⁸. All singly excited states (24) were used for the configuration interaction calculations.

The assumption is made that the molecules under investigation are planar, and that the thiophene or furan rings are in *trans* position. There are some reports in the literature that bithiophenes are twisted in the vapour phase²⁹ and in non-polar solvents³. Electron diffraction studies on 2,2'-bithiophene vapour²⁹ are the only report in the literature on the structural investigations of bithiophenes. Further, the work of Almenningen *et al.*²⁹ shows that the thiophene rings in 2,2'-bithiophene are in a *trans* position and have practically the same dimensions as in thiophene itself³⁰ (see Table II). This justifies an assumption of the similar geometries for the remaining molecules studied, *i. e.* the molecules were assumed to be thiophene or furan rings³¹ joined together with a carbon-carbon bond of length 1.40 Å.

* Zahradnik²¹ has shown that the use of a model that does not consider sulphur *d* orbitals gives satisfactory results.

RESULTS AND DISCUSSION

The SCF LCAO MO's and the corresponding energies for 3,3'-bithiophene, 3,3'-bifuran, 2,2'-bithiophene and 2,2'-bifuran are available on request. The molecular orbitals belong to a_u or b_g representations of the symmetry group C_{2h} . In Table III we present the bond orders and charge densities for compounds I—IV. Oxygen and sulphur each contribute 2 electrons to the π system, and from Table III, it is seen that sulphur (I: 1.6205 and III: 1.6165) and oxygen (II: 1.8983 and IV: 1.9184) acquire positive charges in every case. The acquired positive charge is smaller on oxygen than sulphur, due to a larger value of the ionisation potential for oxygen. In other words, the π electrons of oxygen are more firmly bound than those on sulphur.

By using the bond order values we can obtain the bond lengths for

TABLE I

A. Core integrals*	Ref.	B. One center Coulomb integrals
$\beta_{CC} = -2.395$ eV	23	$\gamma_{CC} = 10.84$ eV
$\beta_{CS} = -2.000$ eV	12	$\gamma_{OO} = 15.45$ eV
$\beta_{CO} = -2.115$ eV	24	$\gamma_{SS} = 11.30$ eV
$\delta_{WS} = -8.840$ eV	25	
$\delta_{WO} = -21.740$ eV	24	

* The nomenclature is that of Peacock²³.

2,2'-bithiophene, and compare them with the reported values. A linear relationship between the bond order (p_{ij}) and bond length (L_{ij}) is used:

$$L_{ij} = A + Bp_{ij}$$

Constants A and B depend on the kind of atoms joined in a bond $i-j$. For C—C bonds, $A = 1.517$ and $B = -0.180$ were used³², and for C—S bonds $A = 1.82$ and $B = -0.26$ were used²². The calculated bond lengths for 2,2'-bithiophene are given in Table II. The bond joining two thiophene rings in 2,2'-bithiophene is 1.48 Å, which is longer than the usual aromatic bonds (~ 1.40 Å). We obtained a similar result (1.46 Å), although we used the same β 's for all C—C bonds. This bond has some double bond character, and in

TABLE II
Molecular Geometries

Molecule	Bond	Bond length (Å)	Ref.	Calculated bond length (Å)
2,2'-bithiophene	1—2	1.717	29	1.70
	2—3	1.357		1.38
	3—4	1.433		1.41
	2—2'	1.480		1.46
Thiophene	1—2	1.714	30	
	2—3	1.370		
	3—4	1.423		
Furan	1—2	1.370	31	
	2—3	1.350		
	3—4	1.440		

TABLE III
 Bond Orders and Charge Densities

a) Bond orders				
Bond	3,3'-bithiophene	3,3'-bifuran	2,2'-bithiophene	2,2'-bifuran
1—2	0.4900	0.2677	0.4738	0.2400
2—3	0.7434	0.8276	0.7286	0.8371
3—4	0.5463	0.4685	0.5757	0.4392
4—5	0.7736	0.8620	0.7635	0.8864
5—1	0.4867	0.2678	0.4933	0.2301
2—2'	—	—	0.3075	0.3229
3—3'	0.2702	0.2652	—	—
b) Charge densities				
Atom	3,3'-bithiophene	3,3'-bifuran	2,2'-bithiophene	2,2'-bifuran
1	1.6205	1.8983	1.6165	1.9184
2	1.1144	1.0173	1.0884	1.0111
3	1.0660	1.0304	1.1037	1.0400
4	1.0854	1.0365	1.0840	1.0395
5	1.1138	1.0176	1.1074	0.9911

nature it is similar to bonds joining two benzene rings in biphenyl³³ or two pyridine rings in 2,2'-bipyridine³⁴.

The electronic spectra of the bithiophenes and bifurans have been extensively measured⁴⁻⁷. The UV spectra (λ_{\max} , ϵ_{\max}) are given in Table IV. We present our predicted UV spectra with transition moments along x and y axes for molecules I, II, III and IV in Table V. x axis is defined to lie along the bond connecting two thiophene or two furan rings, while y axis is perpen-

 TABLE IV
 Experimental UV Spectra

Molecule	λ_{\max} (eV)	$\epsilon_{\max} \times 10^3$	Ref.
3,3'-bithiophene	4.77	12.50	4, 5, 7
	5.85	25.10	
3,3'-bifuran	5.18 (s)	5.42	7
	5.36	7.78	
	5.63	7.77	
2,2'-bithiophene	4.12	12.90	4, 7
	5.04	6.00	
2,2'-bifuran	4.20	12.40	6, 7
	4.32	15.10	
	4.41	18.50	
	4.52	18.40	
	4.61	16.70	
	4.84	9.10	
	5.56	2.10	
5.71	2.05		

TABLE V

Calculated Transition Energies (eV) and Transition Moments

Only the first eight transitions in every case are recorded. Transitions are classified by symmetry.

(a) 3,3'-bithiophene

ΔE (eV)	M_x	M_y	$M^2 = M_x^2 + M_y^2$	Symmetry
5.098	-0.842	-0.817	1.377	B _u
5.227	0.0	0.0	0.0	A _g
5.548	0.036	-0.314	0.100	B _u
5.785	0.0	0.0	0.0	A _g
6.091	-1.532	0.522	2.620	B _u
6.397	-0.500	-0.065	0.254	B _u
6.554	0.0	0.0	0.0	A _g
6.733	0.0	0.0	0.0	A _g

(b) 3,3'-bifuran

ΔE (eV)	M_x	M_y	$M^2 = M_x^2 + M_y^2$	Symmetry
5.053	-0.023	0.978	0.956	B _u
5.141	0.0	0.0	0.0	A _g
5.289	0.0	0.0	0.0	A _g
5.643	0.047	-0.062	0.006	B _u
6.005	1.243	-0.198	1.584	B _u
6.546	0.886	0.307	0.879	B _u
6.622	0.0	0.0	0.0	A _g
7.415	0.0	0.0	0.0	A _g

(c) 2,2'-bithiophene

ΔE (eV)	M_x	M_y	$M^2 = M_x^2 + M_y^2$	Symmetry
4.354	1.538	0.024	2.365	B _u
5.355	0.0	0.0	0.0	A _g
5.450	0.253	-0.559	0.376	B _u
5.850	0.0	0.0	0.0	A _g
6.111	0.0	0.0	0.0	A _g
6.685	-0.285	-0.897	0.886	B _u
6.884	0.0	0.0	0.0	A _g
7.201	-0.636	1.075	1.559	B _u

(d) 2,2'-bifuran

ΔE (eV)	M_x	M_y	$M^2 = M_x^2 + M_y^2$	Symmetry
4.340	1.444	-0.469	2.307	B _u
5.513	0.0	0.0	0.0	A _g
5.606	0.0	0.0	0.0	A _g
6.099	0.028	-0.070	0.006	B _u
6.311	0.517	-0.812	0.926	B _u
6.466	0.0	0.0	0.0	A _g
7.847	0.0	0.0	0.0	A _g
8.097	0.126	-0.406	0.181	B _u

dicular to this bond. The molecules I—IV belong to the point group C_{2h} , therefore, only transitions between A_u and B_g states are symmetry allowed. We attribute the calculated values: 5.10 eV (I), 5.05 eV (II), 4.35 eV (III) and 4.34 eV (IV) to the first $\pi-\pi^*$ transition. The corresponding experimentally observed values are: 4.77 eV (I), 5.36 eV (II), 4.12 eV (III) and 4.41 eV (IV), respectively. The difference between the calculated and experimental values is of the order of 0.1 to 0.3 eV, which is a quite good agreement for the approximations used. The agreement for 3,3'-bithiophene and 2,2'-bithiophene obtained by earlier research workers⁸ is a little bit worse for all values of the angle of twist ($\Theta = 0^\circ, 90^\circ$) which they have investigated for each of molecules studied. The best agreement which they found is also for the planar — *trans* model ($\Theta = 0^\circ$). This in part justifies our use of the planar- *trans* model. If there is in molecules I—IV some twisting this suggests that the angle of twisting is probable very small. Therefore, the delocalisation of π -electrons between the rings will not be greatly impeded.

The second $\pi-\pi^*$ transitions are always less intense. The only exception is in the UV spectrum of 3,3'-bithiophene, where the second $\pi-\pi^*$ band is much stronger (about twice) than the first band. This is reproduced in our transition moment calculation.

Remark

After this work was completed and submitted for publication our attention was drawn by a referee to an important paper by Visser, Heeres, Wolters, and Vos (*Acta Cryst.* **B 24** (1968) 467.) in which they have reported x-ray studies on 2,2'-bithiophene, 2,3'-bithiophene, and 3,3'-bithiophene. It is worth pointing out that our assumption of the planar-*trans* model has been substantiated by this work. They have found that in the solid phase the molecules are planar and have a *trans* conformation (two thiophene rings are in *trans* positions regarding the single carbon-carbon bond linking two rings). On the other hand, their measurements of the bond lengths and angles are not very accurate because of the inaccuracies in the intensities. Standard deviations are approximately 0.02 Å for C—S bonds and 0.03 Å for C—C bonds.

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IZVOD

Račun molekularnih orbitala za neke bitiofene i bifurane

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Račun molekularnih orbitala u okviru teorije Parisera, Parra i Poplea primijenjen je na izračunavanje nekih svojstava osnovnog stanja (indeks veze, gustoća naboja, dužina veze) i UV spektara 3,3'-bitiofena, 3,3'-bifurana, 2,2'-bitiofena i 2,2'-bifurana. Postignuto je slaganje između eksperimentalnih podataka iz literature i računski dobivenih rezultata za prvi $\pi-\pi^*$ prijelaz elektrona kod svih ispitivanih molekula.

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